

A COMPUTATIONAL STUDY ON NITROTRIAZINE DERIVATIVES

**A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY**

BY

YAKUP ÇAMUR

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE**

IN

CHEMISTRY

FEBRUARY 2008

Approval of the Thesis:

A COMPUTATIONAL STUDY ON NITROTRIAZINE DERIVATIVES

Submitted by **YAKUP ÇAMUR** in partial fulfillment of the requirements for the degree of **Master of Science in Chemistry Department, Middle East Technical University** by

Prof. Dr. Canan ÖZGEN

Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Ahmet ÖNAL

Head of Department, **Chemistry**

Prof. Dr. Lemi TÜRKER

Supervisor, **Chemistry Dept., METU**

Examining Committee Members

Prof. Dr. Leyla ARAS
Chemistry Dept., METU

Prof. Dr. Lemi TÜRKER
Chemistry Dept., METU

Prof. Dr. Ayhan Sıtkı DEMİR
Chemistry Dept., METU

Prof. Dr. Nihat ÇELEBİ
Chemistry Dept., Abant İzzet Baysal Üniversitesi

Dr. Mehmet Fatih DANIŞMAN
Chemistry Dept., METU

Date : 08.02.2008

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Yakup ÇAMUR

Signature :

ABSTRACT

A COMPUTATIONAL STUDY ON NITROTRIAZINE DERIVATIVES

Çamur, Yakup
M.S., Department of Chemistry
Supervisor: Prof. Dr. Lemi TÜRKER

February 2008, 139 Pages.

In this study, all possible mono, di and trinitro-substituted triazine compounds as potential candidates for high energy density materials (HEDMs) have been investigated by using quantum chemical treatment. Computational chemistry is a valuable tool for estimating the potential candidates for high energy density materials. Geometric features and electronic structures of these nitro-substituted triazines have been systematically studied using *ab initio* and density functional theory (DFT, B3LYP) at the level of 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-pVDZ. Detonation performances were evaluated by the Kamlet-Jacobs equations based on the calculated densities and heats of formation. It is found that **2G** derivative with the predicted densities of 1.9 g/cm³, detonation velocities of 9.43 km/s, and detonation pressures of 40.68 GPa may be novel potential candidates of high energy density materials (HEDMs). Moreover, thermal stabilities were investigated by calculating bond dissociation energies (BDE) at B3LYP/6-311G(d,p) level. Detailed molecular orbital (MO) investigation have been performed on these potential HEDMs.

Key words: Nitrotriazines, *ab initio*, DFT, energetic materials, detonation parameters.

ÖZ

A COMPUTATIONAL STUDY ON NITROTRIAZINE DERIVATIVES

Çamur, Yakup
M.S., Department of Chemistry
Supervisor: Prof. Dr. Lemi TÜRKER

Şubat 2008, 139 Sayfa.

Bu çalışmada bir ve daha fazla nitro grubu bağlı triazin türevleri üzerinde kuantum kimyasını kullanarak araştırma yapılmıştır. Yüksek enerji veren maddelerin patlayıcılık potansiyelini tespit etmede teorik kimya kullanışlı bir alandır. Elde edilen bütün nitrotriazine türevlerinin geometrik özellikleri, elektronik yapıları *ab initio* ve yoğunluk fonksiyon teorisi (DFT) metodları 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-pVDZ temel seviyeleri kullanılarak sistematik olarak tespit edilmeye çalışılmıştır. Patlama performansları yoğunluklar ve oluşum ısıları yardımıyla, Kamlet-Jakobs denklemleri kullanılarak hesaplanmıştır. **2G** türevine ait yoğunluk 1.9 g/cm^3 , patlama hızı 9.43 km/s ve patlama basıncı 40.68 GPa olarak bulunmuş olup, yüksek enerji veren yeni bir madde adayı olabilir. Bunların yanında homolitik bağ kopma enerjileri kullanılarak, elde edilen bütün bileşiklerin termal dayanıklılıkları B3LYP/6-311G(d,p) temel seviyesinde tespit edilmiştir. Detaylı moleküler orbital araştırmaları da bu maddeler üzerinde yapılmıştır.

Anahtar Kelimeler: Nitrotriazinler, *ab initio*, DFT, enerjik materyaller, patlama parametreleri.

to ferhan

and

to my family

ACKNOWLEDGEMENT

I would like to express my sincere appreciation to my supervisor Prof. Dr. Lemi TÜRKER for his advice, support and guidance throughout the research.

I would like to thank to my labmates Selçuk Gümüş and Taner Atalar for their suggestions, endless help and close interest as a friend.

I would like to thank my friends Hayrettin Dursun, İbrahim Hakan Sapmazlı, Mahmut Pala and Metin Yılmaz for their supports and friendships.

Finally, my special appreciation and gratitude is devoted to my family for their endless encouragement and moral support, which makes everything possible.

TABLE OF CONTENTS

ABSTRACT	iv
ÖZ	v
ACKNOWLEDGEMENTS	vii
TABLE OF CONTENTS	viii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xiii
LIST OF ABBREVIATIONS.....	xiv
CHAPTER	
1. INTRODUCTION	
1.1 Triazine Structures.....	1
1.1.1 The 1,3,5-Triazines.....	2
1.1.2 The 1,2,4-Triazines.....	3
1.1.3 The 1,2,3-Triazines.....	4
1.1.4 Nitrotriazine Derivatives.....	5
2. EXPLOSIVES	
2.1 Introduction.....	8
2.2 Classification of Explosives.....	9
2.3 Nitration and Nitrating Agents.....	13
2.4 General Information on Nitro Compounds.....	16
2.5 Reactivity of the Nitro Group.....	16
2.6 Nitro Compounds as Explosives.....	17
2.7 Thermochemistry of Explosives.....	18
2.7.1 Oxygen Balance.....	18

2.7.2 Heats of Formation.....	22
2.7.3 Heat of Explosion.....	24
2.7.4 Detonation.....	25
3. COMPUTATIONAL CHEMISTRY	
3.1 Introduction.....	27
3.2 Semiempirical Methods.....	29
3.2.1 The Austin Model 1 Method	30
3.2.2 Parameterization Method 3.....	31
3.3 <i>Ab initio</i> Methods.....	32
3.3.1 Hartree-Fock Approximation.....	32
3.3.2 Correlation.....	35
3.4 Density Functional Theory.....	37
3.4.1 Basic Theory.....	37
3.5 Using Existing Basis Sets.....	39
3.5.1 Notation.....	40
4. RESULTS AND DISCUSSIONS	
4.1 Method of Calculations.....	43
4.2 General Structural Considerations on Nitrotriazines.....	44
4.3 Geometries.....	47
4.3.1 Bond Lengths.....	51
4.3.2 Bond Angles and Dihedral Angles.....	54
4.4 Nucleus Independent Chemical Shifts (NICS).....	59
4.5 Energetics.....	60
4.6 Bond Dissociation Energies (BDE).....	64
4.7 The Frontier Molecular Orbital Energies.....	66
4.8 Predicted Densities and Detonation of The Nitrotriazine Derivatives...68	
5. CONCLUSIONS.....	72
REFERENCES.....	73
APPENDICES	
A. Total Energies Tables.....	79
B. Z-Matrix Tables.....	90

LIST OF TABLES

TABLES

Table 1.1	Physical properties and structures of s-triazine, pyrimidine and pyridine.....	2
Table 1.2	The Chemical formulas and nomenclature of nitrotriazines.....	5
Table 2.1	Oxygen balance of some explosives.....	19
Table 4.1	Optimized structural parameters of nitro-1,3,5-triazines calculated at B3LYP/cc-pVDZ.....	56
Table 4.2	Optimized structural parameters of nitro-1,2,4-triazines calculated at B3LYP/cc-pVDZ	57
Table 4.3	Optimized structural parameters of nitro-1,2,3-triazines calculated at B3LYP/cc-pVDZ	58
Table 4.4	NICS values for the nitrotriazine structures calculated at B3LYP/6-11G(d,p) method.....	60
Table 4.5	Calculated total energies (in a.u.) for nitrotriazine derivatives at different theoretical levels.....	62
Table 4.6	Calculated total energies (in a.u.) for nitrotriazine derivatives at different theoretical levels.....	63
Table 4.7	Calculated total energies (including zero-point vibrational energies) of nitrotriazine molecules, fragments and NO ₂ at the equilibrium geometries and resulting bond dissociation energies (BDE).....	66
Table 4.8	The HOMO and LUMO energies (ϵ) of nitrotriazine derivatives....	67
Table 4.9	The HOMO and LUMO energies (ϵ) of nitrotriazine derivatives....	68
Table 4.10	Methods for Calculating the N, M, and Q Parameters of the C _a H _b O _c N _d Explosive ^{a,b}	69

Table 4.11	Predicted densities and detonation properties of the nitrotriazine structures.....	70
Table A1	Calculated energy data for the 1A at HF level with 5 different basis sets.....	79
Table A2	Calculated energy data for the 1A at B3LYP level with 5 different basis sets.....	80
Table A3	Calculated energy data for the 1B at HF level with 5 different basis sets.....	80
Table A4	Calculated energy data for the 1B at B3LYP level with 5 different basis sets.....	80
Table A5	Calculated energy data for the 1C at HF level with 5 different basis sets.....	81
Table A6	Calculated energy data for the 1C at B3LYP level with 5 different basis sets.....	81
Table A7	Calculated energy data for the 2A at HF level with 5 different basis sets.....	81
Table A8	Calculated energy data for the 2A at B3LYP level with 5 different basis sets.....	82
Table A9	Calculated energy data for the 2B at HF level with 5 different basis sets.....	82
Table A10	Calculated energy data for the 2B at B3LYP level with 5 different basis sets.....	82
Table A11	Calculated energy data for the 2C at HF level with 5 different basis sets.....	83
Table A12	Calculated energy data for the 2C at B3LYP level with 5 different basis sets.....	83
Table A13	Calculated energy data for the 2D at HF level with 5 different basis sets.....	83
Table A14	Calculated energy data for the 2D at B3LYP level with 5 different basis sets.....	84
Table A15	Calculated energy data for the 2E at HF level with 5 different basis sets.....	84

Table A16	Calculated energy data for the 2E at B3LYP level with 5 different basis sets.....	84
Table A17	Calculated energy data for the 2F at HF level with 5 different basis sets.....	85
Table A18	Calculated energy data for the 2F at B3LYP level with 5 different basis sets.....	85
Table A19	Calculated energy data for the 2G at HF level with 5 different basis sets.....	85
Table A20	Calculated energy data for the 2G at B3LYP level with 5 different basis sets.....	86
Table A21	Calculated energy data for the 3A at HF level with 5 different basis sets.....	86
Table A22	Calculated energy data for the 3A at B3LYP level with 5 different basis sets.....	86
Table A23	Calculated energy data for the 3B at HF level with 5 different basis sets.....	87
Table A24	Calculated energy data for the 3B at B3LYP level with 5 different basis sets.....	87
Table A25	Calculated energy data for the 3C at HF level with 5 different basis sets.....	87
Table A26	Calculated energy data for the 3C at B3LYP level with 5 different basis sets.....	88
Table A27	Calculated energy data for the 3D at HF level with 5 different basis sets.....	88
Table A28	Calculated energy data for the 3D at B3LYP level with 5 different basis sets.....	88
Table A29	Calculated energy data for the 3E at HF level with 5 different basis sets.....	89
Table A30	Calculated energy data for the 3E at B3LYP level with 5 different basis sets.....	89

LIST OF FIGURES

FIGURES

Figure 1.1	Nomenclature and structures of triazines.....	1
Figure 1.2	Chemical structures of nitro-triazines.....	6
Figure 2.1	Chemical structures and names of some explosives.....	19
Figure 2.2	The effect of the oxygen balance on the heat of explosion.....	21
Figure 2.3	Energy is taken into break the bonds of RDX into its constituent elements, then energy is released when new bonds are formed.....	23
Figure 2.4	Schematic diagram of the irreversible explosion process.....	24
Figure 2.5	Change in velocity of detonation as a function of density for a secondary explosive, i.e. TNT.....	26
Figure 3.1	Two arrangements of electrons around the nucleus of an atom having the same probability within HF theory, but not in correlated calculations.....	35
Figure 4.1	Some groups common in explosives and their isoconjugates.....	45
Figure 4.2	Isoconjugates of nitrotriazines studied.....	46
Figure 4.3	Geometric structures and numbering of nitro-triazine structures....	48
Figure 4.4	Geometry optimized structures of nitrotriazines at B3LYP/cc-pVDZ level.....	50
Figure 4.5	3D-electrostatic potential maps of the nitrotriazines.....	53

LIST OF ABBREVIATIONS

Å	Angstrom
AO	Atomic Orbital
AM1	Austin Model 1
B3LYP	Becke's three parameter exchange hybrid functional with Lee, Yang, Parr (LYP) correlation functional
BDE	Bond Dissociation Energy
CBS	Complete Basis Set
CC	Coupled Cluster Theory
CCSD	Coupled cluster theory with single and double excitations
CCSD(T)	Coupled cluster theory with single and double excitations and noniterative inclusion of triples
CCSDT	Coupled cluster theory with single and double excitations and inclusion of connected triples excitations
CI	Configuration Interaction
CIS	Configuration Interaction Single-Excitation
CISD	Configuration Interaction Single-and-Double-Excitation
CPU	Central Processing Unit
DFT	Density Functional Theory
GIAO	Gauge Invariant Atomic Orbital
GTO	Gaussian Type Orbital
GVB	Generalized Valence Bond
HEDM	High Energy Density Material
HF	Hartree-Fock Theory
HOF	Heat of Formation
HOMO	Highest Occupied Molecular Orbital

LDA	Local Density Approximation
LDSA	Local Density-Spin Approximation
LSDA	Local Spin-Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
MCSCF	Multi-Configurational Self-Consistent Field Theory
MM	Molecular Mechanics
MNDO	Modified Neglect of Diatomic Overlap
MPn	Møller-Plesset nth-order Perturbation Theory
MO	Molecular Orbital
NICS	Nucleus Independent Chemical Shift
NMR	Nuclear Magnetic Resonance
PM3	Parameterization Method 3
RHF	Restricted Hartree-Fock Theory
Ψ	Wave function (state function)
ROHF	Restricted Open-Shell Hartree-Fock Theory
SE	Semiempirical
SCF	Self-Consistent Field
STO	Slater Type Orbital
UHF	Unrestricted Hartree-Fock
ZPVE	Zero point vibrational energy

CHAPTER 1

INTRODUCTION

1.1 Triazine Structures

The six-membered heterocycle consisting of three nitrogen atoms and three carbon atoms alternately located in the ring is known as the symmetrical triazine ring system (**1**) [1]. This heterocycle is ordinarily abbreviated as *s-triazine* (or sym-triazine). The other two isomeric six-membered heterocycles containing three nitrogen and three carbon atoms in the ring are asymmetrical triazine (**2**) [1], designated *as-triazine* (asymm-triazine) and vicinal triazine (**3**) [1], designated *v-triazine* (vic-triazine).

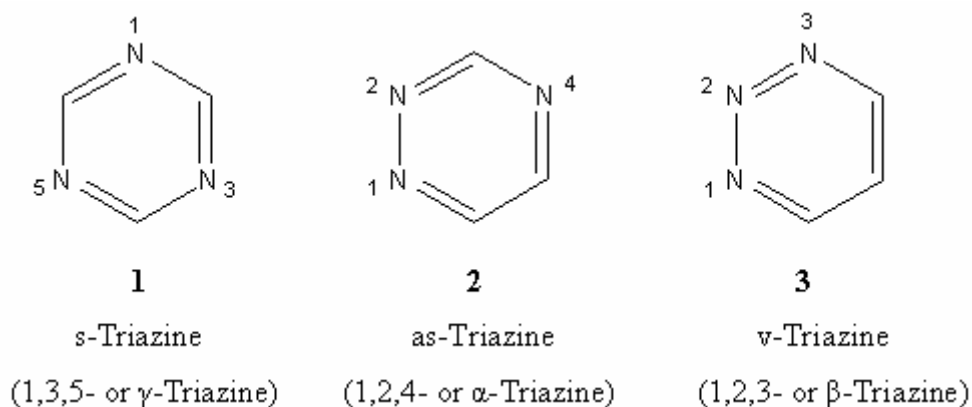


Figure 1.1 Nomenclature and structures of triazines

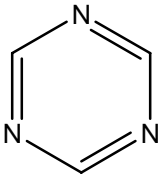
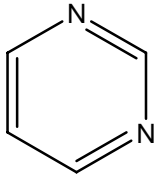
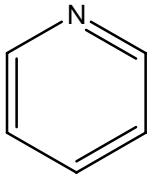
1.1.1 The 1,3,5-Triazine

The symmetrical triazine ring system (**1**) is ordinarily abbreviated as *s-triazine* (or sym-triazine), although the designation *1,3,5-triazine* is also common, particularly in the British literature. In this convention the numbers refer to positions of the ring-nitrogen atoms. In the early German literature, the *s-triazine* system was known as kyanidine (cyanidine) or γ -*triazine*. The designation *s-triazine* is preferred by both *Chemical Abstracts* and *The Ring Index* [2]. Ring-nitrogen positions 1, 3, and 5 are equivalent, as are ring-carbon positions 2, 4, and 6.

s-Triazine is an extremely volatile crystalline solid which melts [3,4], at 86°C and boils at 114°C at one atmosphere. It is easily soluble [3] in ether and in ethanol at -5°C. The relatively high melting point and extreme volatility are in accord with a highly symmetrical molecular structure. Because of its volatility, *s*-triazine can be isolated from reaction mixtures by entrainment in a stream of nitrogen or dry air. The density of the highly refracting rhombohedral crystals has been determined [5] to be approximately 1.38 g/cm³. The heat of combustion for *s*-triazine has been calculated to be 424.4, the heat of fusion, 40.2, the heat of vaporization, 12.15, and the resonance energy, 20.0, all in kcal. per mole [6].

Table 1.1 Physical properties and structures of *s*-triazine, pyrimidine and pyridine

	B.p., °C (760 mm.)	M.p., °C	Resonance energy (kcal./mole)
<i>s</i> -Triazine	114	86	20
Pyrimidine	123	22	26
Pyridine	116	- 42	31

		
<i>s</i> -Triazine	Pyrimidine	Pyridine

s-Triazine exhibits a high degree of thermal stability; it can be purified without appreciable loss by repeated distillation over metallic sodium. A comparison of the melting and boiling points of s-triazine, pyrimidine, and pyridine is of interest in this connection [7]. In this series, introduction of ring-nitrogen atoms has little effect on the boiling points but causes a linear increase in the melting points. The resonance energy of s-triazine [8] is the lowest of the series.

1.1.2 The 1,2,4-Triazine

Compounds with ring system **2** are most systematically named as *1,2,4-triazines*. The name *isotriazine* is occasionally found, especially in the Italian literature [10-11]. *α-Triazine*, another name for this ring system, seems to have arisen from a proposal by Widman [12]. Probably the most commonly used name for compound **2** is *as-triazine*, where *as-* denotes asymmetry. It leads to somewhat shorter and simpler names and is preferred by *The Ring Index* [2] and *Chemical Abstracts*.

So far as we know, no 1,2,4-triazine has found widespread use. A compound, once believed to be a 1,2,4-triazine, was for a time sold as a sweetening agent under the name “glucin” and apparently attained some popularity in Europe. A U.S. patent, issued to Shoemaker and Loane [13] has claims covering the use of 1,2,4-triazines as additives for lubricating oils; the permissible substituents listed include alkyl, aryl, aralkyl, alkoxy, mercapto, or amino groups or halogens. However, patent gives only one example of reduction to practice and this does not mention the use of 1,2,4-triazines. Some 1,2,4-triazines are known to be dyes for wool but it is doubtful whether they are actually used for this purpose. U.S. patents issued to Wolf and Pfister [14-23] state that certain 1,2,4-benzotriazine derivatives show promise in the treatment of malaria.

1.1.3 The 1,2,3-Triazine

The systematic designation, *1,2,3-triazine*, is still widely used for compound **3**. However, both *Chemical Abstracts* and *The Ring Index* [2] prefer the name, *v-triazine*, where v- denotes vicinal nitrogen atoms. *The Ring Index* uses both v- and 1,2,3-prefixes in the naming of condensed systems. A much less satisfactory name-fortunately seldom used-is β -*triazine*. The origin of the β -designation is not clear. It seems to have arisen, though, from a suggestion by Widman [12].

No naturally occurring compounds containing 1,2,3-triazine rings have been reported. This is not surprising, in the view of great reactivity of this type of ring. Although the first synthesis of a 1,2,3-triazine was reported in 1874, we still know little about this group of compounds. A few systematic studies of these compounds were made in the last decade or so of the nineteenth century and the first part of the present century.

We know that the 1,2,3-triazine ring is easily opened. Refined techniques will indeed be necessary to carry out reactions and keep the triazine ring intact. We easily see that many opportunities still exist for significant contributions in this field [24].

1.1.4 Nitrotriazine Derivatives

When we attach nitro group(s) to the 1,3,5-triazine (**1**), 1,2,4-triazine (**2**) and 1,2,3-triazine (**3**) structures, we obtain fifteen different nitrotriazine structures which are listed in Table 1.2 and shown in Figure 1.2.

Table 1.2 The Empirical formulas and nomenclature of nitrotriazines

	Empirical Formula	Nomenclature
1A	$C_3H_2O_2N_4$	2-nitro-1,3,5-triazine
1B	$C_3H_1O_4N_5$	2,4-dinitro-1,3,5-triazine
1C	$C_3O_6N_6$	2,4,6-trinitro-1,3,5-triazine
2A	$C_3H_2O_2N_4$	3-nitro-1,2,4-triazine
2B	$C_3H_2O_2N_4$	6-nitro-1,2,4-triazine
2C	$C_3H_2O_2N_4$	5-nitro-1,2,4-triazine
2D	$C_3H_1O_4N_5$	3,6-dinitro-1,2,4-triazine
2E	$C_3H_1O_4N_5$	3,5-dinitro-1,2,4-triazine
2F	$C_3H_1O_4N_5$	5,6-dinitro-1,2,4-triazine
2G	$C_3O_6N_6$	3,5,6-trinitro-1,2,4-triazine
3A	$C_3H_2O_2N_4$	4-nitro-1,2,3-triazine
3B	$C_3H_2O_2N_4$	5-nitro-1,2,3-triazine
3C	$C_3H_1O_4N_5$	4,5-dinitro-1,2,3-triazine
3D	$C_3H_1O_4N_5$	4,6-dinitro-1,2,3-triazine
3E	$C_3O_6N_6$	4,5,6-trinitro-1,2,3-triazine

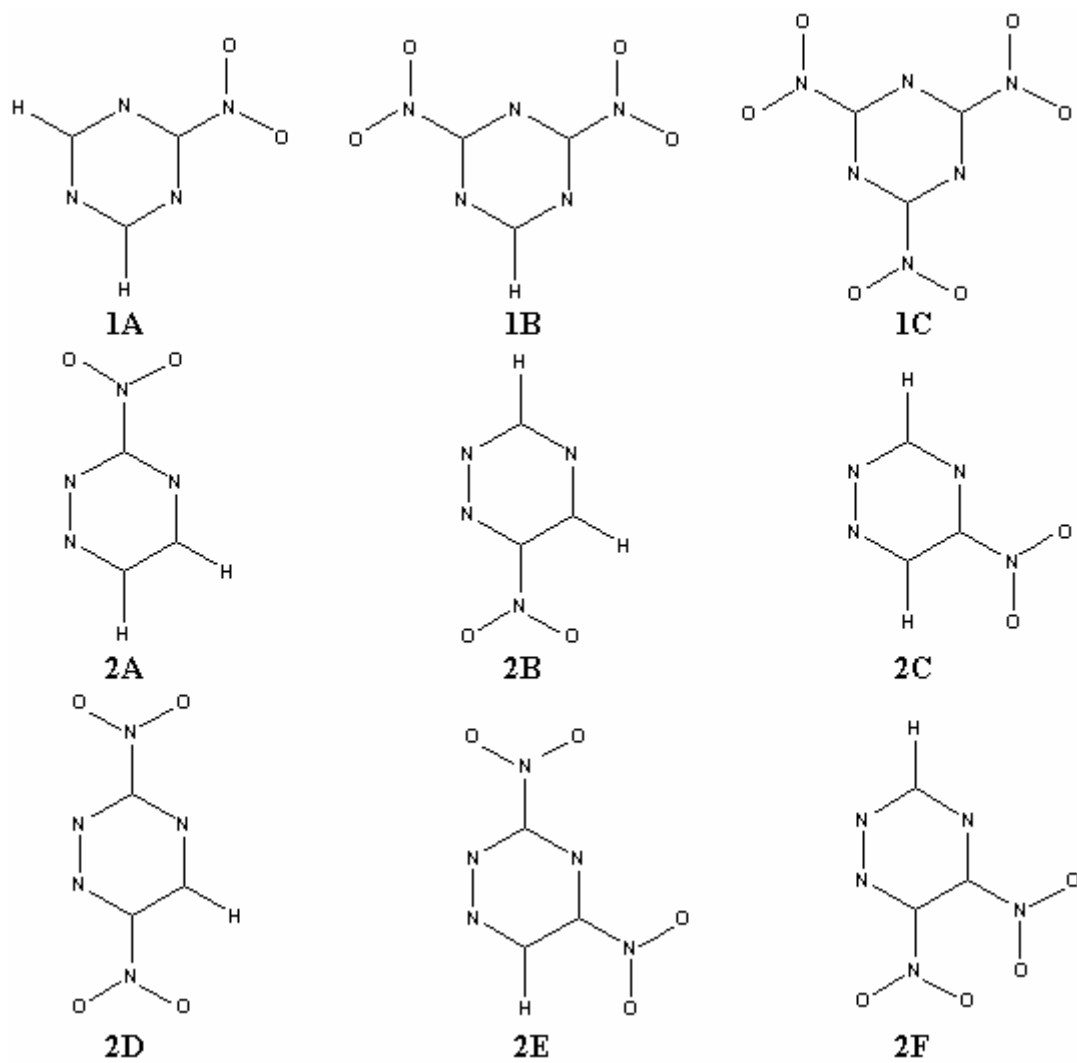


Figure 1.2 Chemical structures of nitro-triazines

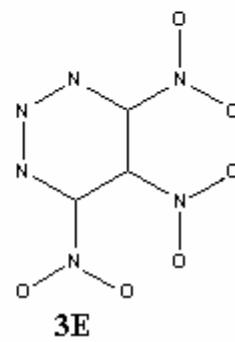
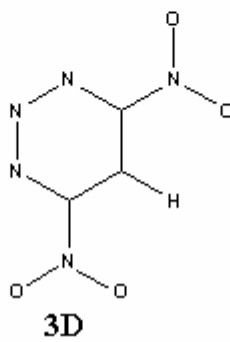
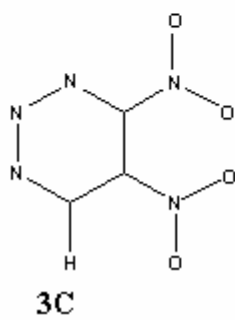
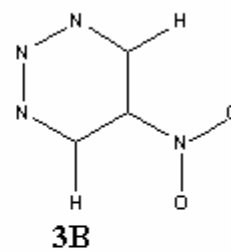
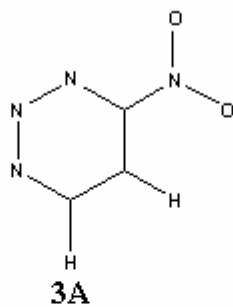
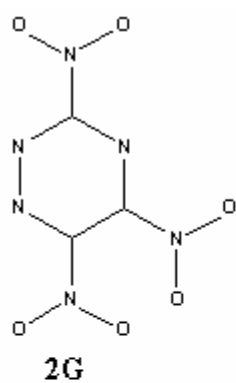


Figure 1.2 continued

CHAPTER 2

EXPLOSIVES

2.1 Introduction

An explosive is a material, either a pure single substance or a mixture of substances, which is capable of producing an explosion by its own energy. An explosion is a loud noise and the sudden going away of things from the place where they have been. Sometimes it may only be the air in the neighborhood of the material or the gas from the explosion which goes away. Our simple definition makes mention of the one single attribute which all explosives possess. It will be necessary to add other ideas to it if we wish to describe the explosive properties of any particular substance. The production of heat alone by the inherent energy of the substance which produces it will be enough to constitute the substance an explosive. Cuprous acetylide explodes by decomposing into copper and carbon and heat, no gas whatever, but the sudden heat causes a sudden expansion of the air in the neighborhood, and the result is an unequivocal explosion. All explosive substances produce heat; nearly all of them produce gas. The change is invariably accompanied by the liberation of energy. The products of the explosion represent a lower energy level than did the explosive before it had produced the explosion. Explosives commonly require some stimulus, like a blow or a spark, to provoke them to liberate their energy, that is, to undergo the change which produces the explosion, but the stimulus which “sets off” the explosive does not contribute to

the energy of the explosion. The various stimuli to which explosives respond and the manner of their responses in producing explosions provide a convenient basis for the classification of these interesting materials.

2.2 Classification of Explosives

Classification of explosive materials is based on various criteria. They may be classified both from the chemical point of view and according to their uses. From the chemical viewpoint, explosives can be distinguished as individual chemical explosives and mixtures. The main subclasses of the former are divided into : 1) nitro compounds, 2) nitric esters, 3) nitramines, 4) derivatives of chloric and perchloric acids, 5) azides, 6) various compounds capable of producing an explosion, for example fulminates, acetylides, nitrogen rich compounds such as tetrazene, peroxides and ozonides, etc.

Individual substances are explosive if their molecules contain groups which confer upon them explosive properties. The first attempt at a systematic approach to the relation between the explosive properties of a molecule and its structure was made by van't Hoff [25]. He pointed out that the explosive molecules generally contain the following groups. 1) O-O linkage in peroxides, ozone and ozonides, 2) O-Cl in chlorides and perchlorates, 3) N-Cl in nitrogen chloride, 4) N=O in nitro compounds, nitric acid esters and salts, 5) N=N in diazo compounds, hydrazoic acid, its salts and esters, 6) N=C in fulminates and cyanogen, 7) C≡C in acetylene and acetylides. A further effort to establish a relationship between explosive properties and structure was made by Pletz [26]. He proposed the theory of "explosophores" and "auxoploses" in a way analogous to Witt's suggestion of chromophores and auxochromes in the dyes, and Ehrlich's toxophores and autotoxes in chemotherapeutics. According to Pletz the explosive properties of any substance depend upon the presence of definite structural groupings, called explosophores. The auxoploses fortify or modify the explosive properties conferred by the explosophore. Pletz divided all explosives into eight classes containing the following groups as explosophores :

- (1) $-\text{NO}_2$ and $-\text{ONO}_2$ in both organic and inorganic substances
- (2) $-\text{N}=\text{N}-$ and $-\text{N}=\text{N}=\text{N}-$ in inorganic and organic azides
- (3) $-\text{N}=\text{C}$ in fulminates
- (4) $-\text{NX}_2$, for example in NCl_3 (X: a halogen)
- (5) $-\text{O}-\text{O}-$ and $-\text{O}-\text{O}-\text{O}-$ in inorganic and organic peroxides and ozonides, respectively
- (6) $-\text{OClO}_2$ and $-\text{OClO}_3$ in inorganic and organic chlorates and perchlorates, respectively
- (7) $-\text{C}\equiv\text{C}-$ in acetylene and metal acetylides
- (8) M-C metal bonded with carbon in some organometallic compounds.

Although this classification is in principle correct, the distinction between the terms “explosophore” and “auxoplose” is very vague and of little practical value. A further step in the classification of explosives was made by Lothrop and Handrick [27], who collected and classified all the available information on the performance of explosives and related it to four factors. Those are the oxygen balance, “plosophoric” groups, “auxoplosive” groups and heat of explosion.

A plosophore has been defined as a group of atoms which is capable of forming an explosive compound on introduction into a hydrocarbon. According to these authors there exist two classes of plosophores differing sharply in effectiveness and consistency in producing power. Hence, it is suggested that these be called “primary” and “secondary” plosophores. Primary plosophores include aromatic and aliphatic nitro groups, nitrate esters, and the nitramine group. The secondary plosophores include groups such as azo, azide, nitroso, peroxide, ozonide, perchlorate, etc. If more than one type of these groups is present, such a molecule may be named a hybrid according to Lothrop and Handrick [27].

Groups which do not themselves produce explosive properties, but may influence them (in the same way that auxochromic groups vary the color intensity and shade of a dye), are called auxoplosives by these authors. As examples of such groups, we may quote hydroxyl, carboxyl, chlorine, sulfur, ether, oxygen, amine, etc.

Although the classification of groups existing in explosive molecules suggested by Lothrop and Handrick [27] may generally be accepted, their far-reaching postulations concerning a close relation between the oxygen balance and performance of explosives aroused strong criticism [28], because the oxygen present, for example, in carbonyl or hydroxyl groups, has little effect on the performance of an explosive. This is due to the high heat of formation of C-O and C-O-H bonds. The low value of the explosive power of oxygen atoms bonded with carbon triple bonds has great significance in relation to the performance of explosives. Because of that reason, the performance of picric acid (trinitrophenol) is only very slightly higher than that of and hydrogen atoms in such a group as COOH had already been stressed by Stettbacher [29], who has pointed out that an exception is provided by peroxides and ozonides which form exothermic bond that considerably enhance explosive performance. However, the slightly better performance of picric acid compared with trinitrobenzene is probably the result of the former's greater ability to detonate. The ease of detonation of picric and styphnic acids as compared with trinitrobenzene is well known. Smolenski and Czuba pointed out that dinitrophenol detonates more readily than dinitrobenzene [30]. From the classic work of Wöhler and Wenzelberg, it is also well known that the sensitivity to impact of aromatic nitro compounds increases with increase in the number of substituents for a given member of the nitro groups [31].

According to their uses explosives are divided into i) primary explosives or initiators ii) high explosives, and iii) propellants (low explosives). Primary explosives and their mixtures are divided into those used for filling ignition caps and those used in detonators [32]. High explosives may be classified according to their physical properties as powdery, meltable, semi-meltable and plastic. On the other hand, propellants may be grouped on the basis of chemical composition into gun powder and similar mixtures, nitrocellulose (single base) and nitroglycerine (double base) powders. With respect to their uses and some properties they are divided into black powder, smokeless and flashless powders, and rocket propellants.

(i) *Primary explosives or initiators* explode or detonate when they are heated or subjected to shock. They do not burn; Sometimes they do not even contain the elements necessary for combustion. The materials themselves explode, and the explosion results whether they are confined or not. They differ from secondary explosives in that they undergo a very rapid transition from burning to detonation and have ability to transmit the detonation to less sensitive explosives. On detonation the molecules in the explosive dissociate and produce a tremendous amount of heat and/or shock. This will in turn initiate a second, more stable explosive. Typical primary explosives which are widely used are lead azide, lead styphnate (trinitroresorcinate), lead mononitroresorcinate (LMNR), potassium dinitrobenzofurazan (KDNBF), barium styphnate and potassium perchlorate. Other primary explosive materials which are not frequently used today are mercury azide, potassium chlorate and mercury fulminate.

(ii) *High explosives* detonate under the influence of the shock of the explosion of a suitable primary explosive. They do not function by burning; in fact, not all of them are combustible, but most of them can be ignited by a flame and in small amount generally burn tranquilly and can be extinguished easily. If heated to a high temperature by external heat or by their own combustion, they sometimes explode. They differ from primary explosives in not being exploded readily by heat or by shock, and generally in being more brisant and powerful. They exert a mechanical effect upon whatever is near them when they explode, whether they are confined or not. Examples: dynamite, trinitrotoluene, tetryl, picric acid, nitrocellulose, nitroglycerin, liquid oxygen mixed with wood pulp, fuming nitric acid mixed with nitrobenzene, compressed acetylene and cyanogen, ammonium nitrate and perchlorate, nitroguanidine. It is evident that we cannot describe a substance by saying that it is "very explosive." We must specify whether it is sensitive to fire and to shock, whether it is really powerful or merely brisant, or both, whether it is fast or slow. Likewise, in the discussions in the thesis, we must distinguish carefully between sensitivity, stability, and reactivity. A substance may be extremely reactive chemically but perfectly stable in the absence of anything with which it may react. A substance may be exploded readily by a slight shock,

but it may be stable if left to itself. Another may require the shock of a powerful detonator to make it explode but may be subject to spontaneous decomposition. The three classes of explosive materials overlap somewhat, for the behavior of a number of them is determined by the nature of the stimuli to which they are subjected and by the manner in which they are used. Black powder has probably never been known, even in the hideous explosions which have sometimes occurred at black powder mills, to do anything but burn. Smokeless powder which is made from colloided nitrocellulose, especially if it exists in a state of fine subdivision, is a vigorous high explosive and may be detonated by means of a sufficiently powerful initiator. In the gun it is lighted by a flame and functions as a propellant. Nitroglycerin, trinitrotoluene, nitroguanidine, and other high explosives are used in admixture with nitrocellulose in smokeless powders. Fulminate of mercury if compressed very strongly becomes "dead pressed" and loses its power to detonate from flame, but retains its power to burn, and will detonate from the shock of the explosion of less highly compressed mercury fulminate. Lead azide, however, always explodes from shock, from fire, and from friction.

(iii) *Propellants or low explosives* are combustible materials, containing within themselves all oxygen needful for their combustion, which burn but do not explode, and function by producing gas which produces an explosion. Examples: black powder, smokeless powder. Explosives of this class differ widely among themselves in the rate at which they deliver their energy. There are slow powders and fast powders for different uses. The kick of a shotgun is quite different from the persistent push against the shoulder of a high-powered military rifle in which a slower burning and more powerful powder is used.

2.3 Nitration and Nitrating Agents

Nitration is one of the earliest known organic chemical reactions. It is mentioned in the writings of the alchemists. As early as in the first half of the 18th century, Glauber obtained picric acid by the action of nitric acid on wool and horn. Soon reactions between nitric acid and a variety of organic substances became one

of the alchemical reactions most frequently used. They were usually carried out by heating a substance with nitric acid, often to boiling point. Thus, picric acid was obtained from certain organic substances such as indigo, silk, resins, etc.

In 1833 Braconnot obtained nitric esters of cellulose and starch by the action of nitric acid on plant fibers and starch, at low temperature. In 1834 Mitscherlich obtained nitrobenzene. But it is only since 1842, when Zinin reduced nitrobenzene to aniline, that rapid development of the chemistry of nitro compounds and their application to organic industry has occurred.

At present, nitration is one of the most widely applied direct substitution reactions. This is due to several factors, for example nitration usually proceeds easily, its products can readily be separated from the spent acid, and there is a wide range of possibilities in the practical use of nitro compounds, both as intermediates and end products. The presence of a nitro group in the starting product made it possible to obtain a number of basic organic intermediates such as aniline and benzidine. Also, dyes with more than one nitro group, such as picric acid were obtained. It has been found that higher nitrated nitro compounds and nitric acid esters have explosive properties and are of practical importance. However, some nitro compounds have found applicability in perfumes. Medicinal properties have lately been discovered in certain nitro compounds, e.g. chloramphenicol.

Nitration is a reaction which has contributed greatly to the development of the substitution rule [33]. Although nitration had been well known and widely used for many years both in the laboratory and in the industry, little known about the nature and mechanism of this reaction in the past. However, in the last couple of decades much progress has been made in this field. With the aid of the new techniques offered by modern physics and physical chemistry and by the application of the modern electronic theory of chemical bonds, certain intricate problems have been elucidated in the course of extensive research. Nitration can be carried out either directly by introduction of the nitro group in place of hydrogen atom or by adding it to a double bond, or else indirectly. These methods employ,

(1) concentrated nitric acid

(2) mixtures of concentrated nitric acid and concentrated sulfuric acid (or oleum) in different proportions which are usually known as nitrating mixtures

- (3) dilute nitric acid
- (4) alkali nitrates in the presence of sulfuric acid
- (5) nitrogen dioxide
- (6) nitrogen dioxide in the presence of catalysts.
- (7) a solution of nitrogen dioxide in sulfuric acid

Sometimes in laboratory experiments and in industry more expensive nitrating agents may be used, some of these are solutions of nitric acid in inert organic solvents (chloroform, carbon tetrachloride, ether, nitromethane, etc.), or a solution of nitric acid in phosphoric or acetic acids or in acetic anhydride. For nitrating on the laboratory scale, mixtures of nitric acid ester or acyl nitrates, e.g. acetyl nitrate CH_3CONO_2 , and sulfuric acid may also be used.

Also, several lesser known nitrating agents exist, which can find practical use on a laboratory scale. These are metal nitrates in the presence of acetic acid or acetic anhydride, described by Menke [34], nitroguanidine in solution in sulfuric acid, used for the nitration of aromatic amines and phenols and tetranitromethane and hexanitroethane in an alkaline medium, used by Schmidt [35].

Besides these direct methods of introducing nitro groups, several indirect methods are also known that involve in the introduction of a group which can readily be substituted by a nitro group. In one of these which is widely used in the nitration of phenols, a compound is sulfonated and subsequently, by reaction with nitric acid, the sulfo group is replaced by the nitro group.

Other indirect nitration methods applied on an industrial scale, for nitrating phenols, comprise: first introduction of a nitroso groups into the phenol and then oxidizing it to the nitro group. The other method involves oxidation of a primary amino group to the nitro group.

In experimental work, indirect methods of introducing nitro groups find wide application as, for example, the substitution of a halogen (iodine or bromine in an alkyl iodide or bromide) by the nitro group, by means of silver nitrite (the Viktor Meyer reaction), and the new modification of this method described recently by Kornblum et al. [36, 37], in which alkyl halides are reacted with sodium nitrite.

In aromatic compounds, an amino group may be substituted by the nitro group by diazotization and reacting with nitric acid in the presence of cuprous salts (the Sandmeyer reaction). This method is used for laboratory work only and is described in textbooks on preparative organic chemistry.

Three types of nitration reactions are distinguished with respect to the chemical structure of compounds resulting from nitration processes. These are :

(1) C-nitration, leading to the formation of “true” nitro compounds, having the nitro group attached to a carbon atom: C-NO₂, such as aromatic and aliphatic nitro compounds.

(2) O-nitration, leading to the formation of nitric acid esters, with the nitro group attached to an oxygen atom: C-O-NO₂, for example trinitroglycerine, ethylene glycol dinitrate, etc.

(3) N-nitration, leading to the formation of nitramines with the nitro group attached to a nitrogen atom of an amine or amide group: N-NO₂, eg., nitrourea.

2.4 General Information on Nitro Compounds

Nitro compounds are substances in which the nitro group is directly attached to a carbon atom: -C-NO₂. Depending on how many hydrogen atoms linked with a carbon, they are known as primary (-CH₂-NO₂), secondary (CH-NO₂) and tertiary (C-NO₂) nitro compounds. All aromatic nitro compounds are tertiary derivatives. Aliphatic or aryl-aliphatic nitro compounds can be primary, secondary and tertiary [32].

2.5 Reactivity of the Nitro Group

Aromatic nitro compounds which are of course tertiary, form a separate group of compounds, differing from the aliphatic derivatives in many respects. For this reason they deserve special attention and are widely used in dye and ammunition industry. The attachment of nitro groups to the aromatic ring affects their reactivity. For example, nitro groups in *ortho* and *para* positions in relation to each other are rather reactive, and one of them can be substituted relatively easily.

Only the nitro groups in the *meta* position to each other are stable. Thus, one of the nitro groups in the unsymmetrical trinitrotoluene's (isomers or TNT) can readily be substituted. This is a consequence of the substitution rule, that the nitro group directs a new entrant group towards *meta* position [32].

2.6 Nitro Compounds as Explosives

Among aliphatic nitro compounds nitromethane was recognized as an explosive material long time after its discovery. Tetranitromethane is not explosive but can form an explosive when mixed with combustible substances. Tetranitromethane in the mixture acts as an oxygen carrier. As explosives nitro derivatives of aromatic compounds are of greatest practical importance. It is usually considered that only those nitro compounds possess explosive properties which contain at least two nitro groups attached to one benzene ring. However, Berthelot [38] noticed as long ago, in 1887 that the presence of even one nitro group is sufficient to increase the ease of thermal decomposition of an aromatic compound. This was later confirmed by Datta and Chatterje [39], and Condit and Haynor [40] when studying the temperatures of thermal decomposition of nitro compounds. Nevertheless, among aromatic nitro compounds only those which have three or more nitro groups of one benzene ring (and some of those which have two) exhibit distinctly marked explosive properties. Among the compounds which have two nitro groups, only dinitrobenzenes and dinitrotoluenes are recognized as explosives while dinitronaphthalenes are on the borderline between explosive and non-explosive substances. Trinitronaphthalenes have explosive properties similar to those of dinitrobenzene, since the ratio between number of nitro groups and carbon atoms is approximately the same for both compounds. For this reason, generally mononitro compounds are considered only from the viewpoint of their utilization as intermediates for the preparation of higher nitrated products. Aromatic nitro compounds are obtained from the corresponding aromatic compounds by classical nitration methods using mixtures of nitric and sulfuric acids [32]. Explosive aromatic nitro compounds exhibit a high degree of chemical

stability and undergo no changes during storage. They differ from other explosives by possessing a low sensitivity to impact and friction.

2.7 Thermochemistry of Explosives

Thermochemistry is an important part of explosive chemistry: it provides information on the type of chemical reactions, energy changes, mechanisms and kinetics which occur when a material undergoes an explosion.

When an explosive reaction takes place, the explosive molecule breaks apart into its constituent atoms. This is quickly followed by a rearrangement of the atoms into a series of small, stable molecules. These molecules are usually water (H_2O), carbondioxide (CO_2), carbon monoxide (CO) and nitrogen (N_2). There are also molecules of hydrogen (H_2), carbon (C), aluminium oxide (Al_2O_3), sulfur dioxide (SO_2), etc., found in the products of some explosives. The nature of the products depends upon the amount of oxygen available during the reaction. This supply of oxygen depends in turn upon the quantity of oxidizing atoms which are present in the explosive materials.

2.7.1 Oxygen Balance

If the amount of oxygen present in the explosive molecule is insufficient for the complete oxidation a negative oxygen balance results; this can be seen in the molecule of TNT. Nitroglycerine, however, has a high portion of oxygen, more than required for complete oxidation of its fuel elements and therefore has a positive oxygen balance. This oxygen balance can be defined as the amount of oxygen, expressed in weight percent, liberated as a result of the complete conversion of the explosive material to carbon dioxide, water, sulfur dioxide, aluminium oxide, etc.

It can be seen from Table 2.1 that explosive substances may have a positive or negative oxygen balance. The oxygen balance provides information on the types of gases liberated. If the oxygen balance is large and negative then there is not enough oxygen for carbondioxide to be formed. Consequently, toxic gases such as

carbon monoxide will be liberated. This is very important for commercial explosives as the amount of toxic gases liberated must be kept to a minimum.

Table 2.1 Oxygen balance of some explosives

Explosive substance	Empirical Formula	Oxygen balance/% weight
Ammonium nitrate	NH_4NO_3	+19.99
Nitroglycerine	$\text{C}_3\text{H}_5\text{N}_3\text{O}_9$	+3.50
EGDN	$\text{C}_2\text{H}_4\text{N}_2\text{O}_6$	0.00
PETN	$\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$	-10.13
RDX	$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$	-21.60
HMX	$\text{C}_4\text{H}_8\text{N}_8\text{O}_8$	-21.62
Nitroguanidine	$\text{CH}_4\text{N}_4\text{O}_2$	-30.70
Picric acid	$\text{C}_6\text{H}_3\text{N}_3\text{O}_7$	-45.40
Tetryl	$\text{C}_7\text{H}_5\text{N}_5\text{O}_8$	-47.39
TATB	$\text{C}_6\text{H}_6\text{N}_6\text{O}_6$	-55.80
HSN	$\text{C}_{14}\text{H}_6\text{N}_6\text{O}_{12}$	-67.60
TNT	$\text{C}_7\text{H}_5\text{N}_3\text{O}_6$	-74.00

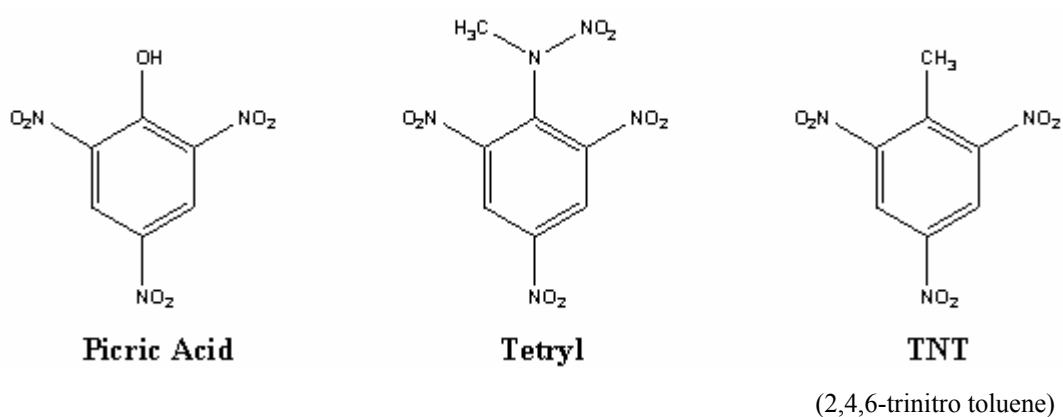
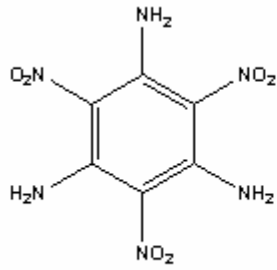
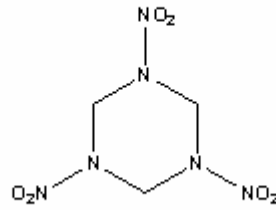


Figure 2.1 Chemical structures and names of some explosives

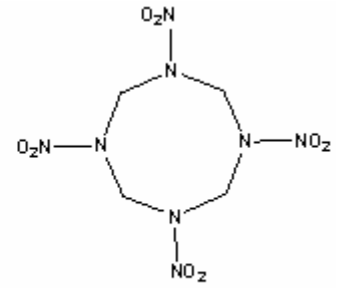


TATB

(1,3,5-triamino-2,4,6-trinitrobenzene)
(cyclotetramethylenetrinitramine)

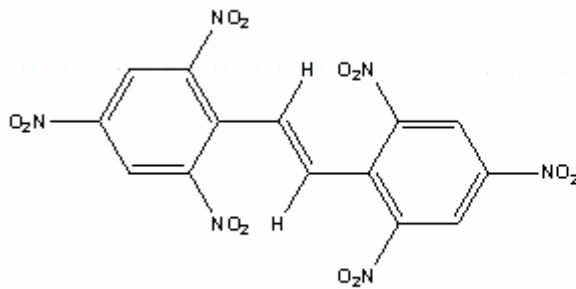


RDX



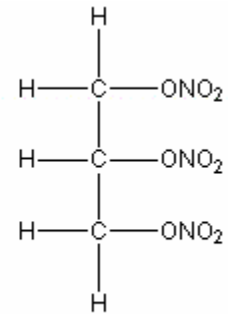
HMX

(cycloheximethylenetrinitramine)

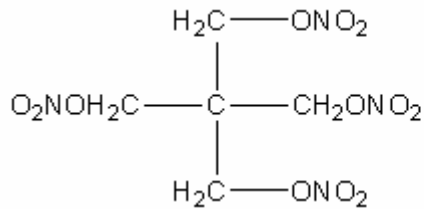


HNS

(hexanitrostilbene)

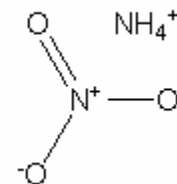


Nitroglycerine

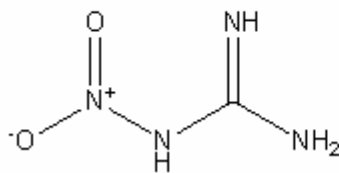


PETN

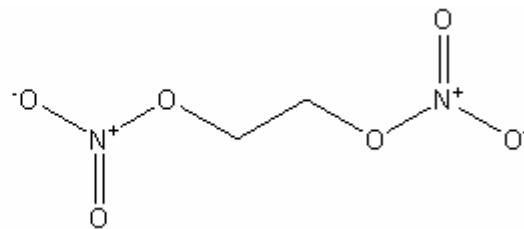
(pentaerythritol tetranitrate)



Ammonium Nitrate



Nitroguanidine



EGDN

(ethylene glycol dinitrate)

Figure 2.1 Continued

The oxygen balance does not provide information on the energy changes which take place during an explosion. This information can be obtained by calculating the heat liberated during decomposition of explosive substances, known as the 'heat of explosion'. In order to calculate the heat of explosion, the decomposition products of the explosive must be determined, since the magnitude of the heat of explosion is dependent upon the thermodynamic state of its products. The decomposition process will be by detonation in the case of primary and secondary explosives, and burning in the case of gunpowders and propellants.

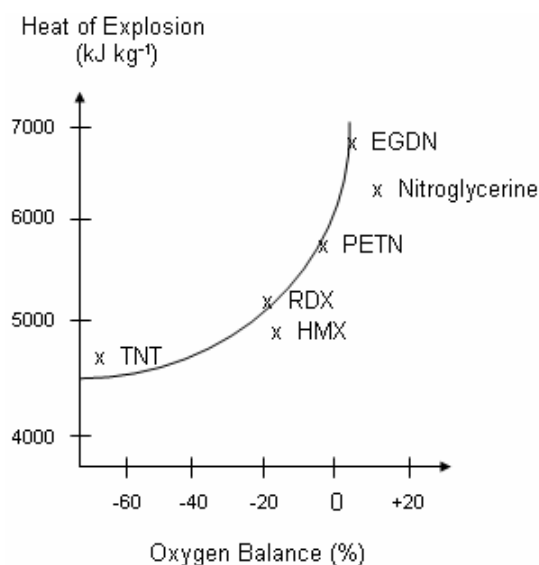


Figure 2.2 The effect of the oxygen balance on the heat of explosion

The heat of explosion reaches a maximum for an oxygen balance of zero, since this corresponds to the stoichiometric oxidation of carbon to carbon dioxide and hydrogen to water. The oxygen balance can therefore be used to optimize the composition of the explosive to give an oxygen balance as close to zero as possible.

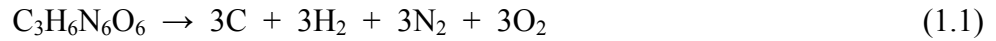
The effect of the oxygen balance on the heat of explosion can be seen from Figure 2.2.

2.7.2 Heats of Formation

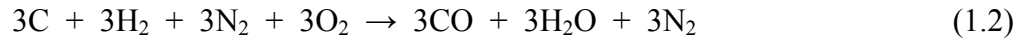
The heats of formation for a reaction containing explosive chemicals can be described as the total heat evolved when a given quantity of a substance is completely oxidized in an excess amount of oxygen, resulting in the formation of carbon dioxide, water and sulfur dioxide. For explosive substances which do not contain sufficient oxygen in its molecule for complete oxidation, i.e. TNT, products such as carbon monoxide, carbon and hydrogen gas are formed. The energy liberated during the formation of these products is known as the 'heat of explosion'. If these products are then isolated and allowed to burn in excess oxygen to form substances like carbon dioxide, water, etc., the heat evolved added to the heat of explosion would be equal to the 'heat of combustion'. Consequently, the value for the heat of combustion is higher than the value for the heat of explosion for the substances which have insufficient oxygen for complete oxidation. For explosive substances with positive oxygen balance, i.e. nitroglycerine, there is generally no difference between the value for the heat of explosion and that of the heat of combustion.

The value for the heat of formation can be negative or positive. If the value is negative, heat is liberated during the reaction and the reaction is exothermic; whereas if the value is positive, heat is absorbed during the reaction and the reaction is endothermic. For reactions involving explosive components the reaction is always exothermic. In an exothermic reaction the energy evolved may appear in many forms, but for practical purposes it is usually obtained in the form of heat. The energy liberated when explosive deflagrate is called the 'heat of deflagration', whereas the energy liberated by detonating explosives is called the 'heat of detonation' in kJ mol^{-1} or the 'heat of explosion' in kJ kg^{-1} .

In a chemical reaction involving explosives, energy is initially required to break the bonds of explosive into its constituent elements as shown in Reaction 1.1 for RDX.



These elements quickly form new bonds with the release of a greater quantity of energy as shown in Reaction 1.2.



The molecules of an explosive are first raised to a higher energy level through input of the ‘heats of atomization’ in order to break their interatomic bonds. Then the atoms rearrange themselves into new molecules, releasing a larger quantity of heat and dropping to an energy level lower than the original as shown in Figure 2.3.

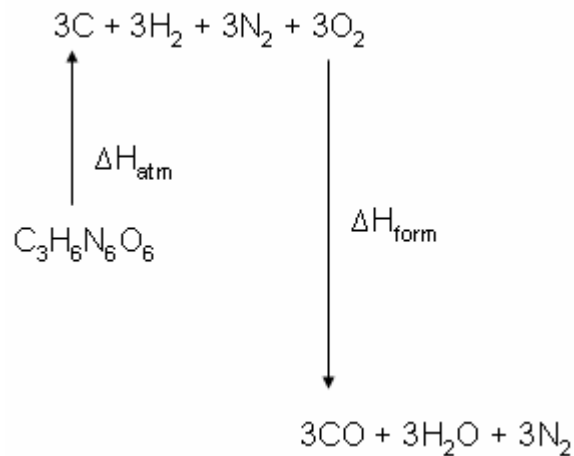


Figure 2.3 Energy is taken in to break the bonds of RDX into its constituent elements, then energy is released when new bonds are formed

The thermodynamic path presented in Figure 2.3 will most likely not be the same as the ‘kinetic path’. For instance, the reaction may take place in several stages involving complex systems of reaction chains, etc. Nevertheless, the energy evolved depends only on the initial and final states and not on the intermediate

ones. Once the reaction is completed, the net heat evolved is exactly the same as if the reactant molecules were first dissociated into their atoms, and then reacted directly to form the final products (Hess's Law).

2.7.3 Heat of Explosion

When an explosive is initiated either to burning or detonation, its energy is released in the form of heat. The liberation of heat under adiabatic conditions is called the 'heat of explosion', denoted by the letter Q . The heat of explosion provides information about the work capacity of the explosive, where the effective propellants and secondary explosives generally have high values of Q . For secondary explosives in detonating devices, the heat of explosion is conventionally expressed in terms of constant volume conditions Q_v .

Consider an explosive which is initiated by a stimulus of negligible thermal proportions. The explosion can be represented by the irreversible process as shown in Figure 2.4, where Q is the value of the heat ultimately lost to the surroundings.

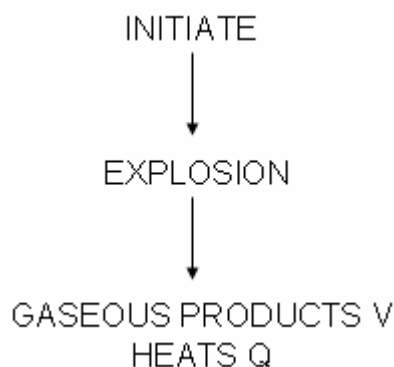


Figure 2.4 Schematic diagram of the irreversible explosion process

Under constant volume conditions Q_v can be calculated from the Standard internal energies of formation for the products $\Delta U^\circ_{f(\text{products})}$ and Standard internal energies of formation for the explosive components $\Delta U^\circ_{f(\text{explosive components})}$ as shown in Equation 1.3.

$$Q_v = \Sigma \Delta U^\circ_{f(\text{products})} - \Delta U^\circ_{f(\text{explosive components})} \quad (1.3)$$

A similar expression is given for the heat of explosion under constant pressure conditions as shown in Equation 1.4, where ΔH°_f represents the corresponding standard enthalpies of formation:

$$Q_p = \Sigma \Delta H^\circ_{f(\text{products})} - \Delta H^\circ_{f(\text{explosive components})} \quad (1.4)$$

In considering the thermochemistry of solid and liquid explosives, it is usually adequate, for practical purposes, to treat the state functions ΔH and ΔU as approximately the same. Consequently, heats, or entalpy terms, tend to be used for both constant pressure and constant volume conditions.

Therefore, the heat of explosion Q can be calculated from the difference between the sum of energies for the formation of the explosive components and the sum of the energies for the formation of the explosion products, as shown in Equation 1.5.

$$Q = \Delta H_{(\text{reaction})} = \Sigma \Delta H_{f(\text{products})} - \Delta H_{f(\text{explosive components})} \quad (1.5)$$

Since the conditions of loading density, temperature, pressure, etc., are not taken into consideration, the calculated values do not exactly agree with those obtained experimentally.

The value for Q in kJ kg^{-1} is generally derived from the heat of detonation ΔH_d in kJ mol^{-1} .

2.7.4 Detonation

When a loud, sharp bang is heard similar to a grenade or a bomb exploding it is known as detonation. It can be achieved either by burning to detonation or by

an initial shock. Explosive substances which on initiation decompose via the passage of a shockwave rather than a thermal mechanism are called detonating explosives. The velocity of the shockwave in solid or liquid explosive is between 1500 and 9000 m s⁻¹. Detonation velocity is an important parameter to determine the performance of an explosive. Generally, high explosives (secondary explosives) have high value of detonation velocity. Therefore, the velocity of detonation for secondary explosives is generally higher than that for primary explosives.

For homogeneous commercial-type explosives the velocity of detonation increases and then decreases as the compaction density of the explosive composition increases. The compaction of heterogeneous explosives makes the transition from deflagration to detonation very difficult.

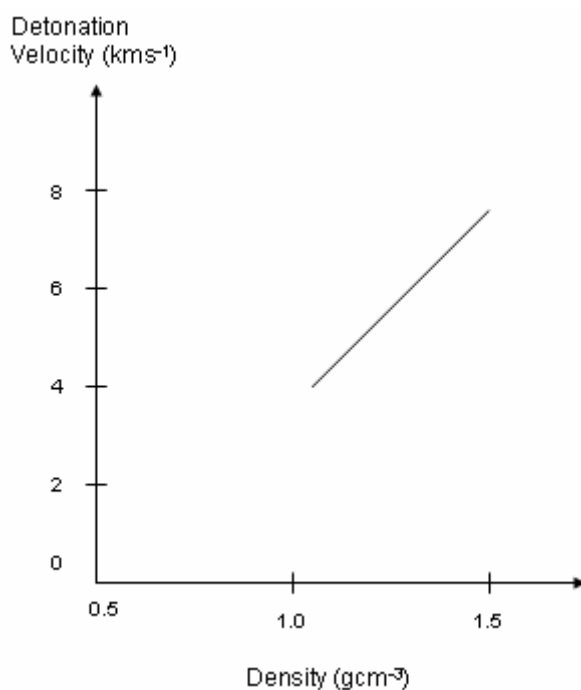


Figure 2.5 Change in velocity of detonation as a function of density for a secondary explosive, i.e. TNT

For homogeneous, military-type explosives the velocity of detonation will increase as the compaction density of the explosive composition increases as shown in Figure 2.5.

CHAPTER 3

COMPUTATIONAL CHEMISTRY

3.1. Introduction

Computational chemistry is used in a number of different ways. One particularly important way is to model a molecular system prior to synthesizing that molecule in the laboratory. Although computational models may not be perfect, they are often good enough to rule out 90% of possible compounds as being unsuitable for their intended use. This is very useful information because synthesizing a single compound could require months of labor and raw materials, and generate toxic waste. A second use of computational chemistry is in understanding a problem more completely. There are some properties of a molecule that can be obtained computationally more easily than by experimental means. There are also insights into molecular bonding, which can be obtained from the results of computations, that cannot be obtained from any experimental method. Thus, many experimental chemists are now using computational modeling to gain additional understanding of the compounds being examined in the laboratory. As computational chemistry has become easier to use, professional computational chemists have shifted their attention to more difficult modeling problems. No matter how easy computational chemistry becomes, there will always be problems so difficult that only an expert in the field can tackle them.

Computational chemistry (also called molecular modelling; the two terms mean about the same thing) is a set of techniques for investigating chemical problems on a computer. Questions commonly investigated computationally are :

- *Molecular geometry* : The shapes of molecules – bond lengths, angles, and dihedrals.
- *Energies of molecules and transition states* : This tells us which isomer is favored at equilibrium, and (from transition state and reactant energies) how fast a reaction should go.
- *Chemical reactivity* : For example, knowing where the electrons are concentrated (nucleophilic sites) and where they want to go (electrophilic sites) enables us to predict where various kinds of reagents will attack a molecule.
- *IR, UV, and NMR spectra* : These can be calculated, and if the molecule is unknown, someone trying to make it knows what to look for.
- *The interaction of a substrate with an enzyme* : Seeing how a molecule fits into the active site of an enzyme is one approach to designing better drugs.
- *The physical properties of substances* : These depend on the properties of individual molecules and on how the molecules interact in the bulk material. For example, the strength and melting point of a polymer (e.g. a plastic) depend on how well the molecules fit together and on how strong the forces between them are. People who investigate things like this work in the field of materials science.

In studying these questions computational chemists have a selection of methods at their disposal. The main tools available belong to five broad classes as described below :

- Molecular mechanics (MM)
- Semiempirical (SE) methods
- *Ab initio* methods
- Density functional theory
- Molecular dynamics and Monte Carlo simulations

3.2 Semiempirical Methods

Semiempirical calculations are set up with the same general structure as a HF calculation in that they have a Hamiltonian and a wave function. Within this framework, certain pieces of information are approximated or completely omitted. Usually, the core electrons are not included in the calculation and only a minimal basis set is used. Also, some of the two-electron integrals are omitted. In order to correct for the errors introduced by omitting part of the calculation, the method is parameterized. Parameters to estimate the omitted values are obtained by fitting the results to experimental data or *ab initio* calculations. Often, these parameters replace some of the integrals that are excluded.

The advantage of semiempirical calculations is that they are much faster than *ab initio* calculations. The disadvantage of semiempirical calculations is that the results can be erratic and fewer properties can be predicted reliably. If the molecule being computed is similar to molecules in the database used to parameterize the method, then the results may be very good. If the molecule being computed is significantly different from anything in the parameterization set, the answers may be very poor. For example, the carbon atoms in cyclopropane and cubane have considerably different bond angles from those in most other compounds; thus, these molecules may not be predicted well unless they were included in the parameterization. However, semiempirical methods are not as sensitive to the parameterization set as are molecular mechanics calculations.

Semiempirical methods are parameterized to reproduce various results. Most often, geometry and energy (usually the heat of formation) are used. Some researchers have extended this by including dipole moments, heats of reaction, and

ionization potentials in the parameterization set. A few methods have been parameterized to reproduce a specific property, such as electronic spectra or NMR chemical shifts. Semiempirical calculations can be used to compute properties other than those in the parameterization set.

Many semiempirical methods compute energies as heats of formation. The researcher should not add zero-point corrections to these energies because the thermodynamic corrections are implicit in the parameterization.

Semiempirical calculations have been very successful in the description of organic chemistry, where there are only a few elements used extensively and the molecules are of moderate size. Some semiempirical methods have been devised specifically for the description of inorganic chemistry as well. The followings are some of the commonly used semiempirical methods.

3.2.1 The Austin Model 1 Method

The Austin Model 1 (AM1) method is still popular for modeling organic compounds. AM1 generally predicts the heats of formation (ΔH_f) more accurately than MNDO, although a few exceptions involving Br atoms have been documented. Depending on the nature of the system and information desired, either AM1 or PM3 will often give the most accurate results obtainable for organic molecules with semiempirical methods.

There are some known strengths and limitations in the results obtained from these methods. AM1 tends to predict results for aluminum better than PM3. It tends to poorly predict nitrogen pyramidalization. AM1 tends to give O-Si-O bonds that are not bent enough. There are some known limitations to AM1 energies, such as predicting rotational barriers to be one-third the actual barrier and predicting five-membered rings to be too stable. The predicted heat of formation tends to be inaccurate for molecules with a large amount of charge localization. Geometries involving phosphorus are predicted poorly. There are systematic errors in alkyl group energies predicting them to be too stable. Nitro groups are too positive in energy. The peroxide bond is too short by about 0.17Å. Hydrogen bonds are predicted to have the correct strength, but often the wrong orientation. On average,

AM1 does not predict energies and geometries better than PM3. Computed bond enthalpies are consistently low.

3.2.2 Parameterization Method 3

Parameterization method 3 (PM3) uses nearly the same equations as the AM1 method along with an improved set of parameters. The PM3 method is also currently extremely popular for organic systems. It is more accurate than AM1 for hydrogen bond angles, but AM1 is more accurate for hydrogen bond energies. The PM3 and AM1 methods are also more popular than other semiempirical methods due to the availability of algorithms for including solvation effects in these calculations.

There are also some known strengths and limitations of PM3. Overall heats of formation are more accurate than with AM1. Hypervalent molecules are also predicted more accurately. PM3 tends to predict that the barrier to rotation around the C-N bond in peptides is too low. Bonds between Si and the halide atoms are too short. PM3 also tends to predict incorrect electronic states for germanium compounds. It tends to predict sp^3 nitrogen as always being pyramidal. Some spurious minima are predicted. Proton affinities are not accurate. Some polycyclic rings are not flat. The predicted charge on nitrogen is incorrect. Nonbonded distances are too short. Hydrogen bonds are too short by about 0.1\AA , but the orientation is usually correct. On average, PM3 predicts energies and bond lengths more accurately than AM1.

Semiempirical methods can provide results accurate enough to be useful, particularly for organic molecules with computation requirements low enough to make them convenient on PC. These methods are generally good for predicting molecular geometries and energetics. Semiempirical methods can be used for predicting vibrational modes and transition structures, but do so less reliably than *ab initio* methods. Semiempirical calculations generally give poor results for van der Waals and dispersion intermolecular forces, due to the lack of diffuse basis functions.

3.3 *Ab initio* Methods

The term *ab initio* is Latin for “from the beginning.” This name is given to computations that are derived directly from theoretical principles with no inclusion of experimental data. Various approximations are involved in *ab initio*. The approximations made are usually mathematical approximations, such as using a simpler functional form for a function or finding an approximate solution to a differential equation.

3.3.1 Hartree-Fock Approximation

The most common type of *ab initio* calculation is called a Hartree-Fock calculation (abbreviated HF), in which the primary approximation is the central field approximation. This means that the Coulombic electron-electron repulsion is taken into account by integrating the repulsion term. This gives the average effect of repulsion, but not the explicit repulsion interaction. This is a variational calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy. The energies are calculated in units called Hartrees (1 Hartree = 27.2116 eV). Because of the central field approximation, energies from HF calculations are always greater than the exact energy and tend to a limiting value called the Hartree-Fock limit as the basis set is improved.

One of the advantages of this method is that it breaks the many-electron Schrödinger equation [41] into many simpler one-electron equations. Each one-electron equation is solved to yield a single-electron wave function, called an orbital, and an energy, called an orbital energy. The orbital describes the behavior of an electron in the net field of all the other electrons.

The second approximation in HF calculations is due to the fact that the wave function must be described by some mathematical function, which is known exactly for only a few one-electron systems. The functions used most often are linear combinations of Gaussian-type orbitals $\exp(-ar^2)$, abbreviated as GTO. The wave function is formed from linear combinations of atomic orbitals or, stated more correctly, from linear combinations of basis functions. Because of this

approximation, most HF calculations give a computed energy greater than the Hartree-Fock limit. The exact set of basis functions used is often specified by an abbreviation, such as STO-3G or 6-311++G(d,p).

The Gaussian functions are multiplied by an angular function in order to give the orbital the symmetry of a s, p, d, and so on. A constant angular term yields s symmetry. Angular terms of x, y, z give p symmetry. Angular terms of xy, xz, yz, x^2-y^2 , $4z^2-2x^2-2y^2$ yield d symmetry. This pattern can be continued for the other orbitals.

These orbitals are then combined into a determinant. This is done to satisfy two requirements of quantum mechanics. One is that the electrons must be indistinguishable. By having a linear combination of orbitals in which each electron appears in each orbital, it is only possible to say that an electron was put in a particular orbital but not which electron it is. The second requirement is that the wave function for fermions (an electron is a fermion) must be antisymmetric with respect to interchanging two particles. Thus, if electron 1 and electron 2 are switched, the sign of the total wave function must change and only the sign can change. This is satisfied by a determinant because switching two electrons is equivalent to interchanging two columns of the determinant, which changes its sign.

The functions put into the determinant do not need to be individual GTO functions, called Gaussian primitives. They can be a weighted sum of basis functions on the same atom or different atoms. Sums of functions on the same atom are often used to make the calculation run faster. Sums of basis functions on different atoms are used to give the orbital a particular symmetry. For example, a water molecule with C_{2v} symmetry will have orbitals that transform as A1, A2, B1, B2, which are the irreducible representations of the C_{2v} point group. The resulting orbitals that use functions from multiple atoms are called molecular orbitals. This is done to make the calculation run much faster. Any overlap integral over orbitals of different symmetry does not need to be computed because it is zero by symmetry.

The steps in a Hartree-Fock calculation start with an initial guess for the orbital coefficients, usually using a semiempirical method. This function is used to calculate an energy and a new set of orbital coefficients, which can then be used to

obtain a new set, and so on. This procedure continues iteratively until the energies and orbital coefficients remain constant from one iteration to the next. This is called having the calculation converge. There is no guarantee the calculation will converge. In cases where it does not, some technical expertise is required to fix the problem. This iterative procedure is called a self-consistent field procedure (SCF). Some researchers refer to these as SCF calculations to distinguish them from the earlier method created by Hartree, but HF is used more widely.

A variation on the HF procedure is the way that orbitals are constructed to reflect paired or unpaired electrons. If the molecule has a singlet spin, then the same orbital spatial function can be used for both the α and β spin electrons in each pair. This is called the restricted Hartree-Fock method (RHF).

There are two techniques for constructing HF wave functions of molecules with unpaired electrons. One technique is to use two completely separate sets of orbitals for the α and β electrons. This is called an unrestricted Hartree-Fock wave function (UHF) [42]. This means that paired electrons will not have the same spatial distribution. This introduces an error into the calculation, called spin contamination. Spin contamination might introduce an insignificant error or the error could be large enough to make the results unusable depending on the chemical system involved. UHF calculation are popular because they are easy to implement and run fairly efficiently.

Another way of constructing wave functions for open-shell molecules is the restricted open shell Hartree-Fock method (ROHF). In this method, the paired electrons share the same spatial orbital; thus, there is no spin contamination. The ROHF technique is more difficult to implement than UHF and may require slightly more CPU time to execute. ROHF is primarily used for cases where spin contamination is large using UHF.

For singlet spin molecules at the equilibrium geometry, RHF and UHF wave functions are almost always identical. RHF wave functions are used for singlets because the calculation takes less CPU time. In a few rare cases, a singlet molecule has biradical resonance structures and UHF will give a better description of the molecule (i.e., ozone).

The RHF scheme results in forcing electrons to remain paired. This means that the calculation will fail to reflect cases where the electrons should uncouple. For example, a series of RHF calculations for H_2 with successively longer bond lengths will show that H_2 dissociates into H^+ and H^- , rather than two H atoms. This limitation must be considered whenever processes involving pairing and unpairing of electrons are modeled. This is responsible for certain systematic errors in HF results, such as activation energies that are too high, bond lengths slightly too short, vibrational frequencies too high, and dipole moments and atomic charges that are too large. UHF wave functions usually dissociate correctly.

3.3.2 Correlation

One of the limitations of HF calculations is that they do not include electron correlation. This means that HF takes into account the average effect of electron repulsion, but not the explicit electron-electron interaction. Within HF theory the probability of finding an electron at some location around an atom is determined by the distance from the nucleus but not the distance to the other electrons as shown in Figure 3.1. This is not physically true, but it is the consequence of the central field approximation, which defines the HF method.

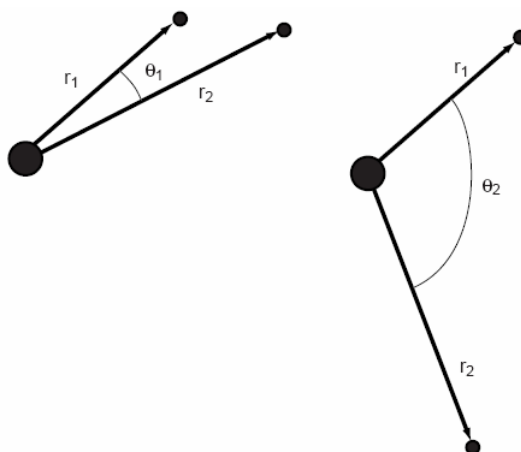


Figure 3.1 Two arrangements of electrons around the nucleus of an atom having the same probability within HF theory, but not in correlated calculations

A number of types of calculations begin with a HF calculation and then correct for correlation. Some of these methods are Møller-Plesset [43] perturbation theory (MPn, where n is the order of correction), the generalized valence bond (GVB) method, multi-configurational self-consistent field (MCSCF), configuration interaction (CI), and coupled cluster theory (CC) [44-46]. As a group, these methods are referred to as correlated calculations. Correlation is important for many different reasons. Including correlation generally improves the accuracy of computed energies and molecular geometries. For organic molecules, correlation is an extra correction for very-high-accuracy work, but is not generally needed to obtain quantitative results. One exception to this rule are compounds exhibiting Jahn-Teller distortions, which often require correlation to give quantitatively correct results. An extreme case is transition metal systems, which often require correlation in order to obtain results that are qualitatively correct.

In general, *ab initio* calculations give very good qualitative results and can yield increasingly accurate quantitative results as the molecules in question become smaller. The advantage of *ab initio* methods is that they eventually converge to the exact solution once all the approximations are made sufficiently small in magnitude. In general, the relative accuracy of results is

$$\text{HF} \ll \text{MP2} < \text{CISD} \approx \text{MP4} \approx \text{CCSD} < \text{CCSD(T)} < \text{CCSDT} < \text{Full CI}$$

However, this convergence is not monotonic. Sometimes, the smallest calculation gives a very accurate result for a given property. There are four sources of error in *ab initio* calculations:

1. The Born-Oppenheimer approximation
2. The use of an incomplete basis set
3. Incomplete correlation
4. The omission of relativistic effects

The disadvantage of *ab initio* methods is that they are expensive. These methods often take enormous amounts of computer CPU time, memory, and disk space. The HF method scales as N^4 , where N is the number of basis functions. This

means that a calculation twice as big takes 16 times as long (2^4) to complete. Correlated calculations often scale much worse than this. In practice, extremely accurate solutions are only obtainable when the molecule contains a dozen electrons or less. However, results with an accuracy rivaling that of many experimental techniques can be obtained for moderate-size organic molecules. The minimally correlated methods, such as MP2 and GVB, are often used when correlation is important to the description of large molecules.

3.4 Density Functional Theory

Density functional theory (DFT) has become very popular in recent years. This is justified based on the pragmatic observation that it is less computationally intensive than other methods with similar accuracy. This theory has been developed more recently than other *ab initio* methods. Because of this, there are classes of problems not yet explored with this theory, making it all the more crucial to test the accuracy of the method before applying it to unknown systems.

3.4.1 Basic Theory

The premise behind DFT is that the energy of a molecule can be determined from the electron density instead of a wave function. This theory originated with a theorem by Hohenberg and Kohn [47] that stated this was possible. The original theorem applied only to finding the ground-state electronic energy of a molecule. A practical application of this theory was developed by Kohn and Sham [48] who formulated a method similar in structure to the Hartree-Fock method.

In this formulation, the electron density is expressed as a linear combination of basis functions similar in mathematical form to HF orbitals. A determinant is then formed from these functions, called Kohn-Sham orbitals. It is the electron density from this determinant of orbitals that is used to compute the energy. This procedure is necessary because Fermion systems can only have electron densities that arise from an antisymmetric wave function. There has been some debate over the interpretation of Kohn-Sham orbitals. It is certain that they are not mathematically equivalent to either HF orbitals or natural orbitals from correlated

calculations. However, Kohn-Sham orbitals do describe the behavior of electrons in a molecule, just as the other orbitals mentioned do. DFT orbital eigenvalues do not match the energies obtained from photoelectron spectroscopy experiments as well as HF orbital energies do. The questions still being debated are how to assign similarities and how to physically interpret the differences.

A density functional is then used to obtain the energy for the electron density. A functional is a function of a function, in this case, the electron density. The exact density functional is not known. Therefore, there is a whole list of different functionals that may have advantages or disadvantages. Some of these functionals were developed from fundamental quantum mechanics and some were developed by parameterizing functions to best reproduce experimental results. Thus, there are in essence *ab initio* and semiempirical versions of DFT. DFT tends to be classified either as an *ab initio* method or in a class by itself.

The advantage of using electron density is that the integrals for Coulomb repulsion need be done only over the electron density, which is a three-dimensional function, thus scaling as N^3 . Furthermore, at least some electron correlation can be included in the calculation. This results in faster calculations than HF calculations (which scale as N^4) and computations that are a bit more accurate as well. The better DFT functionals give results with an accuracy similar to that of an MP2 calculation.

Density functionals can be broken down into several classes. The simplest is called the $X\alpha$ method. This type of calculation includes electron exchange but not correlation. It was introduced by J. C. Slater [49], who in attempting to make an approximation to Hartree-Fock [50,51] unwittingly discovered the simplest form of DFT. The $X\alpha$ method is similar in accuracy to HF and sometimes better.

The simplest approximation to the complete problem is one based only on the electron density, called a local density approximation (LDA). For high-spin systems, this is called the local spin density approximation (LSDA). LDA calculations have been widely used for band structure calculations. Their performance is less impressive for molecular calculations, where both qualitative and quantitative errors are encountered. For example, bonds tend to be too short

and too strong. In recent years, LDA, LSDA, and VWN (the Vosko, Wilks, and Nusair [52] functional) have become synonymous in the literature.

A more complex set of functionals utilizes the electron density and its gradient. These are called gradient-corrected methods. There are also hybrid methods that combine functionals from other methods with pieces of a Hartree-Fock calculation, usually the exchange integrals.

In general, gradient-corrected or hybrid calculations give the most accurate results. However, there are a few cases where $X\alpha$ and LDA do quite well. LDA is known to give less accurate geometries and predicts binding energies significantly too large. The current generation of hybrid functionals [53] are a bit more accurate than the present gradient-corrected techniques.

Given the fact that DFT is newer than the other *ab initio* methods, it is quite likely that conventional wisdom over which technique works best will shift with the creation of new techniques in the not too distant future. DFT's recent heavy usage has been due to the often optimal accuracy versus CPU time. The B3LYP method with basis sets of 6-31G* or larger is the method of choice for many organic molecule calculations. Unfortunately, there is no systematic way to improve DFT calculations, thus making them unusable for very-high-accuracy work.

3.5 Using Existing Basis Sets

A basis set is a set of functions used to describe the shape of the orbitals in an atom. Molecular orbitals and entire wave functions are created by taking linear combinations of basis functions and angular functions. Most semiempirical methods use a predefined basis set. When *ab initio* or density functional theory calculations are done, a basis set must be specified. Although it is possible to create a basis set from scratch, most calculations are done using existing basis sets. The type of calculation performed and basis set chosen are the two biggest factors in determining the accuracy of results.

3.5.1 Notation

Most calculations today are done by choosing an existing segmented Gaussian type orbitals (GTO) basis set. These basis sets are identified by one of a number of notation schemes. These abbreviations are often used as the designator for the basis set in the input to *ab initio* computational chemistry programs. The following is a look at the notation for identifying some commonly available contracted GTO basis sets.

The smallest basis sets are called minimal basis sets. The most popular minimal basis set is the **STO-3G** set. This notation indicates that the basis set approximates the shape of a STO orbital by using a single contraction of three GTO orbitals. One such contraction would then be used for each orbital, which is the definition of a minimal basis. Minimal basis sets are used for very large molecules, qualitative results, and in certain cases quantitative results. There are **STO-nG** basis sets for $n = 2-6$.

Another family of basis sets, commonly referred to as the Pople basis sets, are indicated by such a notation **6-31G** [54]. This notation means that each core orbital is described by a single contraction of six GTO primitives and each valence shell orbital is described by two contractions, one with three primitives and the other with one primitive. These basis sets are very popular, particularly for organic molecules. Other Pople basis sets in this set are 3-21G [55], 4-31G, 4-22G, 6-21G, 6-311G [56], and 7-41G.

The Pople basis set notation can be modified by adding one or two asterisks, such as 6-31G* or 6-31G(d,p). A single asterisk means that a set of d primitives has been added to atoms other than hydrogen. Two asterisks mean that a set of p primitives has been added to hydrogen as well. These are called polarization functions because they give the wave function more flexibility to change shape. Adding polarization functions usually decreases the variational total energy by about the same amount as adding another contraction. However, this energy change is almost completely systematic, so it changes the relative energies very little. Polarization functions are used because they often result in more accurate computed geometries and vibrational frequencies.

The **3-21G*** basis is an exception to the notation above. In this particular case, the d functions are added only to 2nd row atoms, Al through Ar. In order to indicate this difference, this basis is sometimes given the notation **3-21G(*)**. One or two plus signs can also be added, such as **6-31+G*** or **6-31++G***. A single plus sign indicates that diffuse functions have been added to atoms other than hydrogen. The second plus sign indicates that diffuse functions are being used for all atoms. These diffuse functions are primitives with small exponents, thus describing the shape of the wave function far from the nucleus. Diffuse functions are used for anions, which have larger electron density distributions. They are also used for describing interactions at long distances, such as van der Waals interactions. The effect of adding diffuse functions is usually to change the relative energies of the various geometries associated with these systems. Basis sets with diffuse functions are also called augmented basis sets. Very diffuse orbitals are called Rydberg orbitals since they are used to describe Rydberg states of molecules.

As the Pople basis sets have further expanded to include several sets of polarization functions, f functions and so on, there has been a need for a new notation. In recent years, the types of functions being added have been indicated in parentheses. An example of this notation is **6-31G(dp,p)** which means that extra sets of p and d functions have been added to nonhydrogens and an extra set of p functions have been added to hydrogens. Thus, this example is synonymous with **6-31+G(d,p)**.

Many basis sets are just identified by the author's surname and the number of primitive functions. Some examples of this are the Huzinaga, Dunning, and Duijneveldt basis sets. For example, **D95** and **D95V** are basis sets created by Dunning with nine s primitives and five p primitives. The **V** implies one particular contraction scheme for the valence orbitals. Another example would be a basis set listed as "Duijneveldt 13s8p".

In order to describe the number of primitives and contractions more directly, the notation **(6s,5p)→(1s,3p)** or **(6s,5p)→(1s,3p)** is sometimes used. This example indicates that six s primitives and five p primitives are contracted into one s contraction and three p contractions. Thus, this might be a description of the 6-311G basis set. However, this notation is not precise enough to tell whether the

three p contractions consist of three, one, and one primitives or two, two, and one primitives. The notation **(6,311)** or (6,221) is used to distinguish these cases. Some authors use round parentheses () to denote the number of primitives and square brackets [] to denote the number of contractions.

An older, but still used, notation specifies how many contractions are present. For example, the acronym **TZV** stands for triple-zeta valence, meaning that there are three valence contractions, such as in a 6-311G basis. The acronyms **SZ** and **DZ** stand for single zeta and double zeta, respectively. A **P** in this notation indicates the use of polarization functions. Since this notation has been used for describing a number of basis sets, the name of the set creator is usually included in the basis set name (i.e., Ahlrichs VDZ). If the author's name is not included, either the Dunning-Hay set is implied or the set that came with the software package being used is implied.

An extension of this last notation is **aug-cc-pVDZ**. The “aug” denotes that this is an augmented basis (diffuse functions are included). The “cc” denotes that this is a correlation-consistent basis, meaning that the functions were optimized for best performance with correlated calculations. The “p” denotes that polarization functions are included on all atoms. The “VDZ” stands for valence double zeta, meaning that the valence orbitals are described by two contractions. There is a family of correlation consistent basis sets created by Dunning and coworkers. These sets have become popular for high-accuracy correlated calculations. They have shown that large basis sets with high-angular-momentum polarization functions have a greater effect on the accuracy of correlated calculations than HF calculations. Because this family of basis sets was developed in a systematic way, many properties converge asymptotically as larger basis sets are chosen. This fact has been exploited by fitting the results of the same calculation with several basis sets to an exponential decay to predict the infinite basis set limit for HF calculations. A similar procedure has been used to predict the full CI limit from multireference valence CI calculations. This extrapolation has only been tested for total energies and a few other properties. The technique should be applicable to any property showing asymptotic convergence, but there is not yet a sufficient volume of literature to predict how accurate this extrapolation will be.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Method of Calculation

The Gaussian 03 package [57] was used as the calculation tool. Full optimization of all the bond lengths, bond angles and torsional angles was initially achieved by using molecular mechanics and then AM1 Self-Consistent Field Molecular Orbital (SCF-MO) methods successive by [58] at RHF level. The results from the AM1 method were selected as input and the structures were further optimized by employing spin-restricted Hartree-Fock (RHF) approach at the level [59-61] of the 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-pVDZ basis sets. Also, geometry optimizations were achieved within the framework of density functional theory (DFT, B3LYP) [62,63] at the level of 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-pVDZ (restricted closed-shell) bases sets. The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [64]. The term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [65] and Lee, Yang, Parr (LYP) correlation correction functional [66,67]. In order to compare the bond strengths, homolytic bond dissociation energy (BDE) calculations were performed at the levels of UB3LYP/6-311G(d,p). The homolytic BDE [68,69] is defined for the present case as: $BDE = E(X) + E(R) - E(R-X)$, where E stands for the respective total electronic energy corrected for the zero-point energy for each parent structure and the fragments (R and X) of the low-energy R-X bond scission reaction.

Nucleus independent chemical shift (NICS) calculations at the center of rings were performed on all the molecules using the gauge invariant atomic orbital (GIAO) approach [70] at the B3LYP/6-31G(d,p) level. The B3LYP/6-31G(d,p) optimized geometries were used for the NICS calculations.

For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface.

4.2 General Structural Considerations on Nitrotriazines

Wide variety of explosives exist and employed in usage. They have some common structural features. Usually, they are classified according to the types of groups present in their structures like nitro explosives, azides, nitramines etc. However, a deeper look into the groups considered primarily responsible for the explosive character of the compounds reveals that aliphatic or aromatic nitro compounds, aliphatic nitro esters, nitrogen halides etc., all have a common topological assembly of various atoms, that is the isoconjugate of methylenepropenyl dianion [71]. This moiety is a non-Kekule alternating hydrocarbon structure. Figure 4.1 shows certain explosive groups (explosophores) and their isoconjugate non-Kekule alternant hydrocarbon structures. As seen there, when a nitro group is attached to a conjugated system, automatically an embedded non-Kekule moiety emerges. Although, the whole system becomes a Kekule or non-Kekule depending on the position of the attached nitro group, the embedded non-Kekule moiety isoconjugate with methylenepropenyl dianion system engenders a local unstable assembly of bonds due to the mesomeric and inductive electron attracting nature of the nitro group. If the nitro group is linked to a carbon atom in a π -structure, the effect of NO_2 group could be partly reduced by delocalization of electrons from the main body of the system to the nitro group. However, if this flow of electrons are hindered by some other electron withdrawing

groups present at some other positions of the molecule, the local non-Kekule character due to the methylenepropenyl dianion system becomes more pronounced, hence unstability should increase. This is a general trend in practice.

Triazine nuclei (**1**, **2**, **3**) are isoconjugate with benzene skeleton. The lone-pairs of nitrogen atoms in the structure of triazines lie in the σ -plane, thus the orbital of nitrogens accommodating these electrons are orthogonal to the π -skeleton. Thus, π -skeleton of triazines, like benzene contains six electrons but because of the electronegativity of aza-nitrogens it has a polarized π -skeleton. Due to some obvious structural reasons, the triazine nuclei presently considered are even alternant systems. All the mono-nitration products of triazines (**1A**, **2A**, **2B**, **2C**, **3A**, **3B**) are isoconjugate with odd alternant hydrocarbon system. In the case of dinitro structures, **1B**, **2E** and **3D** are isoconjugate with non-Kekule alternant hydrocarbon systems, but **2D**, **2F** and **3C** have even alternant hydrocarbon isoconjugates. In the case of trinitro products, the symmetrical derivative (**1C**) has a non-Kekule, whereas **2G** and **3E** have odd alternant hydrocarbon isoconjugates.

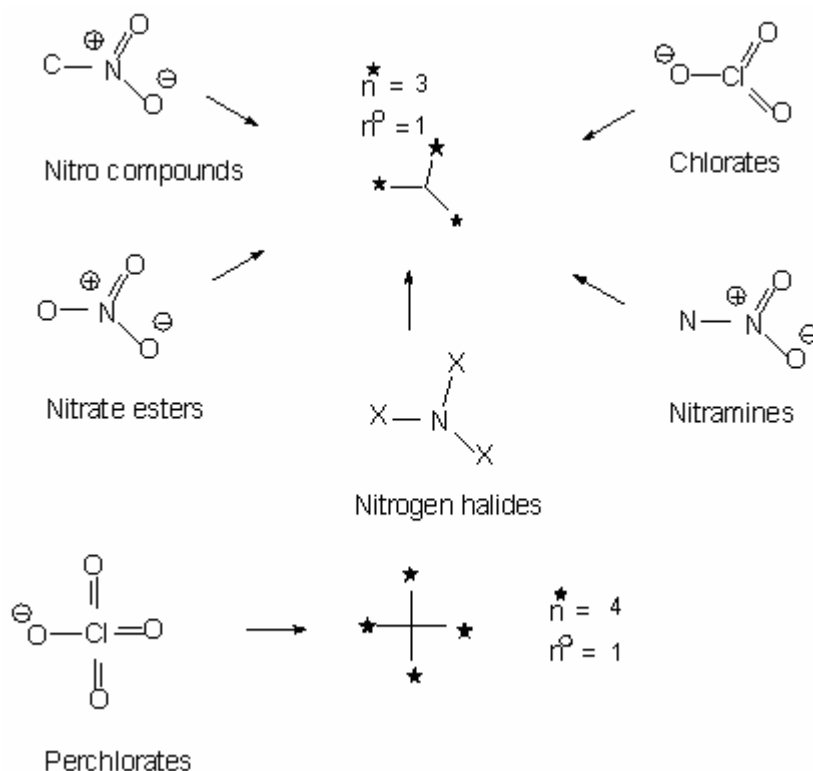


Figure 4.1 Some groups common in explosives and their isoconjugates

Nitro group is an odd conjugate system containing three atoms and four π -electrons, thus it is isoconjugate with the allyl anion. Although, in nitro compounds, the nitro group is attached to the adjacent aromatic system through the central, inactive atom of its isoconjugate allyl anion, it is not a – E substituent but according to Dewar, it is a + E substituent [72,73]. Considering NO_2 structure, the negatively charged oxygen cannot donate or attract electrons to or from the adjacent conjugate system, but delocalization of electrons is possible to the NO group in NO_2 structure. Although, the oxygen atoms in NO_2 group are identical through resonance, one of them cannot be conjugated with the adjacent aromatic system. Hence, a nitro group acts as a nitroso group in the whole π -skeleton of the molecule. Following the Dewar's treatment of nitro groups, all the non-Kekule as well as the odd and even structures in Figure 4.2 become even alternant systems. Certain instability is associated with non-Kekule compounds. Since, the Dewar's treatment abolishes non-Kekule character, all the nitrotriazines deserve to be treated in detail by using high level molecular orbital calculations.

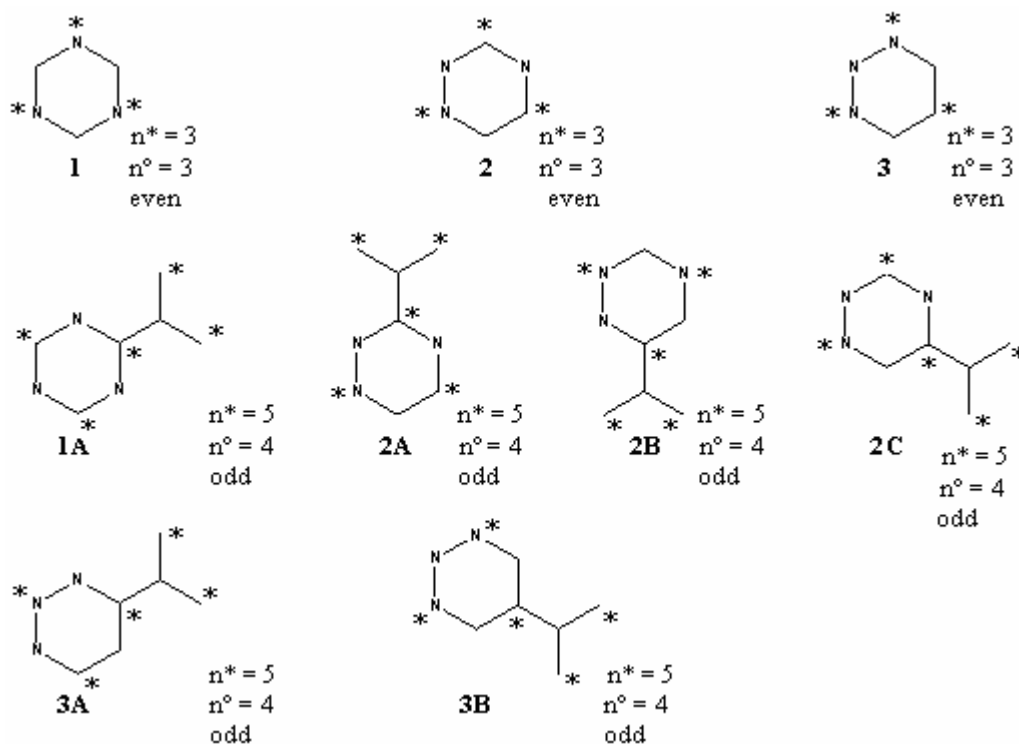


Figure 4.2 Isoconjugates of nitrotriazines studied

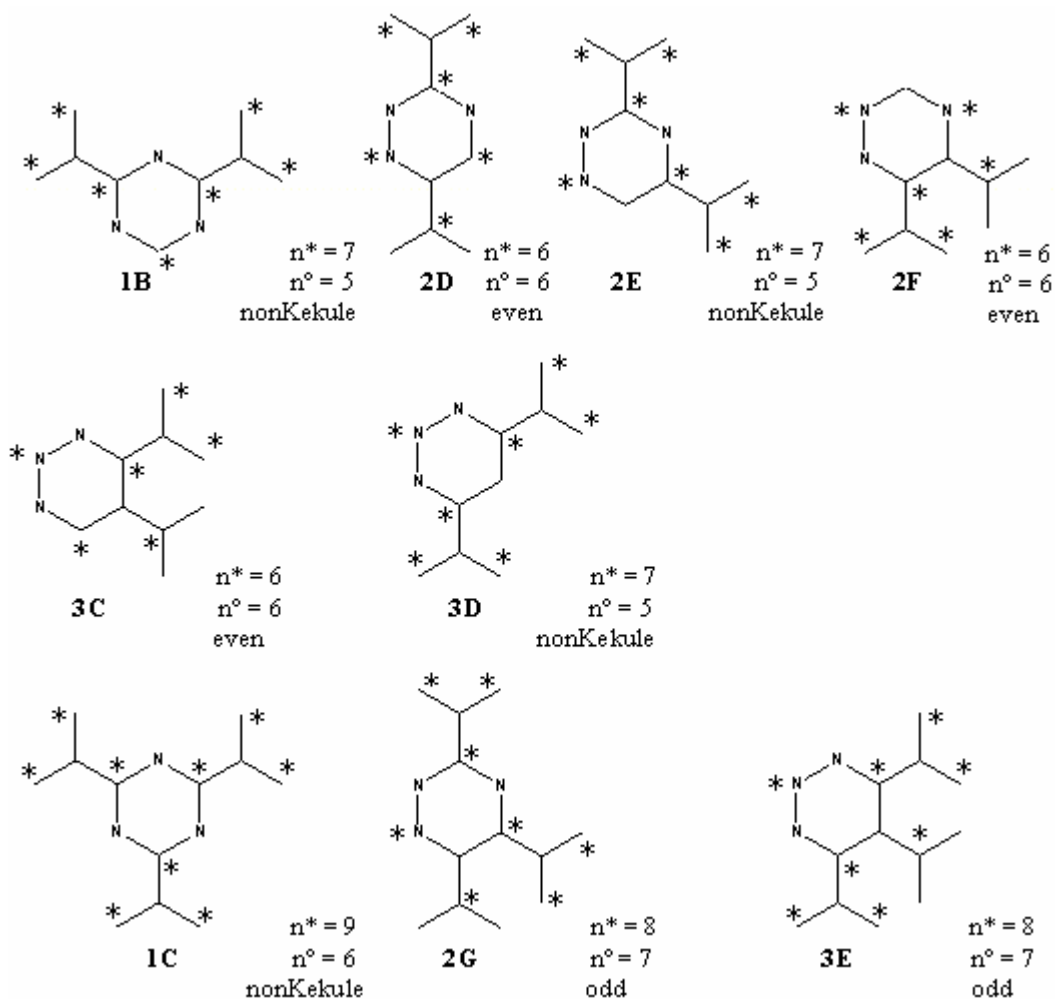


Figure 4.2 Continued

4.3 The Geometries

Figure 4.3 shows the geometric structures and atomic numbering of the nitrotriazine derivatives; 2-nitro-1,3,5-triazine (**1A**), 2,4-dinitro-1,3,5-triazine (**1B**), 2,4,6-trinitro-1,3,5-triazine (**1C**), 3-nitro-1,2,4-triazine (**2A**), 6-nitro-1,2,4-triazine (**2B**), 5-nitro-1,2,4-triazine (**2C**), 3,6-dinitro-1,2,4-triazine (**2D**), 3,5-dinitro-1,2,4-triazine (**2E**), 5,6-dinitro-1,2,4-triazine (**2F**), 3,5,6-trinitro-1,2,4-triazine (**2G**), 4-nitro-1,2,3-triazine (**3A**), 5-nitro-1,2,3-triazine (**3B**), 4,5-dinitro-1,2,3-triazine (**3C**), 4,6-dinitro-1,2,3-triazine (**3D**), 4,5,6-trinitro-1,2,3-triazine (**3E**).

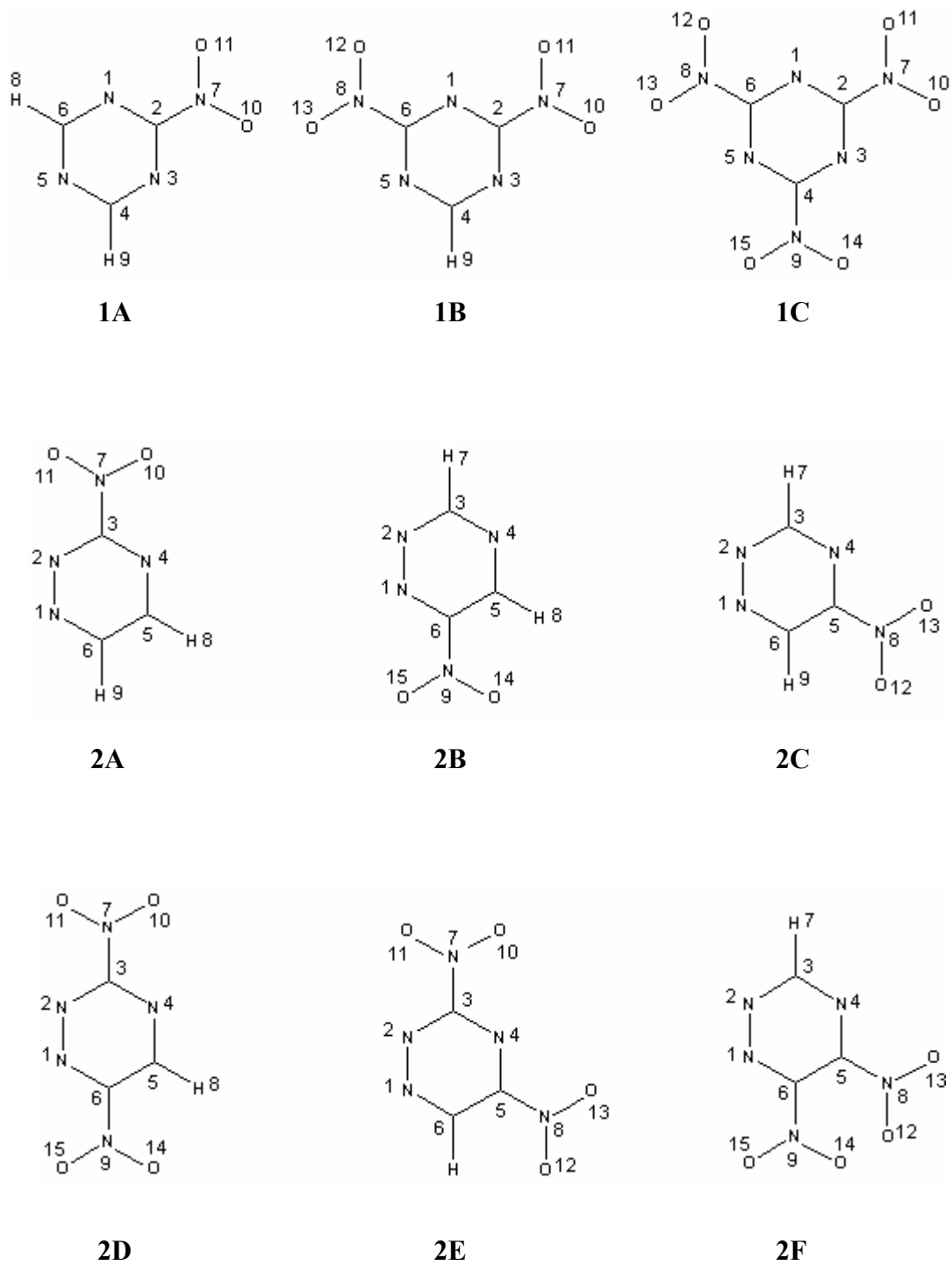
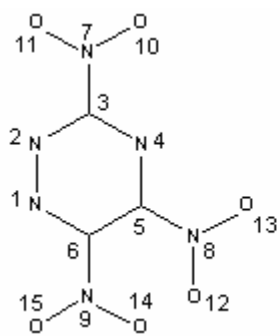
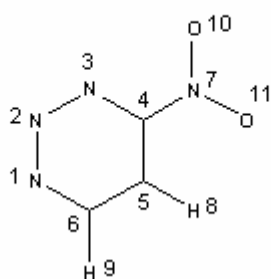


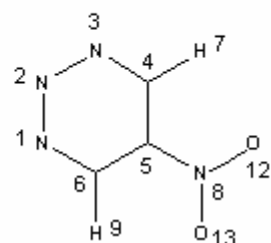
Figure 4.3 Chemical structures and numbering of nitro-triazine structures



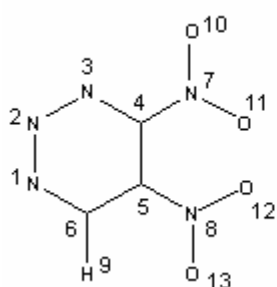
2G



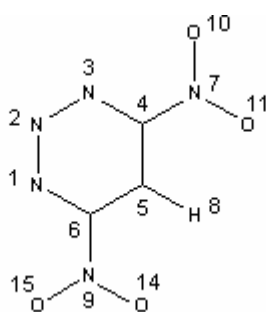
3A



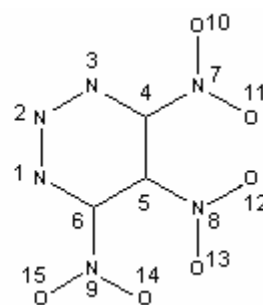
3B



3C



3D



3E

Figure 4.3 continued

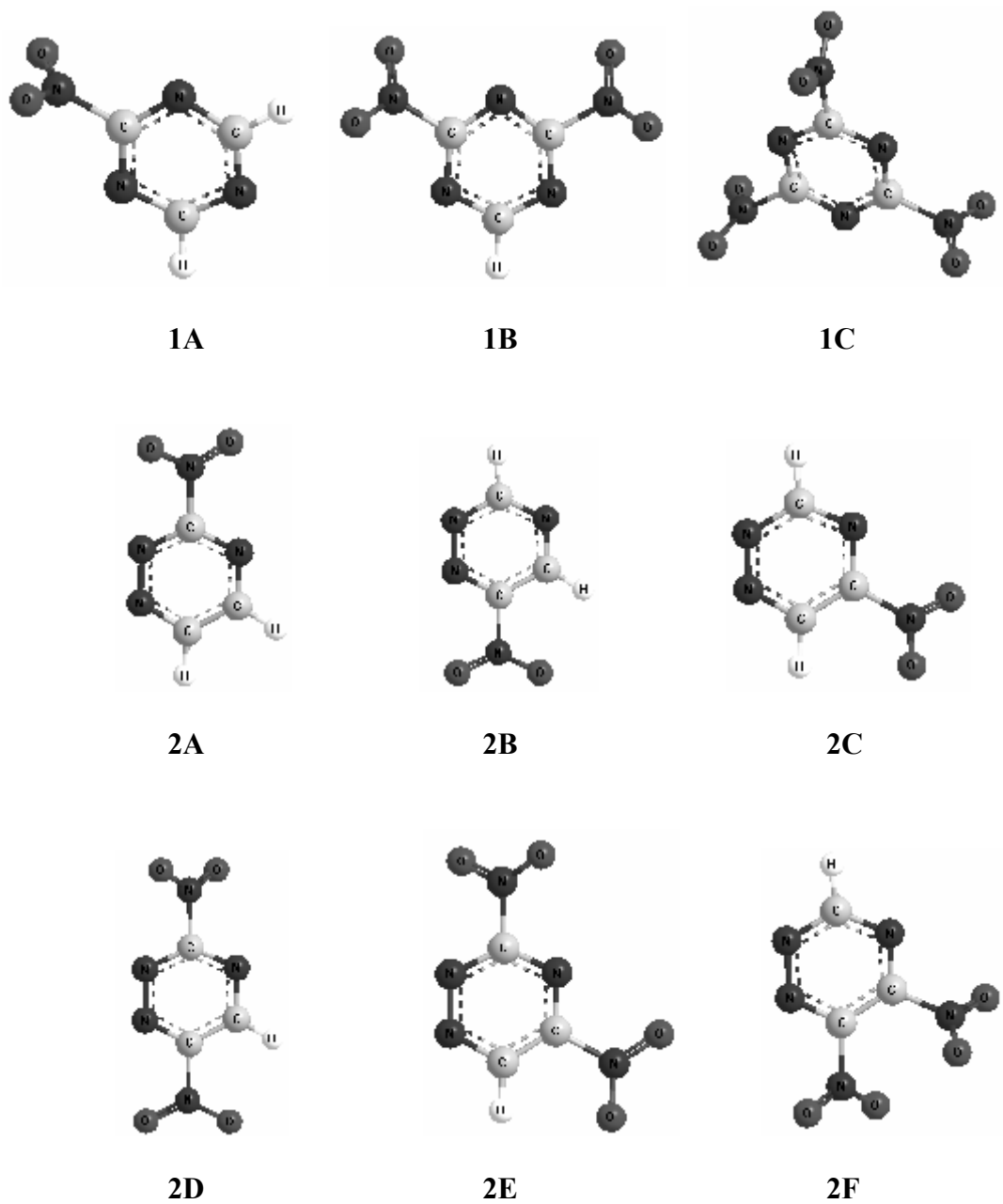


Figure 4.4 Geometry optimized structures of nitrotriazines at B3LYP/cc-pVDZ level

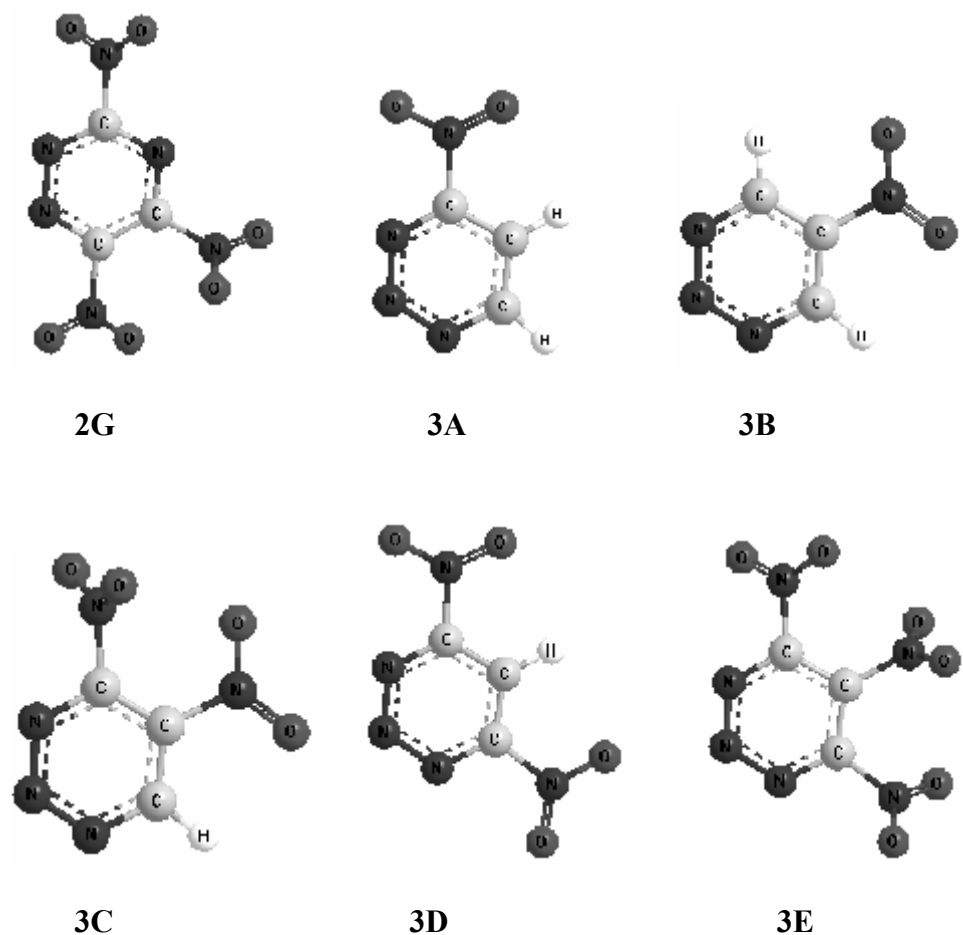


Figure 4.4 continued

4.3.1 Bond Lengths

Some structural data of the present systems have been given in Tables 4.1-4.3. The three-dimensional electrostatic potential maps of the nitrotriazines are shown in Figure 4.5. The dark loops indicate negative charge development for a particular system. As can be seen from the figures the negative charge is located on the nitro groups as expected due to the electron withdrawing character of the nitro groups. However, charge development on nitro substituents decreases with increasing number of nitro groups in the structure.

For each of the systems we studied, there are six C-N bonds in the 1,3,5 triazine ring, four C-N bonds, one N-N bond and one C-C bond in the 1,2,4 triazine ring, two C-N bonds, two N-N bonds and two C-C bonds in the 1,2,3 triazine ring. Bond lengths are tabulated in Table 4.1.

It is obtained that the longest C-N bond in all the triazine rings corresponds to C3-N4 bond of molecule **2F**, which is 1.3448 Å, the shortest one due to the C5-N4 bond of molecule **2F**, which is 1.309 Å. Consequently, all these C-N bonds in triazine rings are much shorter than the normal C-N single bond that is referred to 1.49 Å [74]. The same results are obtained for bond lengths of the N-N and C-C bonds in the triazine rings which lie in the range of 1.3228–1.3337 Å and 1.3846–1.4030 Å, respectively and are also smaller than that of the normal N-N single bond (1.45 Å) and C-C single bond (1.54 Å).

From data in Tables 4.1-4.3, it is observed that the shortest N-O bond in all the nitro groups corresponds to the N7-O10 and N9-O15 of molecule **3E** (1.2106 Å), while the longest one turns out to be N9-O14 bond of molecule **2B** (1.2267 Å). Thus, all the N-O bonds in nitro groups are around the normal N-O double bond of a nitro group (about 1.2 Å) [74].

The same analyses have been carried out for all the C-NO₂ bonds. From the data in Tables 4.1-4.3, all the C-NO₂ bond lengths are in the range of 1.4796–1.5230 Å and they are around the normal C-N single bond which is referred to 1.49 Å [74].

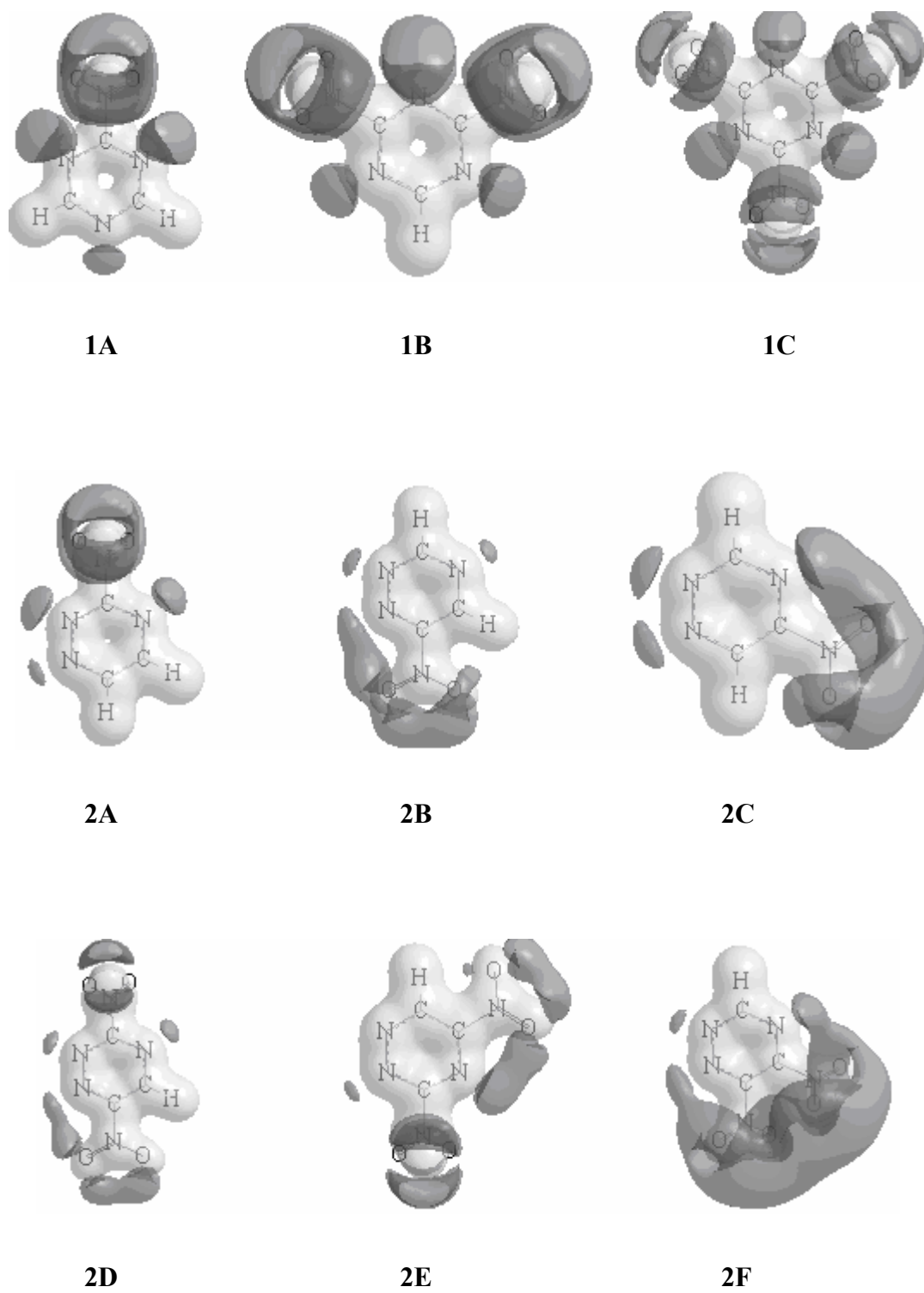


Figure 4.5 3D-electrostatic potential maps of the nitrotriazines

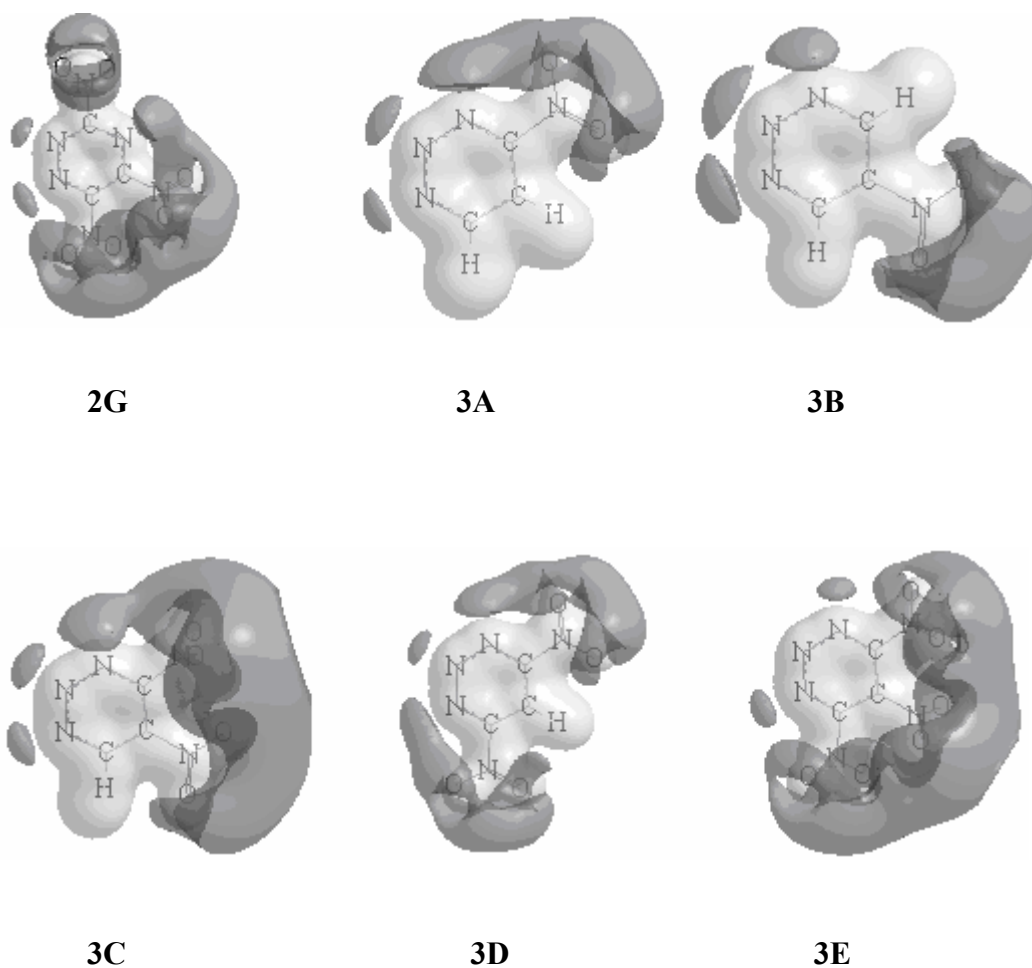


Figure 4.5 continued

4.3.2 Bond Angles and Dihedral Angles

In 1,3,5-triazine, 1,2,4-triazine and 1,2,3-triazine molecules (**1**, **2**, **3**), N-C(NO₂)-N bond angles (involving the bonds connecting the nitro substituents to the main ring) are greater than C(NO₂)-N-C(NO₂) bond angles. This behavior can be explained as follows: all angles in benzene ring are 120°, indicating a perfect hexagon. However, in the case of nitro-1,3,5-triazines the hexagon is distorted by the insertion of three nitrogen atoms. Since nitrogen is more electronegative than carbon, the distribution of the π -electrons in triazines ring is not uniform leading to a less successful delocalization of π -electrons. Thus, the π -electrons of the system

are more located around three nitrogens, in which the N-C(NO₂)-N bond angles increase. In our case, nitro substitution at position 2 in **1A**, at positions 2 and 4 in **1B**, at positions 2, 4 and 6 in **1C** increase the N-C-N bond angle up to 125-128°. This is quite reasonable, since nitro group pulls the lone pair electrons of the nitrogens toward itself increasing π -electron density around N-C(NO₂)-N angle (but decreasing on the other side), which results an increase in the N-C(NO₂)-N angle. Generally, the N-C(NO₂)-N bond angles are decreasing with the increasing number of nitro groups. Structure **1C** has dihedral angles of 180°, so it is in the same plane with the main ring resulting a better π -conjugation.

In nitro-1,2,4-triazine molecules (**2A**, **2B**, **2C**, **2D**, **2E**, **2F**, **2G**), N-C-N bond angles are greater than N-N-C, N-C-C and C-N-C bond angles. The **2A** has the greater bond angle (N2-C3-N4) of 129.7117°, while **2E** has the smaller bond angle (C3-N4-C5) of 112.5966°.

In nitro-1,2,3-triazine molecules (**3A**, **3B**, **3C**, **3D**, **3E**), the **3D** has the greater bond angle (N3-C4-C5) of 124.5461° and has the lower bond angle (C4-C5-C6) of 111.535°.

Table 4.1 Optimized structural parameters of nitro-1,3,5-triazines calculated at B3LYP/cc-pVDZ level

Bond	IA	IB	IC
N1-C2	1.3219	1.3253	1.3237
C2-N3	1.3219	1.3221	1.3237
N3-C4	1.3412	1.3400	1.3237
C4-N5	1.3373	1.3400	1.3237
N5-C6	1.3373	1.3221	1.3237
C6-N1	1.3412	1.3253	1.3237
C2-N7	1.5061	1.5033	1.5230
C6-N8	-	1.5033	1.5229
C4-N9	-	-	1.5229
N7-O10	1.2179	1.2170	1.2144
N7-O11	1.2179	1.2164	1.2144
N8-O12	-	1.2164	1.2145
N8-O13	-	1.2170	1.2145
N9-O14	-	-	1.2145
N9-O15	-	-	1.2145
N1-C2-N3	128.8884	128.3755	127.6633
C2-N3-C4	112.6038	113.1695	112.3357
N3-C4-N5	125.7550	125.3223	127.6663
C4-N5-C6	114.3482	113.1696	112.3327
N5-C6-N1	125.7550	128.3754	127.6663
C6-N1-C2	112.6038	111.4354	112.3357
N3-C2-N7-O11	141.4608	-139.5164	180.0000
N5-C6-N8-O12	-	139.5059	180.0000
N5-C4-N9-O14	-	-	-180.0000

The unit of bond length is Å, bond angles and dihedral angles are degree.

Table 4.2 Optimized structural parameters of nitro-1,2,4-triazines calculated at B3LYP/cc-pVDZ level

Bond	2A	2B	2C	2D	2E	2F	2G
N1-N2	1.3337	1.3313	1.3311	1.3305	1.3313	1.3307	1.3306
N2-C3	1.3246	1.3394	1.3376	1.3277	1.3256	1.3361	1.3249
C3-N4	1.3276	1.3428	1.3435	1.3284	1.3288	1.3448	1.3307
N4-C5	1.3313	1.3300	1.3115	1.3302	1.3126	1.3111	1.3123
C5-C6	1.4022	1.3990	1.3961	1.4011	1.3982	1.4005	1.4030
C6-N1	1.3355	1.3196	1.3375	1.3205	1.3377	1.3197	1.3205
C3-N7	1.4999	-	-	1.4955	1.4986	-	1.4967
C5-N8	-	-	1.5056	-	1.5047	1.4928	1.4918
C6-N9	-	1.4964	-	1.4964	-	1.4873	1.4872
N7-O10	1.2190	-	-	1.2179	1.2176	-	1.2170
N7-O11	1.2177	-	-	1.2167	1.2165	-	1.2156
N8-O12	-	-	1.2250	-	1.2241	1.2206	1.2197
N8-O13	-	-	1.2133	-	1.2118	1.2125	1.2113
N9-O14	-	1.2267	-	1.2257	-	1.2234	1.2224
N9-O15	-	1.2131	-	1.2119	-	1.2125	1.2113
N1-N2-C3	116.8183	117.6180	118.4377	116.4212	117.2397	117.7005	116.5732
N2-C3-N4	129.7117	127.3835	126.5874	129.6657	128.9150	126.5159	128.8124
C3-N4-C5	113.0830	114.7304	113.5674	113.7431	112.5966	114.8408	113.8124
N4-C5-C6	120.3873	118.7924	123.0344	118.6114	122.7189	120.6081	120.4002
C5-C6-N1	121.8175	123.7793	119.6691	123.7604	119.8320	121.4514	121.5757
C6-N1-N2	118.1391	117.6964	118.7040	117.7462	118.6532	118.8710	118.8006
O11-N7-C3-N4	-141.8602	-	-	-135.7623	141.2376	-	139.2362
O13-N8-C5-C6	-	-	-179.9997	-	176.1170	131.7941	131.5668
O14-N9-C6-N1	-	-179.9999	-	-178.4437	-	136.9385	134.7617

The unit of bond length is Å, bond angles and dihedral angles are degree.

Table 4.3 Optimized structural parameters of nitro-1,2,3-triazines calculated at B3LYP/cc-pVDZ level

Bond	3A	3B	3C	3D	3E
N1-N2	1.3227	1.3258	1.3223	1.3266	1.3228
N2-N3	1.3302	1.3258	1.3243	1.3266	1.3228
N3-C4	1.3223	1.3419	1.3305	1.3240	1.3255
C4-C5	1.3846	1.3852	1.3871	1.3859	1.3889
C5-C6	1.3905	1.3852	1.3870	1.3859	1.3889
C6-N1	1.3431	1.3419	1.3417	1.3240	1.3255
C4-N7	1.5063	-	1.4860	1.5069	1.4948
C5-N8	-	1.4796	1.4807	-	1.4835
C6-N9	-	-	-	1.5069	1.4948
N7-O10	1.2123	-	1.2150	1.2114	1.2106
N7-O11	1.2255	-	1.2150	1.2238	1.2217
N8-O12	-	1.2218	1.2199	-	1.2145
N8-O13	-	1.2218	1.2201	-	1.2145
N9-O14	-	-	-	1.2238	1.2217
N9-O15	-	-	-	1.2114	1.2106
N1-N2-N3	121.1475	122.0008	121.5912	120.7256	120.5925
N2-N3-C4	118.9137	119.9491	119.9684	119.3234	120.0286
N3-C4-C5	124.4968	120.4928	121.9583	124.5461	123.2997
C4-C5-C6	113.0354	117.1154	115.0539	111.5354	112.7509
C5-C6-N1	122.3086	120.4928	121.6910	124.5461	123.2997
C6-N1-N2	120.0980	119.9490	119.7371	119.3234	120.0286
O11-N7-C4-N3	-179.9975	-	88.6163	-179.9997	137.6366
O13-N8-C5-C4	-	180.0000	-179.9705	-	119.4027
O15-N9-C6-C5	-	-	-	-179.9998	137.6372

The unit of bond length is Å, bond angles and dihedral angles are degree.

4.4 Nucleus Independent Chemical Shifts (NICS)

Aromaticity continues to be an actively investigated area of chemistry. The simplest criterion for aromatic compounds is that they have to possess cyclic conjugated π -systems containing the proper number of π -electrons (i.e., the Hückel rule). While this criterion is robust enough to predict the aromaticity of a host of neutral and charged ring systems, it is not always a clear indicator of aromaticity for more complex systems (as in our case).

Aromaticity is expressed by a combination of properties in cyclic delocalized systems. In general, aromaticity is discussed in terms of energetic, structural and magnetic criteria [75–80]. In 1996, Schleyer has introduced a simple and efficient probe for aromaticity: Nucleus-independent chemical shift (NICS) [81], which is the computed value of the negative magnetic shielding at some selected point in space, generally, at a ring or cage center. Negative NICS values denote aromaticity (-11.5 for benzene, -11.4 for naphthalene) and positive NICS values denote antiaromaticity (28.8 for cyclobutadiene) while small NICS values indicate non-aromaticity (-2.1 for cyclohexane, -1.1 for adamantane). NICS may be a useful indicator of aromaticity that usually correlates well with the other energetic, structural and magnetic criteria for aromaticity [82-85]. Resonance energies and magnetic susceptibilities are measures of the overall aromaticity of a polycycle, but do not provide information about the individual rings. However, NICS is an effective probe for local aromaticity of individual rings of polycyclic systems.

In the present case, NICS values of the various nitro triazine derivatives have been calculated by the application of density functional theory using the standard 6-31G(d,p) basis set (Table 4.4). All the molecules have been found to be aromatic. This was somewhat expected since for all the cases, the electrons located on the nitrogen atoms (due to its higher electronegativity than carbon atom) have been pulled into the ring by the attachment of very strongly withdrawing nitro group(s). For all series (1, 2 and 3) as the number of nitro groups increases the average NICS values increases. According to the NICS data the most stable compound among the series is **1C**, which can be explained by the symmetry in this

structure. The nitrogens of the triazine system and the three nitro groups are arranged symmetrically in this structure, so that the pulling of electrons into the ring by the electron withdrawing nitro groups is most effective in this case. Therefore, the ring current has been quite strongly increased; leading to a NICS of the greatest negative value. According to the calculated NICS results, the stability order in three nitro triazine derivatives is; **1C** > **2G** > **3E** in very good agreement with the total energies calculated (see Table 4.5 for the total energies). The same argument can hold for the other series.

Table 4.4 NICS values for the nitrotriazine structures calculated at B3LYP/6-31G(d,p) method

Structures	NICS
1A	-6.368
1B	-7.593
1C	-10.677
2A	-5.542
2B	-5.863
2C	-6.305
2D	-6.671
2E	-7.255
2F	-7.396
2G	-8.129
3A	-6.197
3B	-5.941
3C	-7.214
3D	-7.821
3E	-7.960

4.5 Energetics

The nitro substituents in the structure of triazines change its electronic character as well as its chemistry. Theoretically nitro-group can be either coplanar or nonplanar with the aromatic nucleus. In the case of coplanar nitro group, shift of electrons from the aromatic ring to the nitro group occurs through resonance. This

effect produces a flat geometry for the NO₂ group with an sp² hybridized nitrogen atom and a relatively short C(NO₂)-N bond of “partially double” character (see Figure 4.4). The exact balance of these processes is subtle and depends on the possibility of forming resonance structures (the statistical weight of the contributing canonical structures). Tables 4.5 and 4.6 show the calculated total energies of the compounds at spin-restricted Hartree-Fock (RHF) level at the 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-pVDZ basis sets. Also, total energies were achieved within the framework of density functional theory (DFT, B3LYP) at the level of 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-pVDZ (restricted closed-shell), respectively. Total energies are corrected for zero-point vibrational energy (ZPVE). As seen from the table, generally among the calculated total energies of the nitrotriazine compounds a good agreement of stability order was obtained at different levels has been found. In terms of the energy considerations, the stability order is **1A > 2C > 2B > 2A > 3B > 3A** for mono-nitro substituted triazines, for dinitrated triazines **1B > 2E > 2D > 2F > 3D > 3C**, and for the three-nitro substituted triazines **1C > 2G > 3E** at this performed theoretical levels (see Tables 4.5 and 4.6). Smaller energy differences are obtained with the use of correlated methods.

Table 4.5 Calculated total energies (in a.u.) for nitrotriazine structures at different theoretical levels

Structures	B3LYP/ 6-31G(d,p)	B3LYP/ 6-31+G(d,p)	B3LYP/ 6-311G(d,p)	B3LYP/ 6-311+G(d,p)	B3LYP/ cc-pvDZ
1A	-484.785890	-484.807821	-484.907635	-484.921985	-484.820520
1B	-689.263187	-689.280433	-689.442952	-689.464297	-689.319813
1C	-893.734860	-893.773046	-893.971442	-893.997914	-893.813743
2A	-484.743161	-484.764867	-484.863821	-484.878055	-484.778446
2B	-484.746039	-484.766869	-484.866168	-484.879557	-484.781190
2C	-484.747221	-484.768113	-484.867501	-484.880939	-484.782453
2D	-689.222241	-689.252929	-689.400193	-689.406503	-689.279158
2E	-689.223176	-689.253622	-689.401150	-689.421646	-689.280140
2F	-689.217477	-689.248311	-689.395502	-689.416382	-689.274099
2G	-893.689908	-893.730105	-893.925697	-893.953378	-893.768520
3A	-484.721427	-484.742139	-484.840926	-484.854209	-484.757156
3B	-484.721882	-484.742451	-484.841074	-484.854076	-484.757422
3C	-689.191306	-689.221866	-689.368145	-689.388470	-689.248637
3D	-689.200595	-689.229933	-689.377265	-689.396972	-689.258014
3E	-893.659274	-893.698712	-893.893558	-893.920872	-893.738181

The total energies are corrected for ZPVE.

Table 4.6 Calculated total energies (in a.u.) for nitrotriazine structures at different theoretical levels

Structures	RHF/ 6-31G(d,p)	RHF/ 6-31+G(d,p)	RHF/ 6-311G(d,p)	RHF/ 6-311+G(d,p)	RHF/ cc-pVDZ
1A	-482.078629	-482.092877	-482.189502	-482.199995	-482.118520
	-482.580526	-482.658787	-482.653332	-482.672799	-482.305946
1B	-685.519547	-685.540487	-685.685009	-685.700697	-685.581222
	-685.785769	-	-686.364341	-686.393326	-685.882615
1C	-888.954435	-888.981700	-889.174450	-889.195143	-889.038048
	-889.307675	-	-890.138099	-	-889.451916
2A	-482.024931	-482.038863	-482.135088	-482.145364	-482.064899
	-482.218837	-482.250244	-482.616499	-482.666596	-482.266429
2B	-482.028950	-482.042257	-482.138508	-482.148422	-482.068626
	-482.221599	-	-482.616781	-	-482.270751
2C	-482.028210	-482.041460	-482.138003	-482.147757	-482.068079
	-482.221168	-	-482.617168	-	-482.270544
2D	-685.469497	-685.489465	-685.633481	-685.648641	-685.530604
	-685.751332	-739.565225	-686.376885	-686.404992	-685.846372
2E	-685.468417	-685.488089	-685.632436	-685.647516	-685.529667
	-685.749269	-685.792283	-686.375413	-686.403590	-685.844444
2F	-685.461459	-685.481585	-685.625321	-685.640818	-685.522307
	-685.758888	-685.803308	-686.385617	-686.415456	-685.854479
2G	-888.895978	-888.922713	-889.114252	-889.135074	-888.978399
	-889.280704	-889.338562	-890.109866	-	-889.471361
3A	-481.997559	-482.011087	-482.106983	-482.116906	-482.037567
	-482.201611	-	-482.625640	-	-482.249456
3B	-481.997559	-482.011087	-482.106983	-482.116906	-482.037567
	-482.209982	-	-482.388932	-	-482.010535
3C	-685.430165	-685.450392	-685.593384	-685.608674	-685.491332
	-685.742890	-685.787869	-686.367099	-686.396684	-685.837556
3D	-685.440998	-685.460491	-685.604198	-685.619175	-685.502158
	-685.732466	-	-686.355740	-	-685.828194
3E	-888.857188	-888.884128	-889.074520	-889.095600	-888.939651
	-889.272957	-	-890.100890	-	-889.463889

The total energies are corrected for ZPVE.

4.6 Bond Dissociation Energies (BDE)

Another main concern for the explosives is whether they are kinetically stable enough to be of practical interest. So, studies on the bond dissociations are important and essential for understanding the decomposition process of the energetic materials, since they are directly relevant to the sensitivity and stability of the energetic materials [86]. Previous studies [87,88] on the bond dissociation energy (BDE) for the nitro compounds such as nitro aromatic and nitramine molecules have shown that there is a parallel relationship between BDE for the weakest R-NO₂ (or N-NO₂) bond scission in the molecule and its sensitivity. Usually, the larger the BDE value, the lower the sensitivity is. However, this is only applied to the molecules in which R-NO₂ (or N-NO₂) bond is the weakest one. The C-C bond of nitrocubanes is weaker than the C-NO₂ bonds, and initial step in the decomposition is rupture of the cube C-C bond [89]. On the other hand, for designing and evaluating new energetic materials, it is accordingly important to be able to determine computationally the dissociation energies of these bonds. This is complicated, however, by the well-known difficulties involved in describing the electronic structure of nitro molecules. By comparing the computed energies and experimental results, the B3LYP method is able to give best agreement with experimental BDE data [90].

To measure the bond strength and relative stabilities of the title compounds, the BDE of various bond dissociations were calculated. BDE is originally defined as the enthalpy change at 298 K and 1 atm for the chemical bond dissociation in a molecule as follows [91] :



$$\text{BDE(A-B)} = \Delta H^\circ = [\Delta H^\circ_f(\text{A}^*) + \Delta H^\circ_f(\text{B}^*)] - \Delta H^\circ_f(\text{A-B}) \quad (2)$$

where A-B stands for the neutral molecules, A* and B* stand for the corresponding product radicals after the bond dissociation, BDE(A-B) is the bond dissociation enthalpy of bond A-B, ΔH° is the standard heat of reaction in the bond dissociation

process, $\Delta H_f^\circ(A^*)$, $\Delta H_f^\circ(B^*)$, and $\Delta H_f^\circ(A-B)$ are the standard heats of formation for the products and reactant at 298 K, respectively. However, in the present study, the BDE is defined as the difference between the zero-point energy corrected total energies at 0 K of the parent nitrotriazines and those of their corresponding radicals in the unimolecular bond dissociations. This has been successfully and frequently used to measure and determine the bond strength and relative stability of the compounds and corresponding radicals [92-99]. Therefore, the BDEs were computed at 0 K according to the energy changes of the bond dissociation process at the UB3LYP/6-311G(d,p) level: $BDE(A-B) = \Delta H^\circ = [\Delta H_f^\circ(A^*) + \Delta H_f^\circ(B^*)] - \Delta H_f^\circ(A-B)$. The thermal decomposition mechanism can also be determined from the calculated BDE.

Tables 4.7 shows calculated total energies (including zero-point vibrational energies) of nitrotriazine molecules, fragments and NO_2 at the equilibrium geometries and resulting bond dissociation energies (BDE) at UB3LYP/6-311G(d,p) level of theory. On the basis of the BDE for the initial steps in their thermal decompositions, it can be deduced that the relative stability order of these molecules may be in the order : **3B** > **2B** > **2A** > **2D(3)** = **2D(6)** > **1A** > **2E(3)** > **3A** > **2G(3)** > **1B** > **3D** > **2C** > **3C(5)** > **2F(5)** > **1C** > **2F(6)** > **2G(6)** > **3E(4)** = **3E(5)** (see Table 4.7). As seen in the table, BDEs for these compounds are highly position dependent and it is hard to generalize certain trends. According to suggestion of Chung et. al. [100], more than a 20 kcal/mol (83.68 kJ/mol) barrier to dissociation should exist for a molecule to be considered as a viable candidate of high energy density material (HEDM). Therefore, we can conclude that the molecules in Figure 4.3 are all viable candidate of HEDMs.

Table 4.7 Calculated total energies (including zero-point vibrational energies) of nitrotriazine molecules, fragments and NO₂ at the equilibrium geometries and resulting bond dissociation energies (BDE)

	Formula	Parent energy (hartrees)	Fragment energy (hartrees)	NO ₂ energy (hartrees)	BDE (kcal/mol)
1A	C ₃ H ₂ O ₂ N ₄	-484.90764	-279.69924	-205.06338	91.0
1B	C ₃ H ₁ O ₄ N ₅	-689.44295	-484.23677	-205.06338	89.6
1C	C ₃ O ₆ N ₆	-893.97144	-688.76806	-205.06338	87.9
2A	C ₃ H ₂ O ₂ N ₄	-484.86382	-279.65346	-205.06338	92.2
2B	C ₃ H ₂ O ₂ N ₄	-484.86618	-279.65575	-205.06338	92.3
2C	C ₃ H ₂ O ₂ N ₄	-484.86750	-279.66233	-205.06338	89.0
2D(3)	C ₃ H ₁ O ₄ N ₅	-689.40019	-484.19132	-205.06338	91.3
2D(6)	C ₃ H ₁ O ₄ N ₅	-689.40019	-484.19132	-205.06338	91.3
2E(3)	C ₃ H ₁ O ₄ N ₅	-689.40115	-484.19312	-205.06338	90.8
2E(5)	C ₃ H ₁ O ₄ N ₅	-689.40115	-484.19730	-205.06338	88.1
2F(5)	C ₃ H ₁ O ₄ N ₅	-689.39552	-484.19956	-205.06338	83.2
2F(6)	C ₃ H ₁ O ₄ N ₅	-689.39552	-484.19473	-205.06338	86.2
2G(3)	C ₃ O ₆ N ₆	-893.92570	-688.71877	-205.06338	90.1
2G(5)	C ₃ O ₆ N ₆	-893.92570	-688.72981	-205.06338	83.2
2G(6)	C ₃ O ₆ N ₆	-893.92570	-688.72534	-205.06338	86.0
3A	C ₃ H ₂ O ₂ N ₄	-484.84093	-279.63348	-205.06338	90.4
3B	C ₃ H ₂ O ₂ N ₄	-484.84107	-279.62743	-205.06338	94.3
3C(4)	C ₃ H ₂ O ₂ N ₄	-689.36815	-484.17089	-205.06338	84.0
3C(5)	C ₃ H ₂ O ₂ N ₄	-689.36815	-484.16392	-205.06338	88.4
3D	C ₃ H ₁ O ₄ N ₅	-689.37727	-484.17142	-205.06338	89.4
3E(4)	C ₃ O ₆ N ₆	-893.89356	-688.69583	-205.06338	84.3
3E(5)	C ₃ O ₆ N ₆	-893.89356	-688.69590	-205.06338	84.3

Key to the notation : aB(L) stands for the radical obtained from aB nitrotriazine by removing the NO₂ group at position L.

4.7 The Frontier Molecular Orbital Energies

Tables 4.8 and 4.9 show the HOMO and LUMO energies (ϵ) of the nitrotriazines calculated at B3LYP/6-311+G(d,p) and B3LYP/cc-pVDZ level. The energies of the frontier orbitals decrease by increasing the number of nitro substituent on the triazines ring. This is a general trend of electron withdrawing substituents which lower the LUMO and HOMO energy levels. As for the frontier molecular orbital energy gap values, that is the difference between the LUMO and

HOMO energy levels, the order is **1A** > **1B** > **2A** > **1C** > **3E** > **2G** > **2D** > **2F** > **3D** > **3A** > **2B** > **3C** > **2E** > **3B** > **2C** at the B3LYP/6-311+G(d,p) level.

Table 4.8 The HOMO and LUMO energies (ϵ) of nitrotriazine structures calculated at B3LYP/6-311+G(d,p)

Structures	HOMO	LUMO	$\Delta\epsilon$
1A	-0.31860	-0.11790	0.20070
1B	-0.34200	-0.14132	0.20068
1C	-0.35161	-0.18635	0.16526
2A	-0.29299	-0.12721	0.16578
2B	-0.29178	-0.13948	0.15230
2C	-0.28975	-0.14971	0.14004
2D	-0.31617	-0.15649	0.15968
2E	-0.32071	-0.17406	0.14665
2F	-0.31715	-0.15855	0.15860
2G	-0.34453	-0.18236	0.16217
3A	-0.30160	-0.14494	0.15666
3B	-0.30107	-0.15651	0.14456
3C	-0.32585	-0.17418	0.15167
3D	-0.33010	-0.17288	0.15722
3E	-0.34869	-0.18476	0.16393

Energies in eV, $\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$.

Table 4.9 The HOMO and LUMO energies (ϵ) of nitrotriazine structures calculated at B3LYP/cc-pVDZ

Structures	HOMO	LUMO	$\Delta\epsilon$
1A	-0.30347	-0.11248	0.19099
1B	-0.32441	-0.13931	0.18510
1C	-0.33319	-0.16937	0.16382
2A	-0.27722	-0.11271	0.16451
2B	-0.27762	-0.12352	0.15410
2C	-0.27579	-0.13316	0.14263
2D	-0.30683	-0.15078	0.15605
2E	-0.30378	-0.15734	0.14644
2F	-0.30153	-0.14206	0.15947
2G	-0.32562	-0.16553	0.16009
3A	-0.28750	-0.12859	0.15818
3B	-0.28677	-0.13929	0.14748
3C	-0.31019	-0.15946	0.15073
3D	-0.31468	-0.15638	0.15830
3E	-0.33110	-0.16548	0.16562

Energies in eV, $\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$.

4.8 Predicted Densities and Detonation of The Nitrotriazine Structures

According to the suggestion of Chung et. al. [101] a molecule should have more than a 20 kcal/mol (83.68 kJ/mol) barrier to dissociate in order to be considered as a viable candidate for high energy density material (HEDM). Thus we can conclude that the molecules in Figure 4.3 are all viable candidates for HEDMs.

Furthermore, density (ρ) detonation velocity (D), and detonation pressure (P) are the important parameters to evaluate the explosive performances of energetic materials and can be predicted by the empirical Kamlet-Jacob equations [102] as follows :

$$D = 1.01 (\text{N M}^{1/2} \text{Q}^{1/2})^{1/2} (1+130 \rho) \quad (1)$$

$$P = 1.558 \rho^2 \text{N M}^{1/2} \text{Q}^{1/2} \quad (2)$$

where each term in eqs. (1) and (2) is defined as D: detonation velocity in km/s, P: detonation pressure in GPa, ρ : density of a compound in g/cm^3 , N: moles of gaseous detonation products per gram of explosive (in mol/g), M: average molecular weight of gaseous products (in g/mol), Q: chemical energy of detonation in kJ/g.

Table 4.10 Methods for Calculating the N, M, and Q Parameters of the $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ Explosive^{a,b}

stoichiometric ratio			
parameters	$c \geq 2a+b/2$	$2a+b/2 > c \geq b/2$	$b/2 > c$
N	$(b+2c+2d)/4\text{MW}$	$(b+2c+2d)/4\text{MW}$	$(b+d)/2\text{MW}$
M	$4\text{MW}/(b+2c+2d)$	$(56d+88c-8b)/$ $(b+2c+2d)$	$(2b+28d+32c)/$ $(b+d)$
Q	$(28.9b+94.05a+0.239\Delta\text{H}_f^\circ)/$ MW	$[28.9b+94.05(c/2-b/4)+$ $0.239\Delta\text{H}_f^\circ]/\text{MW}$	$(57.8c+0.239\Delta\text{H}_f^\circ)/$ MW

^a $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ denotes the compound composed of the C, H, O, and N elements; a, b, c, and d stand for the number of C, H, O, and N atoms in the compound. ^b N is moles of gaseous detonation products per gram of explosive (in mol/g); MW is the average molecular weight of the gaseous products (in g/mol); Q is the chemical energy of detonation (in kJ/g); M in the formula is the molecular weight of the title compounds (in g/mol); ΔH_f° is the standard heat of formation of the studied compound (in kJ/mol).

Here, the parameters N, M and Q were calculated according to the chemical composition of each explosive [103,104] as listed in Table 4.10. On the other hand, the density of each molecule was predicted from the molecular volume, while the molecular volume of each molecule was obtained from the statistical average of 100 single-point calculations for each optimized structures. The molar volume was defined as inside a contour of 0.001 electrons/Bohr³ density that was evaluated using a Monte Carlo integration implemented in the Gaussian 03 package. This method has been successfully tested on various CHNO molecules and accurately predicts the explosive properties [104-109]. In the present study, single point molecular volume calculations at B3LYP/6-311G(d,p) performed based on the B3LYP/6-311G(d,p) geometry optimized structures. Table 4.11 collects the

predicted densities and detonation properties of the nitrotriazine derivatives. The heats of formation (HOF) values were also calculated and listed in the table. The previously reported studies have proved that the heat of formation (HOF) calculated by the PM3 method are reliable [110-113]. All these data in Table 4.11, gave some clue about the explosive character of the molecules derived from triazine molecules.

Table 4.11 Predicted densities and detonation properties of the nitrotriazine structures

Structures	HOF ^b	Q	V ^c	ρ	D	P	
	OB ₁₀₀	(kJ/mol)	(kJ/g)	(cm ³ /mol)	(g/cm ³)	(km/s)	(GPa)
1A	-63.49	176.12	1165.14	74.34	1.70	7.20	22.24
1B	-23.39	173.03	1372.77	95.19	1.80	8.18	29.67
1C	0	502.21	1861.59	115.44	1.87	9.30	39.23
2A	-63.49	360.43	1514.72	78.70	1.60	7.41	22.62
2B	-63.49	345.59	1486.59	78.03	1.62	7.41	22.80
2C	-63.49	352.03	1498.80	77.11	1.63	7.49	23.44
2D	-23.39	431.52	1733.89	95.84	1.78	8.63	32.89
2E	-23.39	438.51	1743.66	94.90	1.80	8.70	33.64
2F	-23.39	430.52	1732.49	93.54	1.83	8.78	34.51
2G	0	528.51	1890.69	113.81	1.90	9.43	40.68
3A	-63.49	401.77	1593.10	78.80	1.60	7.49	23.14
3B	-63.49	380.58	1552.92	77.75	1.62	7.51	23.47
3C	-23.39	341.29	1607.83	94.57	1.81	8.55	32.53
3D	-23.39	479.07	1800.32	96.62	1.77	8.67	32.98
3E	0	365.76	1710.64	112.06	1.93	9.30	39.91

^a Heat of formation obtained from the calculation at the PM3 level. ^b Average value from 100 single-point volume calculations at the B3LYP/6-311G(d,p) level.

Q: Heat of explosion, V: Volume of explosion, D: Velocity of detonation, P: Pressure of explosion.

It was clear that from mono-substituted to tri-substituted nitrotriazines, density (ρ), velocity of detonation (D) and detonation pressure (P) all increase with the increasing number of the nitro groups. This might show good group additivity on the detonation properties and also supports the claim that introducing more nitro substituents into a molecule usually helps to increase its detonation performance. For RDX and HMX, experimental value of D and P are 8.75 km/s, 9.10 km/s and 34.70 GPa, 39.00 GPa, respectively. Comparing these values with tri-substituted

nitro triazine compounds, **1C** has velocity of detonation value of 9.30 km/s and detonation pressure value of 39.23 GPa, **2G** has velocity of detonation value of 9.43 km/s and detonation pressure value of 40.68 GPa, **3E** has velocity of detonation value of 9.30 km/s and detonation pressure value of 39.91 GPa, one finds them to be more powerful explosives than the famous explosives HMX and RDX. Furthermore, the relative position of the nitro substituent in the triazine compounds affects the detonation properties (see Table 4.11). Especially di- and tri-nitro substituted triazines will be novel potential candidates for high energy density materials (HEDMs) when they are successfully synthesized.

CHAPTER 5

Conclusion

In the present study, stabilities of fifteen nitrotriazine structures as potential candidates for high energy density materials (HEDMs) have been investigated computationally by using quantum chemical treatment. Geometric features, electronic structures of these nitro-substituted triazines have been systematically studied using *ab initio* and density functional theory (DFT, B3LYP) at the level of 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-pVDZ. Detonation performances were evaluated by the Kamlet-Jacobs equations based on the calculated densities and heats of formation. Moreover, thermal stabilities were investigated by calculating bond dissociation energies (BDE) at B3LYP/6-311G(d,p) level.

Of the various nitrotriazines studied, only the trinitrotriazines (**1C**, **2G**, **3E**) are oxygen sufficient material for explosive purposes. The rest is oxygen deficient in varying percentages. Thus, their usage necessitates oxidizing agents to be coupled with. The **2G** derivative has the maximum heat of explosion (1890.69 kJ/g), velocity of detonation (9.43 km/s) and pressure of explosion (40.68 GPa) values among the series of compounds studied. The homolytic bond dissociation energy (for C-NO₂ bond) for **3B** is the maximum among the group. The BDE values of all nitrotriazine molecules lie between 83.2 and 94.3 as kcal/mol nearly 4-5 times of normal value that is 20 kcal/mol. Therefore, it can be concluded that the molecules of nitrotriazines are viable candidate of high energy density materials (HEDMs). Of course, all these predictions presently asserted are within the limitations of the calculation methods used.

REFERENCES

- [1] Patterson, Capell, and Walker, *The Ring Index*, 2nd ed., American Chemical Society, Washington, D.C. New York, 1960, p. 27.
- [2] Patterson and Capell, *The Ring Index*, Reinhold, New York, 1940.
- [3] K. Lonsdale, Proc. Roy. Soc. London, 1937, 149.
- [4] A. Pulman, Rev. sci., 86, 219 (1948)
- [5] J. Liebig, Ann., 10, 32 (1834).
- [6] Edwin M. Smolin and Lorence Rapoport, s-Triazines and Derivatives, Interscience Publishers Inc., New York, 7, (1967).
- [7] Grundmann and Kreutzberger, J. Am. Chem. Soc., 76, 632 (1954).
- [8] Grundmann and Schröder, Chem. Ber., 87, 747 (1954).
- [9] Neri, Gazz. chim. ital., 67, 282, 289, 448, 473, 477, 513 (1937) ; 70, 311, 317, 323 (1940) ; 71, 201 (1941) ; through Chem. Abstracts, 32, 173-175, 1265-69 (1938) : 35, 3260 (1941) : 36, 2865 (1942).
- [10] Neri, Chimica e industria (Italy), 23, 11 (1941) ; through Chem. Abstracts, 35, 3261 (1941).
- [11] Neri and Grimaldi, Gazz. chim. ital., 67, 273, 453, 468 (1937) ; through Chem. Abstracts, 32, 173, 1266-1267 (1938).
- [12] Widman, J. Prakt. Chem., 38, 192 (1888).
- [13] U.S. Patent 2,160,293 (May 30, 1939), to Shoemaker and Loane, assignors to Standard Oil Co. (Indiana).
- [14] U.S. Patent 2,489,351 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [15] U.S. Patent 2,489,352 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [16] U.S. Patent 2,489,353 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.

- [17] U.S. Patent 2,489,354 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [18] U.S. Patent 2,489,355 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [19] U.S. Patent 2,489,356 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [20] U.S. Patent 2,489,357 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [21] U.S. Patent 2,489,358 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [22] U.S. Patent 2,489,359 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [23] U.S. Patent 2,489,364 (Nov. 29, 1949), to Wolf and Pfister, assignors to Merck & Co., Inc.
- [24] John G. Erickson, Paul F. Wiley and V. P. Wystrach, *The Chemistry of Heterocyclic Compounds*, New York, **1-3** (1956).
- [25] Brunswing, H. *Explosivstoffe*. Barth: *Braunschweig*; 1909, p.17.
- [26] Pletz, V.M. *Zh. Obshch. Khim.* 1935, 5, 173.
- [27] Lothrop W.C.; Handrick, G.R. *Chem. Revs.* 1949, 44, 419-445.
- [28] Schmidt, A. *Chimie et Industrie* 1952, 67, 253.
- [29] Stettbacher, A. *Angew. Chem.* 1917, 30, 269.
- [30] Smolenski, D; Czuba, W. *Zeszyty Nauk. Polit. Wroclawskiej, Chemia* 1955, 2, 3-10.
- [31] Wöhler, L; Wenzelberg, O. *Angew. Chem.* 1933, 46, 173-176.
- [32] Urbanski, T. *Chemistry and technology of explosive*, Warszawa, 1961; Vol. 10, 1-3.
- [33] Holleman, A.F. *Die direkte einföhrung von substituenten*, Leipzig, 1910.
- [34] Menke, J.B. *Rec. Trav. Chim.* 1925, 44, 141-149.
- [35] Schmidt, E. *Ber.* 1919, 52, 400.
- [36] Kornblum, N; Larson, H.O.; Blackwood, R.H.; Mooberry, D.D.; Oliveto E.P.; Graham, G.E. *J. Am. Chem. Soc.* 1956, 78, 1497-1501.
- [37] Kornblum, N; Powers J.W. *J. Org. Chem.* 1957, 22, 455-456.

- [38] Berthelot, M. *Compt. Rend.* 1887, 105, 1159.
- [39] Data R.L.; Chatterjee, N.R. *J. Chem. Soc. Trans* 1919, 115, 1006-1010.
- [40] Condit P.C.; Haynor, R.L. *J. Ind. Eng. Chem.* 1949, 41, 1700-1704.
- [41] E. Schrödinger, *Ann. Physik.*, **1926**, 79, 361.
- [42] Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.*, **1954**, 22, 571.
- [43] Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, 46, 618.
- [44] Cizek, J. *J. Chem. Phys.*, **1966**, 45, 4256.
- [45] Cizek, J. *Adv. Chem. Phys.* **1969**, 14, 35.
- [46] Bartlett, R. J. *J. Phys. Chem.* **1989**, 93, 1697.
- [47] Hohenberg, P. ; Kohn, W. *Phys. Rev. B.*, **1964**, 136, 864.
- [48] W. Kohn, L. J. Sham, *Phys. Rev.*, **1965**, 140, A1133.
- [49] J. C. Slater, *Phys. Rev.*, **1930**, 35, 210.
- [50] Hartree, D. R. *Proc. Camb. Phil. Soc.* **1928**, 24, 89.
- [51] Fock. V. *Z. Phys.* **1930**, 61, 161.
- [52] S.J. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.*, **1980**, 58, 1200.
- [53] A. D. Becke, *J. Chem. Phys.*, **1993**, 98, 5648.
- [54] W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, **1972**, 56, 2257.
- [55] J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Amer. Chem. Soc.*, **1980**, 102, 939.
- [56] Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.*, **1984**, 80, 3265.
- [57] M.J. Frisch. G.W. Trucks. H.B. Schlegel. G.E. Scuseria. M.A. Robb. J.R. Cheeseman. J.A. Montgomery Jr.. T. Vreven. K.N. Kudin. J.C. Burant. J.M. Millam. S.S. Iyengar. J. Tomasi. V. Barone. B. Mennucci. M. Cossi. G. Scalmani. N. Rega. G.A. Petersson. H. Nakatsuji. M. Hada. M. Ehara. K. Toyota. R. Fukuda. J. Hasegawa. M. Ishida. T. Nakajima. Y. Honda. O. Kitao. H. Nakai. M. Klene. X. Li. J.E. Knox. H.P. Hratchian. J.B. Cross. C. Adamo. J. Jaramillo. R. Gomperts. R.E. Stratmann. O. Yazyev. A.J. Austin. R. Cammi. C. Pomelli. J.W. Ochterski. P.Y. Ayala. K. Morokuma. G.A. Voth. P. Salvador. J.J. Dannenberg. V.G. Zakrzewski. S. Dapprich. A.D. Daniels. M.C. Strain. O. Farkas. D.K. Malick. A.D. Rabuck. K. Raghavachari. J.B. Foresman. J.V. Ortiz. Q. Cui. A.G. Baboul. S. Clifford. J. Cioslowski. B.B. Stefanov. G. Liu. A. Liashenko. P. Piskorz. I.

- Komaromi. R.L. Martin. D.J. Fox. T. Keith. M.A. Al-Laham. C.Y. Peng. A. Nanayakkara. M. Challacombe. P.M.W. Gill. B. Johnson. W. Chen. M.W. Wong. C. Gonzalez. J.A. Pople. Gaussian 03. Revision B.01. Gaussian Inc. Wallingford. CT. 2004.
- [58] M.J.S. Dewar. E.G. Zoebisch. E.F. Healy. J.J.P. Stewart. *J. Am. Chem. Soc.* 107 (1985) 3902.
- [59] C.C.J. Roothaan. *Rev. Mod. Phys.* 23 (1951) 69.
- [60] A.R. Leach. *Molecular Modelling*. Addison-Wesley/Longman. Reading. MA/London. 1996.
- [61] A. Hinchliffe. *Modelling Molecular Structures*. Wiley. New York. 1996.
- [62] Kohn. W.; Sham. L.J. *Phys. Rev.* 1965. 140. 1133-1138.
- [63] Parr. R.G.; Yang. W. *Density functional theory of atoms and molecules*. Oxford University Press: London. 1989.
- [64] Becke. A.D. *Phys. Rev.* 1988. A 38. 3098-3100.
- [65] Vosko. S.H.; Vilk. L.; Nusair. M. *Can. J. Phys.* 1980. 58. 1200-1211.
- [66] Lee. C.; Yang. W.; Parr. R.G. *Phys. Rev. B* 1988. 37. 785-789.
- [67] Miehlich. B.; Savin. A.; Stoll. H.; Preuss. H. *Chem. Phys. Lett.* 1989. 157. 200-206.
- [68] B.M. Rice. S. Sahu. F.J. Owens. *Density functional calculation of bond dissociation energies for NO₂ scission in some nitroaromatic molecules*. *J. Mol. Struct. (THEOCHEM)* 583 (2002) 69–72. 563
- [69] J. Shao. X. Cheng. X. Yang. *Density functional calculations of bond dissociation energies for removal of the nitrogen dioxide moiety in some nitroaromatic molecules*. *J. Mol. Struct. (THEOCHEM)* 755 (2005) 127–130.
- [70] P. Pulay, J.F. Hinton, K. Wolinski, in: J.A. Tossel (Ed.), *Nuclear Magnetic Shieldings and Molecular Structure*, NATOASI Series C, vol. 386, Kluwer, The Netherlands, 1993, pp. 243-262.
- [71] Türker, L. *J. Mol. Struct. (Theochem)*, 2004, 681, 15-19.
- [72] Dewar, M.J.S. *The molecular orbital theory of organic chemistry*, McGraw-Hill: New York, 1969.

- [73] Dewar, M.J.S; Dougherty, R.C. *PMO Theory of organic chemistry*, Plenum-Rosetta: New York, 1975.
- [74] X.-Z. Cao, T.-Y. Song, X.-Q. Wang, *Inorganic Chemistry*, Higher Education Press, 1987, in Chinese.
- [75] Minkin VI, Glukhovtsev MN, Simkin BY, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley, New York, 1994.
- [76] Schleyer PR, Jiao H, *Pure Appl. Chem.*, 68 (1996) 209.
- [77] Glukhovtsev MN, *J. Chem. Educ.*, 74 (1997) 132.
- [78] Krygowski TM, Cyranski MK, Czarnocki Z, Hafelinger G, Katritzky AR., *Tetrahedron*, 56 (2000) 1783.
- [79] Schleyer PR, (Guest Editor), *Chem. Rev.*, 101 (2001) 1115.
- [80] Cyranski MK, Krygowski TM, Katritzky AR, Schleyer, PR., *J. Org. Chem.*, 67 (2002) 1333.
- [81] Schleyer PR, Maerker C, Dransfeld A, Jiao H, Hommes NJRE., *J. Am. Chem. Soc.*, 118 (1996) 6317.
- [82] Jiao H, Schleyer PR., *J. Phys. Org. Chem.* ,11 (1998) 655.
- [83] Schleyer PR, Kiran B, Simion DV, Sorensen TS, *J. Am. Chem. Soc.*, 122 (2000) 510.
- [84] Quinonero D, Garau C, Frontera A, Ballaster P, Costa A, Deya PM, *Chem. Eur. J.*, 8 (2002) 433.
- [85] Patchkovskii S, Thiel W, *J. Mol. Model.*, 6 (2002) 67.
- [86] Ye, S.; Tonokura, K.; Koshi, M. *Combustion and Flame*, 2003, 132(1/2), 240-246.
- [87] Owens, F.J. *J. Mol. Struct. (Theochem)*, 1985, 121, 213-220.
- [88] Dorset, H.; White, A.; *Aeronautical and maritime research laboratory, defense science and technology organization (DSTO)*. DSTO, Technical Report DSTO-GD-0253, Australia; 2000.
- [89] Owens, F. *J. Mol. Struct. (Theochem)*, 1999, 460, 137-140.
- [90] Lee, J.S. *J. Phys. Chem. A* 2005, 109, 11927-11932
- [91] Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*; CRC Press LLC: Boca Raton, Florida, 2002.
- [92] Owens, F. J. *THEOCHEM* 1996, 370, 11.

- [93] Politzer, P.; Murray, J. S. *THEOCHEM* **1996**, 376, 419.
- [94] Politzer, P.; Lane, P. *THEOCHEM* **1996**, 388, 51.
- [95] Harris, N. J.; Lammertsma, K. *J. Am. Chem. Soc.* **1997**, 119, 6583.
- [96] Rice, B. M.; Sahu, S.; Owens, F. J. *THEOCHEM* **2002**, 583, 69.
- [97] Saraf, S. R.; Rogers, W. J.; Mannan, M. S. *Ind. Eng. Chem. Res.* **2003**, 42, 1341.
- [98] Lu, W. C.; Wang, C. Z.; Nguyen, V.; Schmidt, M. W.; Gordon, M. S.; Ho, K. M. *J. Phys. Chem. A* **2003**, 107, 6936.
- [99] Colvin, K. D.; Strout, D. L. *J. Phys. Chem. A* **2005**, 109, 8011.
- [100] Chung, G.S; Schimidt, M.W.; Gordon, M.S. *J. Phys. Chem. A*, 2000, 104, 5647-5650.
- [101] Chung. G.S; Schimidt. M.W.; Gordon. M.S. *J. Phys. Chem. A*. 2000. 104. 5647-5650.
- [102] Kamlet. M.J.; Jacobs. S.J. *J. Chem. Phys.* 1968. 48. 23-36.
- [103] Zhang. X.H.; Yun. Z.H. *Explosive Chemistry*; National Defense Industry Press: Beijing. 1989.
- [104] Qiu. L.; Xiao. H.M.; Ju. X.H.; Gong. X.D. *Int. J. Quantum Chem.* 2005. 105. 48-56.
- [105] Xiao. J.J.; Zhang. J.; Yang. D.; Xiao. H.M. *Acta Chim. Sin.* 2002. 60. 2110.
- [106] Qiu. L.; Xiao. H.M.; Ju. X.H.; Gong. X.D. *Chin. J. Chem. Phys.* 2005. 18. 541.
- [107] Qiu. L.; Xiao. H.M.; Ju. X.H.; Gong. X.D. *Acta Chim. Sin.* 2005. 63. 377.
- [108] Xu. X.J.; Xiao. H.M.; Gong. X.D.; Ju. X.H.; Chen. Z.X. *J. Phys. Chem.* 2005. 109. 11268-11274.
- [109] Qiu. L.; Xiao. H.; Gong. X.; Ju. X.; Zhu. W. *J. Phys. Chem. A* 2006. 110. 3797-3807.
- [110] Williams. C.I.; Whitehead. M.A. *J. Mol. Struct. (Theochem)* 1997.393. 9-24.
- [111] Xiao. H.M.; Fan. J.F.; Gong. X.D. *Explos. Pyrotech.* 1997. 22. 360-364.
- [112] Ma. X.; Schobert. H.H. *J. Phys. Chem. A* 2000. 104. 1064-1074.
- [113] Xiao. H.M.; Fifing J.; Go. Z.M.; Dong. H.S. *Chem. Phys.* 1998. 226. 15-24.

APPENDIX A

CALCULATED ENERGIES OF ALL NITROTRIAZINE STRUCTURES

- The unit of HF is **hartree/particle**.
- The unit of Zero-point vibrational energy is **joules/mol**.
- The units of Zero-point correction, Thermal correction to Energy, Thermal correction to Enthalpy, Thermal correction to Gibbs Free Energy, Sum of electronic and zero-point Energies, Sum of electronic and thermal Energies, Sum of electronic and thermal Enthalpies, Sum of electronic and thermal Free Energies are **hartree/particle**.
- The unit of Dipole moment is **debye**.
- The unit of HOMO and LUMO is **eV**.

Table A1. Calculated energy data for the **1A** at HF level with 5 different basis sets

2-nitro-1,3,5-triazine (1A)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-482.1528574	-482.1667969	-482.2634125	-482.2736592	-482.1926574
Zero-point vibrational energy(Joules/Mol)	194887.5	194075.9	194050.6	193404.4	194647.4
Zero-point correction (Hartree/Particle)	0.074229	0.073920	0.073910	0.073664	0.074137
Thermal correction to Energy	0.080434	0.080239	0.080119	0.079928	0.080329
Thermal correction to Enthalpy	0.081378	0.081184	0.081063	0.080872	0.081273
Thermal correction to Gibbs Free Energy	0.043053	0.042129	0.042748	0.042365	0.043014
Sum of electronic and zero-point Energies	-482.078629	-482.092877	-482.189502	-482.199995	-482.118520
Sum of electronic and thermal Energies	-482.072423	-482.086558	-482.183293	-482.193732	-482.112328
Sum of electronic and thermal Enthalpies	-482.071479	-482.085613	-482.182349	-482.192787	-482.111384
Sum of electronic and thermal Free Energies	-482.109804	-482.124668	-482.220664	-482.231294	-482.149643
Dipole moment (Debye) Total	4.3676	4.4256	4.4154	4.4842	4.3645
HOMO	-0.46331	-0.47375	-0.46466	-0.47160	-0.46033
LUMO	0.04968	0.04564	0.04986	0.04553	0.04990

Table A2. Calculated energy data for the **1A** at B3LYP level with 5 different basis sets

2-nitro-1,3,5-triazine (1A)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-484.8533307	-484.8750564	-484.9747780	-484.9890015	-484.8877448
Zero-point vibrational energy(Joules/Mol)	177064.9	176525.7	176283.0	175952.9	176499.8
Zero-point correction (Hartree/Particle)	0.067440	0.067235	0.067143	0.067017	0.067225
Thermal correction to Energy	0.074089	0.074027	0.073807	0.073759	0.073882
Thermal correction to Enthalpy	0.075033	0.074971	0.074751	0.074703	0.074826
Thermal correction to Gibbs Free Energy	0.035170	0.034784	0.034844	0.034433	0.034914
Sum of electronic and zero-point Energies	-484.785890	-484.807821	-484.907635	-484.921985	-484.820520
Sum of electronic and thermal Energies	-484.779242	-484.801029	-484.900971	-484.915243	-484.813863
Sum of electronic and thermal Enthalpies	-484.778298	-484.800085	-484.900027	-484.914298	-484.812919
Sum of electronic and thermal Free Energies	-484.818161	-484.840272	-484.939934	-484.954569	-484.852831
Dipole moment (Debye) Total	3.7030	3.8196	3.7522	3.8791	3.6284
HOMO	-0.30555	-0.31798	-0.31121	-0.31860	-0.30347
LUMO	-0.11485	-0.11475	-0.11617	-0.11790	-0.11248

Table A3. Calculated energy data for the **1B** at HF level with 5 different basis sets

2,4-dinitro-1,3,5-triazine (1B)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-685.5968728	-685.6173429	-685.7621045	-685.7773992	-685.6586131
Zero-point vibrational energy(Joules/Mol)	203019.7	201784.4	202413.8	201380.6	203189.2
Zero-point correction (Hartree/Particle)	0.077326	0.076856	0.077095	0.076702	0.077391
Thermal correction to Energy	0.086030	0.085745	0.085797	0.085511	0.086061
Thermal correction to Enthalpy	0.086974	0.086689	0.086741	0.086455	0.087005
Thermal correction to Gibbs Free Energy	0.040893	0.039482	0.040701	0.039933	0.041056
Sum of electronic and zero-point Energies	-685.519547	-685.540487	-685.685009	-685.700697	-685.581222
Sum of electronic and thermal Energies	-685.510843	-685.531598	-685.676307	-685.691889	-685.572552
Sum of electronic and thermal Enthalpies	-685.509899	-685.530654	-685.675363	-685.690944	-685.571608
Sum of electronic and thermal Free Energies	-685.555980	-685.577861	-685.721403	-685.737466	-685.617558
Dipole moment (Debye) Total	4.1352	4.1966	4.1875	4.2527	4.1345
HOMO	-0.48450	-0.49535	-0.48585	-0.49349	-0.48121
LUMO	0.01295	0.01542	0.01417	0.01314	0.01365

Table A4. Calculated energy data for the **1B** at B3LYP level with 5 different basis sets

2,4-dinitro-1,3,5-triazine (1B)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-689.3323909	-689.3518122	-689.5118983	-689.5330020	-689.3889353
Zero-point vibrational energy(Joules/Mol)	181695.5	187405.6	181019.8	180384.5	181480.2
Zero-point correction (Hartree/Particle)	0.069204	0.071379	0.068947	0.068705	0.069122
Thermal correction to Energy	0.078552	0.078081	0.078326	0.078228	0.078470
Thermal correction to Enthalpy	0.079496	0.079025	0.079271	0.079172	0.079414
Thermal correction to Gibbs Free Energy	0.031894	0.038398	0.031591	0.030614	0.031809
Sum of electronic and zero-point Energies	-689.263187	-689.280433	-689.442952	-689.464297	-689.319813
Sum of electronic and thermal Energies	-689.253839	-689.273731	-689.433572	-689.454774	-689.310465
Sum of electronic and thermal Enthalpies	-689.252895	-689.272787	-689.432628	-689.453830	-689.309521
Sum of electronic and thermal Free Energies	-689.300497	-689.313415	-689.480308	-689.502388	-689.357126
Dipole moment (Debye) Total	3.4394	3.4228	3.4864	3.6061	3.3733
HOMO	-0.32704	-0.33756	-0.33282	-0.34200	-0.32441
LUMO	-0.14237	-0.12806	-0.14224	-0.14132	-0.13931

Table A5. Calculated energy data for the **1C** at HF level with 5 different basis sets

2,4,6-trinitro-1,3,5-triazine (1C)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-889.0347462	-889.0614292	-889.2546218	-889.2748030	-889.1185620
Zero-point vibrational energy(Joules/Mol)	210857.4	209329.9	210490.4	209146.8	211389.1
Zero-point correction (Hartree/Particle)	0.080311	0.079730	0.080172	0.079660	0.080514
Thermal correction to Energy	0.091559	0.091195	0.091407	0.091032	0.091723
Thermal correction to Enthalpy	0.092503	0.092139	0.092351	0.091976	0.092667
Thermal correction to Gibbs Free Energy	0.039796	0.038371	0.039726	0.038703	0.040078
Sum of electronic and zero-point Energies	-888.954435	-888.981700	-889.174450	-889.195143	-889.038048
Sum of electronic and thermal Energies	-888.943188	-888.970234	-889.163215	-889.183771	-889.026839
Sum of electronic and thermal Enthalpies	-888.942244	-888.969290	-889.162271	-889.182827	-889.025895
Sum of electronic and thermal Free Energies	-888.994950	-889.023058	-889.214896	-889.236100	-889.078484
Dipole moment (Debye) Total	0.0000	0.0000	0.0000	0.0001	0.0000
HOMO	-0.50339	-0.51290	-0.50477	-0.51121	-0.50031
LUMO	-0.02003	-0.01660	-0.01930	-0.02024	-0.01812

Table A6. Calculated energy data for the **1C** at B3LYP level with 5 different basis sets

2,4,6-trinitro-1,3,5-triazine (1C)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-893.8052072	-893.8430262	-894.0415612	-894.0676098	-893.8842268
Zero-point vibrational energy(Joules/Mol)	184696.3	183732.6	184098.1	182986.1	185055.0
Zero-point correction (Hartree/Particle)	0.070347	0.069980	0.070119	0.069696	0.070484
Thermal correction to Energy	0.079725	0.079388	0.079490	0.079129	0.079841
Thermal correction to Enthalpy	0.080670	0.080332	0.080435	0.080073	0.080785
Thermal correction to Gibbs Free Energy	0.034156	0.034413	0.033913	0.034052	0.034309
Sum of electronic and zero-point Energies	-893.734860	-893.773046	-893.971442	-893.997914	-893.813743
Sum of electronic and thermal Energies	-893.725482	-893.763639	-893.962071	-893.988481	-893.804386
Sum of electronic and thermal Enthalpies	-893.724538	-893.762694	-893.961127	-893.987537	-893.803442
Sum of electronic and thermal Free Energies	-893.771051	-893.808613	-894.007648	-894.033558	-893.849918
Dipole moment (Debye) Total	0.0003	0.0001	0.0001	0.0004	0.0003
HOMO	-0.33550	-0.35022	-0.34202	-0.35161	-0.33319
LUMO	-0.17304	-0.18714	-0.17698	-0.18635	-0.16937

Table A7. Calculated energy data for the **2A** at HF level with 5 different basis sets

3-nitro-1,2,4-triazine (2A)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-482.0980504	-482.1117029	-482.2078517	-482.2178882	-482.1378909
Zero-point vibrational energy(Joules/Mol)	191975.7	191239.9	191041.9	190412.3	191640.4
Zero-point correction (Hartree/Particle)	0.073120	0.072839	0.072764	0.072524	0.072992
Thermal correction to Energy	0.079288	0.079093	0.078942	0.078760	0.079157
Thermal correction to Enthalpy	0.080232	0.080037	0.079886	0.079705	0.080101
Thermal correction to Gibbs Free Energy	0.041515	0.040916	0.041165	0.040723	0.041399
Sum of electronic and zero-point Energies	-482.024931	-482.038863	-482.135088	-482.145364	-482.064899
Sum of electronic and thermal Energies	-482.018762	-482.032610	-482.128910	-482.139128	-482.058734
Sum of electronic and thermal Enthalpies	-482.017818	-482.031666	-482.127966	-482.138184	-482.057790
Sum of electronic and thermal Free Energies	-482.056536	-482.070787	-482.166687	-482.177165	-482.096492
Dipole moment (Debye) Total	6.3677	6.4526	6.3806	6.4904	6.2706
HOMO	-0.44070	-0.44545	-0.44318	-0.44625	-0.43900
LUMO	0.03896	0.02324	0.03448	0.02255	0.03917

Table A8. Calculated energy data for the **2A** at B3LYP level with 5 different basis sets

3-nitro-1,2,4-triazine (2A)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-484.8094460	-484.8309580	-484.9298265	-484.9439297	-484.8445574
Zero-point vibrational energy(Joules/Mol)	174030.1	173521.7	173296.4	172953.8	173576.5
Zero-point correction (Hartree/Particle)	0.066285	0.066091	0.066005	0.065875	0.066112
Thermal correction to Energy	0.072984	0.072892	0.072713	0.072648	0.072818
Thermal correction to Enthalpy	0.073928	0.073836	0.073657	0.073592	0.073762
Thermal correction to Gibbs Free Energy	0.034087	0.033377	0.033808	0.033393	0.033888
Sum of electronic and zero-point Energies	-484.743161	-484.764867	-484.863821	-484.878055	-484.778446
Sum of electronic and thermal Energies	-484.736462	-484.758066	-484.857114	-484.871282	-484.771739
Sum of electronic and thermal Enthalpies	-484.735518	-484.757122	-484.856169	-484.870337	-484.770795
Sum of electronic and thermal Free Energies	-484.775359	-484.797581	-484.896019	-484.910537	-484.810670
Dipole moment (Debye) Total	5.5487	5.8114	5.6102	5.8439	5.3694
HOMO	-0.27830	-0.29240	-0.28435	-0.29299	-0.27722
LUMO	-0.11332	-0.12545	-0.11951	-0.12721	-0.11271

Table A9. Calculated energy data for the **2B** at HF level with 5 different basis sets

6-nitro-1,2,4-triazine (2B)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-482.1021515	-482.1151908	-482.2113291	-482.2209196	-482.1417453
Zero-point vibrational energy(Joules/Mol)	192190.8	191488.8	191191.7	190342.6	191973.3
Zero-point correction (Hartree/Particle)	0.073202	0.072934	0.072821	0.072498	0.073119
Thermal correction to Energy	0.079377	0.079134	0.079023	0.078742	0.079286
Thermal correction to Enthalpy	0.080321	0.080078	0.079967	0.079687	0.080230
Thermal correction to Gibbs Free Energy	0.041169	0.040873	0.040484	0.039930	0.041175
Sum of electronic and zero-point Energies	-482.028950	-482.042257	-482.138508	-482.148422	-482.068626
Sum of electronic and thermal Energies	-482.022775	-482.036057	-482.132306	-482.142177	-482.062459
Sum of electronic and thermal Enthalpies	-482.021830	-482.035113	-482.131362	-482.141233	-482.061515
Sum of electronic and thermal Free Energies	-482.060983	-482.074318	-482.170845	-482.180990	-482.100570
Dipole moment (Debye) Total	3.8787	3.9417	3.8883	3.9585	3.8655
HOMO	-0.44082	-0.44579	-0.44323	-0.44631	-0.43972
LUMO	0.02632	0.01453	0.02486	0.01575	0.02870

Table A10. Calculated energy data for the **2B** at B3LYP level with 5 different basis sets

6-nitro-1,2,4-triazine (2B)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-484.8124049	-484.8329824	-484.9321587	-484.9454224	-484.8474012
Zero-point vibrational energy(Joules/Mol)	174242.4	173580.1	173258.4	172930.6	173838.8
Zero-point correction (Hartree/Particle)	0.066365	0.066113	0.065991	0.065866	0.066212
Thermal correction to Energy	0.073075	0.071955	0.072750	0.072609	0.072916
Thermal correction to Enthalpy	0.074019	0.072899	0.073694	0.073554	0.073860
Thermal correction to Gibbs Free Energy	0.033673	0.035492	0.031874	0.033230	0.033639
Sum of electronic and zero-point Energies	-484.746039	-484.766869	-484.866168	-484.879557	-484.781190
Sum of electronic and thermal Energies	-484.739330	-484.761028	-484.859409	-484.872813	-484.774485
Sum of electronic and thermal Enthalpies	-484.738386	-484.760084	-484.858464	-484.871869	-484.773541
Sum of electronic and thermal Free Energies	-484.778731	-484.797491	-484.900285	-484.912193	-484.813762
Dipole moment (Debye) Total	3.3508	3.6029	3.3935	3.6053	3.2590
HOMO	-0.27879	-0.29088	-0.28420	-0.29178	-0.27762
LUMO	-0.12586	-0.14105	-0.13051	-0.13948	-0.12352

Table A11. Calculated energy data for the **2C** at HF level with 5 different basis sets

5-nitro-1,2,4-triazine (2C)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-482.1013487	-482.1143360	-482.2107315	-482.2201869	-482.1411405
Zero-point vibrational energy(Joules/Mol)	192025.2	191336.4	190948.3	190165.1	191823.5
Zero-point correction (Hartree/Particle)	0.073139	0.072876	0.072728	0.072430	0.073062
Thermal correction to Energy	0.079334	0.079102	0.078029	0.077758	0.079244
Thermal correction to Enthalpy	0.080278	0.080046	0.078973	0.078702	0.080188
Thermal correction to Gibbs Free Energy	0.040639	0.040086	0.042576	0.042257	0.040798
Sum of electronic and zero-point Energies	-482.028210	-482.041460	-482.138003	-482.147757	-482.068079
Sum of electronic and thermal Energies	-482.022015	-482.035234	-482.132703	-482.142429	-482.061897
Sum of electronic and thermal Enthalpies	-482.021071	-482.034290	-482.131758	-482.141485	-482.060953
Sum of electronic and thermal Free Energies	-482.060710	-482.074250	-482.168156	-482.177930	-482.100342
Dipole moment (Debye) Total	1.5986	1.6613	1.6103	1.6785	1.6112
HOMO	-0.43950	-0.44448	-0.44160	-0.44465	-0.43823
LUMO	0.01148	0.00083	0.01014	0.00186	0.01405

Table A12. Calculated energy data for the **2C** at B3LYP level with 5 different basis sets

5-nitro-1,2,4-triazine (2C)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-484.813589	-484.8342796	-484.933534	-484.9467169	-484.8486630
Zero-point vibrational energy(Joules/Mol)	174248.3	173720.1	173289.7	172699.2	173834.8
Zero-point correction (Hartree/Particle)	0.066368	0.066166	0.066003	0.065778	0.066210
Thermal correction to Energy	0.073061	0.072899	0.07273	0.071632	0.072902
Thermal correction to Enthalpy	0.074005	0.073844	0.073674	0.072576	0.073846
Thermal correction to Gibbs Free Energy	0.033893	0.033334	0.033136	0.035114	0.033785
Sum of electronic and zero-point Energies	-484.747221	-484.768113	-484.867501	-484.880939	-484.782453
Sum of electronic and thermal Energies	-484.740528	-484.76138	-484.860773	-484.875085	-484.775761
Sum of electronic and thermal Enthalpies	-484.739584	-484.760436	-484.859829	-484.874141	-484.774817
Sum of electronic and thermal Free Energies	-484.779696	-484.800946	-484.900368	-484.911603	-484.814878
Dipole moment (Debye) Total	1.2216	1.4004	1.2321	1.3869	1.2008
HOMO	-0.27721	-0.28956	-0.28226	-0.28975	-0.27579
LUMO	-0.13557	-0.15034	-0.14025	-0.14971	-0.13316

Table A13. Calculated energy data for the **2D** at HF level with 5 different basis sets

3,6-dinitro-1,2,4-triazine (2D)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-685.545813	-685.5653797	-685.7095106	-685.7242872	-685.6069798
Zero-point vibrational energy(Joules/Mol)	200368.7	199314.1	199615.4	198608.0	200524.8
Zero-point correction (Hartree/Particle)	0.076316	0.075915	0.076029	0.075646	0.076376
Thermal correction to Energy	0.084972	0.084659	0.084704	0.083483	0.085007
Thermal correction to Enthalpy	0.085916	0.085603	0.085648	0.084427	0.085952
Thermal correction to Gibbs Free Energy	0.039877	0.039254	0.039342	0.040961	0.040061
Sum of electronic and zero-point Energies	-685.469497	-685.489465	-685.633481	-685.648641	-685.530604
Sum of electronic and thermal Energies	-685.460841	-685.480721	-685.624807	-685.640804	-685.521972
Sum of electronic and thermal Enthalpies	-685.459897	-685.479776	-685.623863	-685.63986	-685.521028
Sum of electronic and thermal Free Energies	-685.505936	-685.526125	-685.670169	-685.683326	-685.566919
Dipole moment (Debye) Total	2.7396	2.7175	2.7489	2.7411	2.7214
HOMO	-0.47747	-0.48251	-0.47991	-0.48309	-0.47525
LUMO	-0.00914	-0.01368	-0.00872	-0.01568	-0.00663

Table A14. Calculated energy data for the **2D** at B3LYP level with 5 different basis sets

3,6-dinitro-1,2,4-triazine (2D)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-689.2904014	-689.3207533	-689.4680245	-689.4765824	-689.3472688
Zero-point vibrational energy(Joules/Mol)	178954.3	178072.8	178090.9	183992.8	178825.0
Zero-point correction (Hartree/Particle)	0.068160	0.067824	0.067831	0.070079	0.068111
Thermal correction to Energy	0.077532	0.077333	0.077243	0.077493	0.077483
Thermal correction to Enthalpy	0.078476	0.078277	0.078187	0.078437	0.078427
Thermal correction to Gibbs Free Energy	0.030832	0.029657	0.030083	0.036253	0.030796
Sum of electronic and zero-point Energies	-689.222241	-689.252929	-689.400193	-689.406503	-689.279158
Sum of electronic and thermal Energies	-689.21287	-689.243420	-689.390781	-689.399090	-689.269786
Sum of electronic and thermal Enthalpies	-689.211926	-689.242476	-689.389837	-689.398146	-689.268842
Sum of electronic and thermal Free Energies	-689.259569	-689.291097	-689.437941	-689.440330	-689.316472
Dipole moment (Debye) Total	2.4819	2.5022	2.5143	2.5167	2.4174
HOMO	-0.30861	-0.32334	-0.31502	-0.31617	-0.30683
LUMO	-0.15394	-0.16367	-0.15679	-0.15649	-0.15078

Table A15. Calculated energy data for the **2E** at HF level with 5 different basis sets

3,5-dinitro-1,2,4-triazine (2E)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-685.5447231	-685.5639955	-685.7084622	-685.7231507	-685.6060131
Zero-point vibrational energy(Joules/Mol)	200342.0	199293.0	199607.0	198578.3	200446.0
Zero-point correction (Hartree/Particle)	0.076306	0.075907	0.076026	0.075634	0.076346
Thermal correction to Energy	0.084925	0.084611	0.084649	0.084327	0.084952
Thermal correction to Enthalpy	0.085869	0.085556	0.085594	0.085271	0.085897
Thermal correction to Gibbs Free Energy	0.039982	0.039261	0.039766	0.039135	0.040033
Sum of electronic and zero-point Energies	-685.468417	-685.488089	-685.632436	-685.647516	-685.529667
Sum of electronic and thermal Energies	-685.459798	-685.479384	-685.623813	-685.638824	-685.521061
Sum of electronic and thermal Enthalpies	-685.458854	-685.478440	-685.622869	-685.637880	-685.520117
Sum of electronic and thermal Free Energies	-685.504741	-685.524734	-685.668696	-685.684016	-685.565980
Dipole moment (Debye) Total	3.446	3.4559	3.4438	3.4911	3.4106
HOMO	-0.47258	-0.47663	-0.47458	-0.47742	-0.47043
LUMO	-0.01887	-0.02823	-0.01989	-0.02693	-0.01652

Table A16. Calculated energy data for the **2E** at B3LYP level with 5 different basis sets

3,5-dinitro-1,2,4-triazine (2E)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-689.2913090	-689.3214574	-689.4689592	-689.4892157	-689.3482235
Zero-point vibrational energy(Joules/Mol)	178883.1	178102.9	178034.3	177404.2	178751.9
Zero-point correction (Hartree/Particle)	0.068133	0.067836	0.067810	0.067570	0.068083
Thermal correction to Energy	0.077494	0.077307	0.077200	0.077032	0.077444
Thermal correction to Enthalpy	0.078438	0.078251	0.078144	0.077977	0.078388
Thermal correction to Gibbs Free Energy	0.030969	0.030094	0.030446	0.029896	0.030942
Sum of electronic and zero-point Energies	-689.223176	-689.253622	-689.401150	-689.421646	-689.280140
Sum of electronic and thermal Energies	-689.213815	-689.244151	-689.391759	-689.412183	-689.270780
Sum of electronic and thermal Enthalpies	-689.212871	-689.243207	-689.390815	-689.411239	-689.269835
Sum of electronic and thermal Free Energies	-689.260340	-689.291363	-689.438514	-689.459320	-689.317281
Dipole moment (Debye) Total	2.9001	2.9646	2.8943	2.9995	2.8121
HOMO	-0.30581	-0.32046	-0.31170	-0.32071	-0.30378
LUMO	-0.16005	-0.17450	-0.16486	-0.17406	-0.15734

Table A17. Calculated energy data for the **2F** at HF level with 5 different basis sets

5,6-dinitro-1,2,4-triazine (2F)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-685.5379665	-685.5577162	-685.7015664	-685.7167200	-685.5988228
Zero-point vibrational energy(Joules/Mol)	200869.4	199882.7	200181.0	199279.6	200893.4
Zero-point correction (Hartree/Particle)	0.076507	0.076131	0.076245	0.075902	0.076516
Thermal correction to Energy	0.085099	0.084783	0.084840	0.084538	0.085117
Thermal correction to Enthalpy	0.086043	0.085727	0.085784	0.085483	0.086061
Thermal correction to Gibbs Free Energy	0.041094	0.040583	0.040845	0.040446	0.041021
Sum of electronic and zero-point Energies	-685.461459	-685.481585	-685.625321	-685.640818	-685.522307
Sum of electronic and thermal Energies	-685.452868	-685.472934	-685.616727	-685.632182	-685.513706
Sum of electronic and thermal Enthalpies	-685.451923	-685.471989	-685.615783	-685.631237	-685.512762
Sum of electronic and thermal Free Energies	-685.496872	-685.517133	-685.660721	-685.676274	-685.557802
Dipole moment (Debye) Total	4.6104	4.6874	4.6553	4.7377	4.6129
HOMO	-0.47153	-0.47616	-0.47362	-0.47665	-0.46922
LUMO	0.00466	-0.00319	0.00251	-0.00433	0.00678

Table A18. Calculated energy data for the **2F** at B3LYP level with 5 different basis sets

5,6-dinitro-1,2,4-triazine (2F)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-689.2857030	-689.3162257	-689.4634242	-689.4840678	-689.3422223
Zero-point vibrational energy(Joules/Mol)	179127.6	178309.0	178329.5	177708.8	178858.5
Zero-point correction (Hartree/Particle)	0.068226	0.067914	0.067922	0.067686	0.068124
Thermal correction to Energy	0.077590	0.077352	0.076453	0.077110	0.077519
Thermal correction to Enthalpy	0.078534	0.078296	0.077398	0.078055	0.078463
Thermal correction to Gibbs Free Energy	0.031705	0.031164	0.033120	0.031028	0.031376
Sum of electronic and zero-point Energies	-689.217477	-689.248311	-689.395502	-689.416382	-689.274099
Sum of electronic and thermal Energies	-689.208113	-689.238873	-689.386971	-689.406957	-689.264703
Sum of electronic and thermal Enthalpies	-689.207169	-689.237929	-689.386027	-689.406013	-689.263759
Sum of electronic and thermal Free Energies	-689.253998	-689.285061	-689.430304	-689.453040	-689.310847
Dipole moment (Debye) Total	3.7455	4.0444	3.8072	4.0533	3.6577
HOMO	-0.30379	-0.31671	-0.30904	-0.31715	-0.30153
LUMO	-0.14510	-0.15802	-0.14967	-0.15855	-0.14206

Table A19. Calculated energy data for the **2G** at HF level with 5 different basis sets

3,5,6-trinitro-1,2,4-triazine (2G)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-888.9754944	-889.0017153	-889.1935919	-889.2139568	-889.0580536
Zero-point vibrational energy(Joules/Mol)	208769.7	207421.8	208307.0	207107.5	209134.1
Zero-point correction (Hartree/Particle)	0.079516	0.079003	0.079340	0.078883	0.079655
Thermal correction to Energy	0.090649	0.090262	0.090472	0.090099	0.090786
Thermal correction to Enthalpy	0.091594	0.091206	0.091416	0.091043	0.091730
Thermal correction to Gibbs Free Energy	0.039862	0.038925	0.039711	0.039003	0.039942
Sum of electronic and zero-point Energies	-888.895978	-888.922713	-889.114252	-889.135074	-888.978399
Sum of electronic and thermal Energies	-888.884845	-888.911453	-889.103120	-889.123858	-888.967268
Sum of electronic and thermal Enthalpies	-888.883901	-888.910509	-889.102176	-889.122914	-888.966323
Sum of electronic and thermal Free Energies	-888.935632	-888.962790	-889.153881	-889.174954	-889.018112
Dipole moment (Debye) Total	0.6339	0.6756	0.6487	0.6841	0.6431
HOMO	-0.49838	-0.50266	-0.49989	-0.50361	-0.49590
LUMO	-0.02774	-0.03404	-0.02938	-0.03505	-0.02550

Table A20. Calculated energy data for the **2G** at B3LYP level with 5 different basis sets

3,5,6-trinitro-1,2,4-triazine (2G)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-893.7597500	-893.7995232	-893.9952482	-894.0226170	-893.8383680
Zero-point vibrational energy(Joules/Mol)	183369.7	182258.2	182605.7	181786.6	183385.1
Zero-point correction (Hartree/Particle)	0.069842	0.069418	0.069551	0.069239	0.069848
Thermal correction to Energy	0.081965	0.081702	0.081700	0.081482	0.082001
Thermal correction to Enthalpy	0.082909	0.082646	0.082644	0.082426	0.082945
Thermal correction to Gibbs Free Energy	0.028602	0.027475	0.028207	0.027557	0.028395
Sum of electronic and zero-point Energies	-893.689908	-893.730105	-893.925697	-893.953378	-893.768520
Sum of electronic and thermal Energies	-893.677785	-893.717821	-893.913548	-893.941135	-893.756367
Sum of electronic and thermal Enthalpies	-893.676841	-893.716877	-893.912604	-893.940191	-893.755423
Sum of electronic and thermal Free Energies	-893.731148	-893.772048	-893.967041	-893.995060	-893.809973
Dipole moment (Debye) Total	0.2141	0.3805	0.2229	0.3415	0.2049
HOMO	-0.32824	-0.34409	-0.33467	-0.34453	-0.32562
LUMO	-0.16883	-0.18115	-0.17359	-0.18236	-0.16553

Table A21. Calculated energy data for the **3A** at HF level with 5 different basis sets

4-nitro-1,2,3-triazine (3A)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-482.0700047	-482.0832917	-482.1790445	-482.1887060	-482.1098838
Zero-point vibrational energy(Joules/Mol)	190205.7	189574.3	189196.7	188510.3	189868.3
Zero-point correction (Hartree/Particle)	0.072446	0.072205	0.072061	0.071800	0.072317
Thermal correction to Energy	0.078668	0.078441	0.078289	0.078055	0.078536
Thermal correction to Enthalpy	0.079612	0.079385	0.079233	0.078999	0.079480
Thermal correction to Gibbs Free Energy	0.039882	0.039725	0.039678	0.039338	0.039877
Sum of electronic and zero-point Energies	-481.997559	-482.011087	-482.106983	-482.116906	-482.037567
Sum of electronic and thermal Energies	-481.991337	-482.004851	-482.100755	-482.110651	-482.031348
Sum of electronic and thermal Enthalpies	-481.990393	-482.003907	-482.099811	-482.109707	-482.030404
Sum of electronic and thermal Free Energies	-482.030123	-482.043567	-482.139367	-482.149368	-482.070007
Dipole moment (Debye) Total	4.9300	4.9819	4.9100	4.9866	4.8243
HOMO	-0.45594	-0.46099	-0.45779	-0.46100	-0.45430
LUMO	0.01750	0.00520	0.01637	0.00706	0.01906

Table A22. Calculated energy data for the **3A** at B3LYP level with 5 different basis sets

4-nitro-1,2,3-triazine (3A)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-484.7869375	-484.8074339	-484.9060238	-484.9191751	-484.8224942
Zero-point vibrational energy(Joules/Mol)	171999.0	171430.9	170913.7	170569.1	171544.5
Zero-point correction (Hartree/Particle)	0.065511	0.065295	0.065098	0.064966	0.065338
Thermal correction to Energy	0.072261	0.072086	0.071899	0.071782	0.072094
Thermal correction to Enthalpy	0.073206	0.073031	0.072843	0.072726	0.073038
Thermal correction to Gibbs Free Energy	0.032950	0.032302	0.031813	0.031805	0.032787
Sum of electronic and zero-point Energies	-484.721427	-484.742139	-484.840926	-484.854209	-484.757156
Sum of electronic and thermal Energies	-484.714676	-484.735347	-484.834125	-484.847393	-484.750400
Sum of electronic and thermal Enthalpies	-484.713732	-484.734403	-484.833181	-484.846449	-484.749456
Sum of electronic and thermal Free Energies	-484.753988	-484.775132	-484.874211	-484.887370	-484.789707
Dipole moment (Debye) Total	4.4836	4.7380	4.5270	4.7420	4.3096
HOMO	-0.28949	-0.30156	-0.29414	-0.30160	-0.28750
LUMO	-0.13050	-0.14582	-0.13543	-0.14494	-0.12859

Table A23. Calculated energy data for the **3B** at HF level with 5 different basis sets

5-nitro-1,2,3-triazine (3B)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-482.0723644	-482.0853030	-482.1809840	-482.1902358	-482.1119909
Zero-point vibrational energy(Joules/Mol)	190904.1	189994.3	189772.2	188642.6	190642.0
Zero-point correction (Hartree/Particle)	0.072712	0.072365	0.072280	0.071850	0.072612
Thermal correction to Energy	0.078881	0.078575	0.078475	0.078103	0.078783
Thermal correction to Enthalpy	0.079826	0.079519	0.079419	0.079047	0.079727
Thermal correction to Gibbs Free Energy	0.041207	0.040799	0.040704	0.040159	0.041103
Sum of electronic and zero-point Energies	-481.999653	-482.012938	-482.108704	-482.118386	-482.039379
Sum of electronic and thermal Energies	-481.993483	-482.006728	-482.102509	-482.112133	-482.033208
Sum of electronic and thermal Enthalpies	-481.992539	-482.005784	-482.101565	-482.111189	-482.032264
Sum of electronic and thermal Free Energies	-482.031157	-482.044504	-482.140280	-482.150077	-482.070887
Dipole moment (Debye) Total	0.8048	0.7690	0.7892	0.7515	0.7303
HOMO	-0.45467	-0.45992	-0.45616	-0.45963	-0.45282
LUMO	0.00867	-0.00312	0.00673	-0.00191	0.01051

Table A24. Calculated energy data for the **3B** at B3LYP level with 5 different basis sets

5-nitro-1,2,3-triazine (3B)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-484.7875523	-484.8078617	-484.9063261	-484.9190078	-484.8229237
Zero-point vibrational energy(Joules/Mol)	172417.8	171735.4	171320.6	170478.6	171975.6
Zero-point correction (Hartree/Particle)	0.065670	0.065411	0.065253	0.064932	0.065502
Thermal correction to Energy	0.072397	0.072183	0.072014	0.071762	0.072234
Thermal correction to Enthalpy	0.073341	0.073127	0.072958	0.072706	0.073179
Thermal correction to Gibbs Free Energy	0.033588	0.033187	0.033020	0.032457	0.033422
Sum of electronic and zero-point Energies	-484.721882	-484.742451	-484.841074	-484.854076	-484.757422
Sum of electronic and thermal Energies	-484.715155	-484.735679	-484.834312	-484.847246	-484.750689
Sum of electronic and thermal Enthalpies	-484.714211	-484.734735	-484.833368	-484.846301	-484.749745
Sum of electronic and thermal Free Energies	-484.753964	-484.774674	-484.873306	-484.886551	-484.789502
Dipole moment (Debye) Total	1.1338	1.0603	1.1723	1.0982	1.0767
HOMO	-0.28907	-0.30144	-0.29333	-0.30107	-0.28677
LUMO	-0.14154	-0.15689	-0.14684	-0.15651	-0.13929

Table A25. Calculated energy data for the **3C** at HF level with 5 different basis sets

4,5-dinitro-1,2,3-triazine (3C)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-685.5059557	-685.5258362	-685.6688801	-685.6838530	-685.5671539
Zero-point vibrational energy(Joules/Mol)	198988.4	198079.9	198214.5	197382.6	199071.1
Zero-point correction (Hartree/Particle)	0.075791	0.075445	0.075496	0.075179	0.075822
Thermal correction to Energy	0.084471	0.084154	0.084166	0.083864	0.084513
Thermal correction to Enthalpy	0.085416	0.085098	0.085110	0.084808	0.085458
Thermal correction to Gibbs Free Energy	0.039850	0.039512	0.039759	0.039627	0.039665
Sum of electronic and zero-point Energies	-685.430165	-685.450392	-685.593384	-685.608674	-685.491332
Sum of electronic and thermal Energies	-685.421484	-685.441682	-685.584714	-685.599989	-685.482641
Sum of electronic and thermal Enthalpies	-685.420540	-685.440738	-685.583770	-685.599045	-685.481696
Sum of electronic and thermal Free Energies	-685.466105	-685.486324	-685.629121	-685.644226	-685.527489
Dipole moment (Debye) Total	3.4635	3.5102	3.4990	3.5391	3.4647
HOMO	-0.48501	-0.48967	-0.48643	-0.48929	-0.48303
LUMO	-0.01757	-0.02663	-0.01842	-0.02387	-0.01607

Table A26. Calculated energy data for the **3C** at B3LYP level with 5 different basis sets

4,5-dinitro-1,2,3-triazine (3C)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-689.2586503	-689.2890088	-689.4351410	-689.4553045	-689.3159584
Zero-point vibrational energy(Joules/Mol)	176812.1	176282.9	175897.3	175473.4	176752.4
Zero-point correction (Hartree/Particle)	0.067344	0.067143	0.066996	0.066834	0.067321
Thermal correction to Energy	0.076836	0.076622	0.076472	0.076306	0.076808
Thermal correction to Enthalpy	0.077780	0.077566	0.077416	0.077250	0.077752
Thermal correction to Gibbs Free Energy	0.029744	0.029711	0.029969	0.030191	0.030004
Sum of electronic and zero-point Energies	-689.191306	-689.221866	-689.368145	-689.388470	-689.248637
Sum of electronic and thermal Energies	-689.181814	-689.212387	-689.358669	-689.378998	-689.239151
Sum of electronic and thermal Enthalpies	-689.180870	-689.211443	-689.357725	-689.378054	-689.238207
Sum of electronic and thermal Free Energies	-689.228906	-689.259298	-689.405172	-689.425114	-689.285955
Dipole moment (Debye) Total	2.7316	2.9302	2.7940	2.9590	2.6554
HOMO	-0.31303	-0.32611	-0.31768	-0.32585	-0.31019
LUMO	-0.16181	-0.17682	-0.16620	-0.17418	-0.15946

Table A27. Calculated energy data for the **3D** at HF level with 5 different basis sets

4,6-dinitro-1,2,3-triazine (3D)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-685.5165329	-685.5356774	-685.6794235	-685.6939953	-685.5777194
Zero-point vibrational energy(Joules/Mol)	198316.8	197402.7	197504.1	196440.5	198385.7
Zero-point correction (Hartree/Particle)	0.075535	0.075187	0.075225	0.07482	0.075561
Thermal correction to Energy	0.084221	0.083888	0.083906	0.08356	0.084228
Thermal correction to Enthalpy	0.085165	0.084833	0.08485	0.084504	0.085172
Thermal correction to Gibbs Free Energy	0.037733	0.037707	0.037908	0.03716	0.038043
Sum of electronic and zero-point Energies	-685.440998	-685.460491	-685.604198	-685.619175	-685.502158
Sum of electronic and thermal Energies	-685.432312	-685.451789	-685.595518	-685.610435	-685.493491
Sum of electronic and thermal Enthalpies	-685.431368	-685.450845	-685.594573	-685.609491	-685.492547
Sum of electronic and thermal Free Energies	-685.4788	-685.49797	-685.641515	-685.656835	-685.539676
Dipole moment (Debye) Total	1.1978	1.0883	1.1549	1.0803	1.1475
HOMO	-0.48795	-0.4928	-0.48971	-0.493	-0.48607
LUMO	-0.01897	-0.02713	-0.0188	-0.02519	-0.01638

Table A28. Calculated energy data for the **3D** at B3LYP level with 5 different basis sets

4,6-dinitro-1,2,3-triazine (3D)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-689.2679399	-689.2969509	-689.4441414	-689.4635626	-689.3252549
Zero-point vibrational energy(Joules/Mol)	176814.9	175955.1	175583.1	174833.7	176540.4
Zero-point correction (Hartree/Particle)	0.067345	0.067018	0.066876	0.066591	0.067241
Thermal correction to Energy	0.076718	0.076447	0.076318	0.076111	0.076628
Thermal correction to Enthalpy	0.077662	0.077391	0.077263	0.077055	0.077572
Thermal correction to Gibbs Free Energy	0.029904	0.029083	0.028564	0.026625	0.029675
Sum of electronic and zero-point Energies	-689.200595	-689.229933	-689.377265	-689.396972	-689.258014
Sum of electronic and thermal Energies	-689.191222	-689.220504	-689.367823	-689.387452	-689.248627
Sum of electronic and thermal Enthalpies	-689.190278	-689.21956	-689.366879	-689.386508	-689.247683
Sum of electronic and thermal Free Energies	-689.238036	-689.267868	-689.415577	-689.436937	-689.29558
Dipole moment (Debye) Total	1.4676	1.3615	1.4582	1.3783	1.4013
HOMO	-0.31751	-0.3299	-0.32233	-0.3301	-0.31468
LUMO	-0.15929	-0.17378	-0.16352	-0.17288	-0.15638

Table A29. Calculated energy data for the **3E** at HF level with 5 different basis sets

4,5,6-trinitro-1,2,3-triazine (3E)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-888.9361017	-888.9625782	-889.1532050	-889.1738767	-889.0187028
Zero-point vibrational energy(Joules/Mol)	207187.7	205969.8	206588.6	205515.8	207551.7
Zero-point correction (Hartree/Particle)	0.078914	0.078450	0.078685	0.078277	0.079052
Thermal correction to Energy	0.090047	0.089679	0.089826	0.089478	0.090186
Thermal correction to Enthalpy	0.090992	0.090623	0.090770	0.090422	0.091130
Thermal correction to Gibbs Free Energy	0.039688	0.039028	0.039434	0.038978	0.039775
Sum of electronic and zero-point Energies	-888.857188	-888.884128	-889.074520	-889.095600	-888.939651
Sum of electronic and thermal Energies	-888.846054	-888.872899	-889.063379	-889.084399	-888.928517
Sum of electronic and thermal Enthalpies	-888.845110	-888.871955	-889.062435	-889.083455	-888.927573
Sum of electronic and thermal Free Energies	-888.896413	-888.923550	-889.113771	-889.134899	-888.978927
Dipole moment (Debye) Total	1.5789	1.5843	1.6306	1.6562	1.6409
HOMO	-0.5041	-0.51231	-0.50635	-0.51164	-0.50228
LUMO	-0.03176	-0.03972	-0.03348	-0.03898	-0.02968

Table A30. Calculated energy data for the **3E** at B3LYP level with 5 different basis sets

4,5,6-trinitro-1,2,3-triazine (3E)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	cc-pvDZ
HF	-893.7283698	-893.7674034	-893.9622941	-893.9893272	-893.8072866
Zero-point vibrational energy(Joules/Mol)	181411.6	180349.5	180465.6	179728.5	181435.8
Zero-point correction (Hartree/Particle)	0.069096	0.068691	0.068736	0.068455	0.069105
Thermal correction to Energy	0.081232	0.080954	0.080896	0.080693	0.081258
Thermal correction to Enthalpy	0.082176	0.081898	0.081840	0.081637	0.082202
Thermal correction to Gibbs Free Energy	0.028402	0.027614	0.027999	0.027524	0.028323
Sum of electronic and zero-point Energies	-893.659274	-893.698712	-893.893558	-893.920872	-893.738181
Sum of electronic and thermal Energies	-893.647138	-893.686449	-893.881398	-893.908634	-893.726029
Sum of electronic and thermal Enthalpies	-893.646194	-893.685505	-893.880454	-893.907690	-893.725085
Sum of electronic and thermal Free Energies	-893.699968	-893.739790	-893.934295	-893.961803	-893.778963
Dipole moment (Debye) Total	0.7752	0.8942	0.7805	0.8999	0.7775
HOMO	-0.33462	-0.34882	-0.33982	-0.34869	-0.33110
LUMO	-0.16861	-0.18543	-0.17448	-0.18476	-0.16548

APPENDIX B

Cartesian Coordinates of Ground State Geometries of Nitrotriazine Derivatives at HF/6-31G(d,p) Level

2-nitro-1,3,5-triazine (1A)			E = -482.1528574 a.u.	ZPVE = 194.8875 kJ/mol	
Center Number	Atomic Number	Atomic Type	X	Coordinates (Angstroms) Y	Z
1	6	C	0.011583	1.111106	1.708752
2	7	N	0.000000	1.171693	0.388299
3	6	C	0.000000	0.000000	-0.174929
4	7	N	0.000000	-1.171693	0.388299
5	6	C	-0.011583	-1.111106	1.708752
6	7	N	0.000000	0.000000	2.415002
7	7	N	0.000000	0.000000	-1.646826
8	8	O	0.877673	-0.602621	-2.172051
9	8	O	-0.877673	0.602621	-2.172051
10	1	H	0.028732	2.043350	2.241970
11	1	H	-0.028732	-2.043350	2.241970

2,4-dinitro-1,3,5-triazine (1B)			E = -685.5968728 a.u.	ZPVE = 203.0197 kJ/mol	
Center Number	Atomic Number	Atomic Type	X	Coordinates (Angstroms) Y	Z
1	6	C	-1.080184	0.167364	-0.038279
2	7	N	0.000000	-0.556619	0.064284
3	6	C	1.080184	0.167364	-0.038279
4	7	N	1.168932	1.445977	-0.253157
5	6	C	0.000000	2.048023	-0.373182
6	7	N	-1.168932	1.445978	-0.253157
7	7	N	-2.351905	-0.556355	0.103559
8	7	N	2.351905	-0.556355	0.103558
9	8	O	2.498910	-1.493588	-0.607402
10	8	O	3.104090	-0.128709	0.914833
11	8	O	-2.498912	-1.493584	-0.607406
12	8	O	-3.104087	-0.128711	0.914838
13	1	H	0.000000	3.101856	-0.576070

2,4,6-trinitro-1,3,5-triazine (1C)			E = -889.0347462 a.u.	ZPVE = 210.8574 kJ/mol	
Center Number	Atomic Number	Atomic Type	X	Coordinates (Angstroms) Y	Z
1	6	N	-0.139258	1.244503	0.000000
2	7	N	1.086397	0.800515	-0.000001
3	6	N	1.147401	-0.501650	-0.000001
4	7	C	0.150069	-1.341105	-0.000001
5	6	N	-1.008142	-0.742854	0.000000
6	7	O	-1.236465	0.540588	0.000000
7	7	O	-0.302687	2.704996	0.000000
8	7	C	2.493938	-1.090363	0.000000
9	7	N	-2.191251	-1.614632	0.000001
10	8	O	2.688570	-1.927929	0.814783
11	8	O	3.240951	-0.664489	-0.814784
12	8	C	0.325385	3.292339	0.814754
13	8	N	-1.045045	3.138988	-0.814754
14	8	O	-3.013926	-1.364396	0.814775
15	8	O	-2.195935	-2.474512	-0.814772

3-nitro-1,2,4-triazine (2A)

E = -482.0980504 a.u.

ZPVE = 191.9757 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.398271	1.161605	0.235862
2	6	C	1.701242	1.115122	0.236188
3	6	C	2.360011	-0.091284	-0.021157
4	7	N	1.688885	-1.187129	-0.251436
5	7	N	0.379151	-1.144944	-0.224772
6	6	C	-0.173254	0.001603	0.006168
7	7	N	-1.643432	0.004483	0.001157
8	8	O	-2.162007	0.899478	-0.584207
9	8	O	-2.182829	-0.880877	0.578836
10	1	H	2.240161	2.024003	0.432462
11	1	H	3.430420	-0.163557	-0.042359

6-nitro-1,2,4-triazine (2B)

E = -482.1021515 a.u.

ZPVE = 192.1908 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.806351	1.151424	0.000016
2	6	C	0.503110	1.190192	0.000015
3	6	C	-0.193142	-0.017816	0.000000
4	7	N	0.396908	-1.168769	-0.000015
5	7	N	1.700567	-1.202216	-0.000016
6	6	C	2.348102	-0.059908	0.000000
7	7	N	-1.656848	-0.021014	0.000000
8	8	O	-2.217710	-1.060912	0.000032
9	8	O	-2.169387	1.060661	-0.000033
10	1	H	0.000512	2.136825	0.000027
11	1	H	3.419001	-0.125605	-0.000001

5-nitro-1,2,4-triazine (2C)

E = -482.1013487 a.u.

ZPVE = 192.0252 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.399101	-1.168430	0.000026
2	6	C	-0.193382	-0.026839	0.000000
3	6	C	0.496685	1.179823	-0.000026
4	7	N	1.806157	1.152890	-0.000028
5	7	N	2.428323	0.005411	-0.000003
6	6	C	1.725405	-1.099858	0.000028
7	7	N	-1.667622	-0.027392	0.000000
8	8	O	-2.220173	-1.071782	-0.000061
9	8	O	-2.181638	1.051096	0.000063
10	1	H	0.008638	2.131662	-0.000050
11	1	H	2.271889	-2.022282	0.000062

3,6-dinitro-1,2,4-triazine (2D)

E = -685.545813 a.u.

ZPVE = 200.3687 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.708729	1.196339	-0.169559
2	6	C	-0.595414	1.203095	-0.182450
3	6	C	-1.260534	-0.012148	-0.000767
4	7	N	-0.641862	-1.134718	0.164686
5	7	N	0.663593	-1.136269	0.148712
6	6	C	1.248396	0.011520	-0.008587
7	7	N	-2.724857	-0.050206	0.011048
8	7	N	2.715977	-0.027389	0.004376
9	8	O	3.246973	0.761187	0.715194
10	8	O	3.229008	-0.837056	-0.693449
11	8	O	-3.254514	-1.088365	0.194863
12	8	O	-3.257459	1.004631	-0.171569
13	1	H	-1.117816	2.127723	-0.324327

3,5-dinitro-1,2,4-triazine (2E)

E = -685.5447231 a.u.

ZPVE = 200.3420 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.002176	-0.556250	-0.019477
2	6	C	-1.085990	0.130254	-0.007029
3	6	C	-1.091631	1.521315	0.069387
4	7	N	0.052634	2.155873	0.112338
5	7	N	1.166978	1.475548	0.075452
6	6	C	1.086100	0.183741	0.019764
7	7	N	-2.356994	-0.609788	-0.070016
8	7	N	2.363454	-0.541610	0.008984
9	8	O	3.228850	-0.080334	-0.657438
10	8	O	2.405882	-1.524155	0.673732
11	8	O	-2.305684	-1.768052	-0.288693
12	8	O	-3.336140	0.050422	0.104916
13	1	H	-1.991881	2.098681	0.096163

5,6-dinitro-1,2,4-triazine (2F)

E = -685.5379665 a.u.

ZPVE = 200.8694 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.160351	-1.527304	0.032366
2	6	C	0.159036	-0.727074	0.020002
3	6	C	0.360719	0.654166	-0.023934
4	7	N	1.553150	1.143348	-0.041996
5	7	N	2.583513	0.337571	-0.019548
6	6	C	2.361862	-0.949173	0.008240
7	7	N	-1.167185	-1.337470	0.144314
8	7	N	-0.737589	1.608321	-0.140330
9	8	O	-0.638161	2.632173	0.439195
10	8	O	-1.634195	1.252130	-0.842276
11	8	O	-1.452919	-2.162901	-0.650770
12	8	O	-1.806711	-0.952412	1.070473
13	1	H	3.220507	-1.590685	0.017547

3,5,6-trinitro-1,2,4-triazine (2G)

E = -888.9754944 a.u.

ZPVE = 208.7697 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.845674	0.815887	-0.005117
2	6	C	0.411068	0.560105	-0.012421
3	6	C	0.857104	-0.766623	0.010062
4	7	N	0.018156	-1.744205	0.037376
5	7	N	-1.266648	-1.491128	0.030842
6	6	C	-1.622563	-0.249496	0.008296
7	7	N	1.316754	1.709505	0.047221
8	7	N	2.269980	-1.124420	-0.082163
9	7	O	-3.068216	0.008441	0.017512
10	8	O	-3.728048	-0.677415	-0.687334
11	8	O	-3.427224	0.880885	0.736470
12	8	O	2.649141	-2.017741	0.588078
13	8	O	2.892437	-0.470201	-0.860028
14	8	O	2.090627	1.677690	0.949090
15	8	O	1.167552	2.546472	-0.770690

4-nitro-1,2,3-triazine (3A)

E = -482.0700047 a.u.

ZPVE = 190.2057 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.690929	-1.214056	-0.000001
2	7	N	0.399953	-1.153992	-0.000001
3	6	C	-0.189486	0.008860	0.000000
4	6	C	0.476392	1.206196	0.000002
5	6	C	1.845608	1.050348	0.000001
6	7	N	2.411627	-0.143077	-0.000001
7	7	N	-1.663137	-0.011764	0.000000
8	8	O	-2.207563	-1.059272	0.000003
9	8	O	-2.188197	1.062625	-0.000003
10	1	H	-0.021687	2.153151	0.000003
11	1	H	2.517077	1.887826	0.000001

5-nitro-1,2,3-triazine (3B)

E = -482.0723644 a.u.

ZPVE = 190.9041 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.437640	-0.000001	0.000003
2	7	N	1.815232	-1.131844	0.000000
3	6	C	0.494609	-1.169551	-0.000002
4	6	C	-0.223097	-0.000001	-0.000001
5	6	C	0.494610	1.169551	0.000003
6	7	N	1.815230	1.131846	0.000005
7	7	N	-1.674145	0.000000	-0.000003
8	8	O	-2.213352	-1.061487	-0.000004
9	8	O	-2.213351	1.061488	0.000000
10	1	H	0.029595	-2.135259	-0.000004
11	1	H	0.029594	2.135259	0.000003

4,5-dinitro-1,2,3-triazine (3C)

E = -685.5059557 a.u.

ZPVE = 198.9884 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.978431	-1.680811	0.002986
2	7	N	0.686393	-1.778101	0.016535
3	6	C	-0.053169	-0.705756	0.008660
4	6	C	0.497002	0.553921	-0.016964
5	6	C	1.868109	0.581217	-0.024003
6	7	N	2.570713	-0.541610	-0.014293
7	7	N	-1.489403	-0.980401	0.080926
8	7	N	-0.271356	1.783706	-0.076771
9	8	O	-1.989869	-1.413122	-0.898746
10	8	O	-1.407825	1.684153	-0.405526
11	8	O	-1.990440	-0.768523	1.135872
12	8	O	0.311814	2.785198	0.189807
13	1	H	2.415462	1.502587	-0.043093

4,6-dinitro-1,2,3-triazine (3D)

E = -685.5165329 a.u.

ZPVE = 198.3168 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.084391	-0.000033
2	7	N	1.122444	1.445947	-0.000236
3	6	C	1.131646	0.142472	-0.000219
4	6	C	0.000000	-0.635266	0.000006
5	6	C	-1.131646	0.142472	0.000214
6	7	N	-1.122444	1.445947	0.000193
7	7	N	2.456642	-0.501209	-0.000462
8	7	N	-2.456642	-0.501209	0.000478
9	8	O	3.409306	0.194481	-0.000517
10	8	O	2.437952	-1.695168	-0.000578
11	8	O	-2.437952	-1.695168	0.000527
12	8	O	-3.409306	0.194481	0.000617
13	1	H	0.000000	-1.704147	0.000017

4,5,6-trinitro-1,2,3-triazine (3E)

E = -888.9361017 a.u.

ZPVE = 207.1877 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000001	2.553656	0.000000
2	7	N	-1.121189	1.918417	-0.009351
3	6	C	-1.142330	0.613763	-0.012998
4	6	C	0.000000	-0.147413	-0.000004
5	6	C	1.142330	0.613762	0.012990
6	7	N	1.121190	1.918417	0.009348
7	7	N	-2.476789	0.015533	-0.100215
8	7	N	0.000000	-1.604468	-0.000001
9	7	N	2.476788	0.015532	0.100217
10	8	O	2.592567	-0.817826	0.942211
11	8	O	-3.293364	0.422983	0.646749
12	8	O	-0.649714	-2.117669	0.846921
13	8	O	-2.592571	-0.817830	-0.942203
14	8	O	0.649714	-2.117673	-0.846922
15	8	O	3.293368	0.422979	-0.646744

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at HF/6-31+G(d,p) Level**

2-nitro-1,3,5-triazine (1A) E = -482.1667969 a.u. ZPVE = 194.0759 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.004849	1.112267	1.707632
2	7	N	0.000000	1.172654	0.386186
3	6	C	0.000000	0.000000	-0.174658
4	7	N	0.000000	-1.172654	0.386186
5	6	C	-0.004849	-1.112267	1.707632
6	7	N	0.000000	0.000000	2.413163
7	7	N	0.000000	0.000000	-1.645547
8	8	O	1.046241	-0.203976	-2.169090
9	8	O	-1.046241	0.203976	-2.169090
10	1	H	0.012019	2.044243	2.240942
11	1	H	-0.012019	-2.044243	2.240942

2,4-dinitro-1,3,5-triazine (1B) E = -685.6173429 a.u. ZPVE = 201.7844 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.078656	0.169021	-0.025735
2	7	N	0.000000	-0.561281	0.047028
3	6	C	1.078656	0.169020	-0.025737
4	7	N	1.169753	1.456785	-0.173546
5	6	C	0.000001	2.065575	-0.254159
6	7	N	-1.169752	1.456786	-0.173545
7	7	N	-2.349238	-0.561069	0.070404
8	7	N	2.349238	-0.561072	0.070399
9	8	O	2.667616	-1.175972	-0.892625
10	8	O	2.927506	-0.459200	1.101341
11	8	O	-2.667639	-1.175934	-0.892635
12	8	O	-2.927482	-0.459230	1.101362
13	1	H	0.000001	3.129940	-0.390931

2,4,6-trinitro-1,3,5-triazine (1C) E = -889.0614292 a.u. ZPVE = 209.3299 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	N	1.138275	-0.518150	0.000012
2	7	N	1.099625	0.785070	0.000012
3	6	N	-0.120407	1.244850	-0.000001
4	7	C	-1.229702	0.559768	-0.000014
5	6	N	-1.017868	-0.726700	-0.000011
6	7	O	0.130078	-1.344838	0.000001
7	7	O	2.474668	-1.126485	0.000026
8	7	C	-0.261770	2.706368	-0.000002
9	7	N	-2.212898	-1.579883	-0.000025
10	8	O	-0.759827	3.173339	-0.968720
11	8	O	0.137556	3.260137	0.968716
12	8	C	3.128110	-0.928652	-0.968691
13	8	N	2.754577	-1.749184	0.968754
14	8	O	-2.368277	-2.244685	-0.968753
15	8	O	-2.892140	-1.510955	0.968694

3-nitro-1,2,4-triazine (2A)

E = -482.1117029 a.u.

ZPVE = 191.2399 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.395785	1.157559	0.259564
2	6	C	1.699394	1.111755	0.258123
3	6	C	2.359236	-0.090716	-0.022399
4	7	N	1.687746	-1.181757	-0.273640
5	7	N	0.377910	-1.140635	-0.248661
6	6	C	-0.172086	0.001472	0.005422
7	7	N	-1.642199	0.003555	0.000433
8	8	O	-2.160513	0.736057	-0.779619
9	8	O	-2.179603	-0.718601	0.774855
10	1	H	2.237445	2.017149	0.471782
11	1	H	3.429532	-0.162909	-0.044418

6-nitro-1,2,4-triazine (2B)

E = -482.1151908 a.u.

ZPVE = 191.4888 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.807764	1.151231	0.000015
2	6	C	0.504152	1.190959	0.000012
3	6	C	-0.192074	-0.018207	-0.000004
4	7	N	0.397928	-1.168799	-0.000013
5	7	N	1.701229	-1.202766	-0.000016
6	6	C	2.350043	-0.060289	0.000002
7	7	N	-1.658718	-0.021456	-0.000001
8	8	O	-2.221027	-1.060841	0.000031
9	8	O	-2.170728	1.061575	-0.000028
10	1	H	0.003298	2.138438	0.000025
11	1	H	3.420593	-0.126548	0.000008

5-nitro-1,2,4-triazine (2C)

E = -482.1143360 a.u.

ZPVE = 191.3364 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.400399	-1.168570	0.000026
2	6	C	-0.191977	-0.027372	0.000004
3	6	C	0.497310	1.180501	-0.000023
4	7	N	1.807428	1.152310	-0.000023
5	7	N	2.429612	0.005970	0.000002
6	6	C	1.727068	-1.100518	0.000014
7	7	N	-1.669775	-0.027766	0.000004
8	8	O	-2.223455	-1.071890	-0.000045
9	8	O	-2.183188	1.051871	0.000040
10	1	H	0.011284	2.133386	-0.000043
11	1	H	2.273809	-2.022513	0.000061

3,6-dinitro-1,2,4-triazine (2D)

E = -685.5653797 a.u.

ZPVE = 199.3141 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.711416	1.199073	-0.152757
2	6	C	-0.593202	1.206361	-0.162814
3	6	C	-1.258505	-0.013085	-0.000551
4	7	N	-0.640115	-1.137536	0.147070
5	7	N	0.665682	-1.139345	0.135764
6	6	C	1.247696	0.011174	-0.006415
7	7	N	-2.725403	-0.051176	0.009247
8	7	N	2.714644	-0.027748	0.004547
9	8	O	3.238523	0.509625	0.924728
10	8	O	3.232629	-0.583895	-0.906333
11	8	O	-3.256981	-1.092856	0.167840
12	8	O	-3.257312	1.009175	-0.148627
13	1	H	-1.114376	2.134033	-0.289282

3,5-dinitro-1,2,4-triazine (2E)

E = -685.5639955 a.u.

ZPVE = 199.2930 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.006430	-0.556436	0.022392
2	6	C	1.085193	0.124491	0.006108
3	6	C	1.098412	1.515817	-0.074971
4	7	N	-0.043439	2.155659	-0.119574
5	7	N	-1.161359	1.482144	-0.080615
6	6	C	-1.084309	0.190691	-0.019711
7	7	N	2.354815	-0.624243	0.071029
8	7	N	-2.365668	-0.527524	-0.006252
9	8	O	-3.147417	-0.198940	0.823372
10	8	O	-2.493218	-1.372368	-0.831296
11	8	O	2.296273	-1.786069	0.270242
12	8	O	3.339135	0.034467	-0.084032
13	1	H	2.000610	2.090087	-0.103706

5,6-dinitro-1,2,4-triazine (2F)

E = -685.5577162 a.u.

ZPVE = 199.8827 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.151606	-1.535385	0.037972
2	6	C	0.156632	-0.727872	0.019764
3	6	C	0.367816	0.652006	-0.028272
4	7	N	1.563357	1.132522	-0.050686
5	7	N	2.587827	0.320003	-0.027645
6	6	C	2.357442	-0.965649	0.009078
7	7	N	-1.176684	-1.329772	0.142621
8	7	N	-0.727788	1.614232	-0.136767
9	8	O	-0.626672	2.630369	0.456668
10	8	O	-1.626317	1.268633	-0.842748
11	8	O	-1.489017	-2.113170	-0.684763
12	8	O	-1.794403	-0.979505	1.097860
13	1	H	3.211710	-1.612725	0.021995

3,5,6-trinitro-1,2,4-triazine (2G)

E = -889.0017153 a.u.

ZPVE = 207.4218 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.847868	0.816217	-0.001322
2	6	C	0.408472	0.558959	-0.011912
3	6	C	0.854121	-0.768423	0.004559
4	7	N	0.015601	-1.745800	0.024335
5	7	N	-1.269396	-1.492982	0.019464
6	6	C	-1.622118	-0.250822	0.006062
7	7	N	1.316463	1.709656	0.050854
8	7	N	2.270667	-1.123339	-0.081577
9	7	O	-3.067291	0.006936	0.018325
10	8	O	-3.696473	-0.494744	-0.851510
11	8	O	-3.455471	0.696239	0.903018
12	8	O	2.651801	-2.009973	0.597079
13	8	O	2.894924	-0.469708	-0.859756
14	8	O	2.054139	1.702199	0.983821
15	8	O	1.204820	2.521848	-0.798002

4-nitro-1,2,3-triazine (3A)

E = -482.0832917 a.u.

ZPVE = 189.5743 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.691767	-1.214298	-0.000019
2	7	N	-0.400616	-1.153831	-0.000021
3	6	C	0.188204	0.009034	0.000010
4	6	C	-0.477686	1.207088	0.000004
5	6	C	-1.847650	1.050246	0.000023
6	7	N	-2.412817	-0.144259	-0.000003
7	7	N	1.665210	-0.012175	0.000004
8	8	O	2.210488	-1.059444	0.000038
9	8	O	2.190076	1.063425	-0.000039
10	1	H	0.018607	2.155300	0.000023
11	1	H	-2.520392	1.886585	0.000047

5-nitro-1,2,3-triazine (3B)

E = -482.0853030 a.u.

ZPVE = 189.9943 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.438636	-0.000001	0.000004
2	7	N	1.816685	-1.131638	0.000000
3	6	C	0.495329	-1.170345	-0.000002
4	6	C	-0.222279	-0.000001	-0.000001
5	6	C	0.495331	1.170346	0.000001
6	7	N	1.816684	1.131639	0.000005
7	7	N	-1.676000	0.000000	-0.000002
8	8	O	-2.215482	-1.062021	-0.000003
9	8	O	-2.215481	1.062021	-0.000001
10	1	H	0.032691	-2.137183	-0.000004
11	1	H	0.032691	2.137182	0.000005

4,5-dinitro-1,2,3-triazine (3C)

E = -685.5258362 a.u.

ZPVE = 198.0799 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.919943	-1.746761	-0.000203
2	7	N	0.625818	-1.799789	0.013766
3	6	C	-0.076581	-0.702462	0.004190
4	6	C	0.515785	0.538418	-0.019702
5	6	C	1.887795	0.517924	-0.023822
6	7	N	2.551225	-0.629062	-0.015991
7	7	N	-1.523449	-0.934218	0.070492
8	7	N	-0.209770	1.797525	-0.065121
9	8	O	-2.043321	-1.291980	-0.929904
10	8	O	-1.359415	1.739004	-0.355962
11	8	O	-2.012927	-0.770135	1.139772
12	8	O	0.418577	2.778612	0.177914
13	1	H	2.468337	1.418839	-0.039152

4,6-dinitro-1,2,3-triazine (3D)

E = -685.5356774 a.u.

ZPVE = 197.4027 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.084906	-0.000003
2	7	N	1.122541	1.446701	-0.000003
3	6	C	1.131606	0.143424	-0.000001
4	6	C	0.000000	-0.635236	0.000000
5	6	C	-1.131606	0.143423	0.000001
6	7	N	-1.122541	1.446701	-0.000001
7	7	N	2.459591	-0.501239	-0.000002
8	7	N	-2.459591	-0.501239	0.000004
9	8	O	3.413104	0.193855	0.000035
10	8	O	2.440303	-1.696107	-0.000041
11	8	O	-2.440303	-1.696107	0.000035
12	8	O	-3.413104	0.193855	-0.000024
13	1	H	0.000000	-1.704446	0.000001

4,5,6-trinitro-1,2,3-triazine (3E)

E = -888.9625782 a.u.

ZPVE = 205.9698 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000001	2.551349	0.000000
2	7	N	-1.121849	1.917564	-0.012296
3	6	C	-1.141967	0.612539	-0.013618
4	6	C	0.000000	-0.148398	-0.000002
5	6	C	1.141968	0.612538	0.013614
6	7	N	1.121851	1.917563	0.012296
7	7	N	-2.479472	0.016245	-0.100793
8	7	N	-0.000001	-1.606158	0.000001
9	7	N	2.479472	0.016243	0.100795
10	8	O	2.632370	-0.728340	1.017011
11	8	O	-3.260619	0.340438	0.721963
12	8	O	-0.706559	-2.121460	0.800401
13	8	O	-2.632377	-0.728332	-1.017014
14	8	O	0.706557	-2.121461	-0.800404
15	8	O	3.260624	0.340441	-0.721954

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at HF/6-311G(d,p) Level**

2-nitro-1,3,5-triazine (1A) E = -482.2634125 a.u. ZPVE = 194.0506 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.011277	1.109549	1.707561
2	7	N	0.000000	1.170138	0.388071
3	6	C	0.000000	0.000000	-0.172417
4	7	N	0.000000	-1.170138	0.388071
5	6	C	-0.011277	-1.109549	1.707561
6	7	N	0.000000	0.000000	2.413706
7	7	N	0.000000	0.000000	-1.648865
8	8	O	0.888459	-0.576171	-2.170254
9	8	O	-0.888459	0.576171	-2.170254
10	1	H	0.027908	2.042016	2.240473
11	1	H	-0.027908	-2.042016	2.240473

2,4-dinitro-1,3,5-triazine (1B) E = -685.7621045 a.u. ZPVE = 202.4138 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.077460	0.168972	-0.037861
2	7	N	0.000004	-0.555213	0.064247
3	6	C	1.077461	0.168977	-0.037858
4	7	N	1.168082	1.445159	-0.250329
5	6	C	-0.000004	2.046745	-0.368717
6	7	N	-1.168087	1.445151	-0.250332
7	7	N	-2.352773	-0.557642	0.102582
8	7	N	2.352775	-0.557627	0.102585
9	8	O	2.509763	-1.470260	-0.626542
10	8	O	3.088313	-0.151476	0.929953
11	8	O	-2.509702	-1.470354	-0.626459
12	8	O	-3.088371	-0.151417	0.929860
13	1	H	-0.000008	3.101098	-0.569153

2,4,6-trinitro-1,3,5-triazine (1C) E = -889.2546218 a.u. ZPVE = 210.4904 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	N	0.667655	-1.055518	-0.000003
2	7	N	-0.626286	-1.193652	-0.000004
3	6	N	-1.247932	-0.050447	-0.000002
4	7	C	-0.720590	1.139205	0.000002
5	6	N	0.580278	1.105964	0.000004
6	7	O	1.346876	0.054446	0.000001
7	7	O	1.455639	-2.301269	-0.000002
8	7	C	-2.720777	-0.109986	-0.000002
9	7	N	1.265138	2.411254	0.000005
10	8	O	-3.257437	0.534481	0.826692
11	8	O	-3.203666	-0.795666	-0.826698
12	8	C	1.165838	-3.088266	0.826688
13	8	N	2.290906	-2.376620	-0.826692
14	8	O	2.091591	2.553781	0.826701
15	8	O	0.912766	3.172288	-0.826691

3-nitro-1,2,4-triazine (2A)

E = -482.2078517 a.u.

ZPVE = 191.0419 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.398055	1.159398	0.241553
2	6	C	1.699020	1.113458	0.241678
3	6	C	2.357528	-0.092114	-0.021672
4	7	N	1.687292	-1.184520	-0.256958
5	7	N	0.378851	-1.141501	-0.230056
6	6	C	-0.170517	0.001166	0.006342
7	7	N	-1.645013	0.004139	0.001152
8	8	O	-2.158983	0.870813	-0.616263
9	8	O	-2.180497	-0.852566	0.610467
10	1	H	2.237489	2.021798	0.442074
11	1	H	3.427873	-0.165448	-0.043636

6-nitro-1,2,4-triazine (2B)

E = -482.2113291 a.u.

ZPVE = 191.1917 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.806119	1.150621	0.000003
2	6	C	-0.505516	1.189812	0.000004
3	6	C	0.190361	-0.018343	0.000000
4	7	N	-0.397013	-1.166314	-0.000003
5	7	N	-1.699849	-1.200874	-0.000004
6	6	C	-2.346330	-0.061375	0.000000
7	7	N	1.660786	-0.021281	0.000000
8	8	O	2.216040	-1.055458	0.000007
9	8	O	2.169469	1.054971	-0.000008
10	1	H	-0.002604	2.136165	0.000006
11	1	H	-3.417186	-0.127899	0.000000

5-nitro-1,2,4-triazine (2C)

E = -482.2107315 a.u.

ZPVE = 190.9483 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.398760	-1.166380	0.000030
2	6	C	-0.190983	-0.027677	0.000008
3	6	C	0.499476	1.178668	-0.000028
4	7	N	1.806290	1.151205	-0.000028
5	7	N	2.427500	0.004425	0.000001
6	6	C	1.725324	-1.097936	0.000009
7	7	N	-1.672025	-0.027268	0.000005
8	8	O	-2.219214	-1.065998	-0.000074
9	8	O	-2.181966	1.045754	0.000072
10	1	H	0.011931	2.130559	-0.000051
11	1	H	2.270943	-2.020818	0.000077

3,6-dinitro-1,2,4-triazine (2D)

E = -685.7095106 a.u.

ZPVE = 199.6154 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.708839	1.196828	-0.161506
2	6	C	-0.592702	1.204025	-0.174585
3	6	C	-1.257078	-0.012911	-0.000893
4	7	N	-0.640951	-1.133455	0.156533
5	7	N	0.663942	-1.134710	0.140454
6	6	C	1.245409	0.010942	-0.008736
7	7	N	-2.727964	-0.050980	0.011059
8	7	N	2.717256	-0.027956	0.004318
9	8	O	3.242775	0.725849	0.744962
10	8	O	3.228019	-0.802185	-0.722864
11	8	O	-3.252209	-1.080062	0.211361
12	8	O	-3.256858	0.995182	-0.188532
13	1	H	-1.115440	2.129304	-0.310139

3,5-dinitro-1,2,4-triazine (2E)

E = -685.7084622 a.u.

ZPVE = 199.6070 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.001843	-0.555112	-0.017377
2	6	C	-1.082739	0.130489	-0.009902
3	6	C	-1.088573	1.521954	0.056945
4	7	N	0.053107	2.155232	0.094469
5	7	N	1.166392	1.473989	0.064209
6	6	C	1.083762	0.186300	0.018499
7	7	N	-2.359225	-0.612445	-0.069396
8	7	N	2.364403	-0.542058	0.017144
9	8	O	3.210725	-0.116729	-0.684119
10	8	O	2.418215	-1.485344	0.724489
11	8	O	-2.310362	-1.750910	-0.345371
12	8	O	-3.327516	0.031861	0.167868
13	1	H	-1.988836	2.099279	0.080475

5,6-dinitro-1,2,4-triazine (2F)

E = -685.7015664 a.u.

ZPVE = 200.1810 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.173580	-1.514814	0.031185
2	6	C	0.168375	-0.726537	0.019355
3	6	C	0.356814	0.656823	-0.022368
4	7	N	1.539941	1.156710	-0.040870
5	7	N	2.578461	0.361531	-0.019064
6	6	C	2.369809	-0.923773	0.007450
7	7	N	-1.156955	-1.351202	0.143813
8	7	N	-0.754590	1.603970	-0.139457
9	8	O	-0.673828	2.612435	0.454458
10	8	O	-1.631146	1.251334	-0.857107
11	8	O	-1.431069	-2.176412	-0.644581
12	8	O	-1.797404	-0.971779	1.063206
13	1	H	3.234536	-1.557062	0.016318

3,5,6-trinitro-1,2,4-triazine (2G)

E = -889.1935919 a.u.

ZPVE = 208.3070 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.844904	0.814755	-0.006761
2	6	C	0.407910	0.559845	-0.013626
3	6	C	0.854429	-0.766932	0.011380
4	7	N	0.019612	-1.742160	0.037990
5	7	N	-1.265284	-1.489534	0.031218
6	6	C	-1.618834	-0.252208	0.007377
7	7	N	1.316065	1.713895	0.045879
8	7	N	2.272694	-1.125116	-0.080503
9	7	O	-3.068637	0.006422	0.017231
10	8	O	-3.719447	-0.645512	-0.715649
11	8	O	-3.428940	0.843758	0.765446
12	8	O	2.651426	-2.003573	0.596281
13	8	O	2.887766	-0.484375	-0.865314
14	8	O	2.081517	1.685678	0.946171
15	8	O	1.169196	2.542516	-0.770208

4-nitro-1,2,3-triazine (3A)

E = -482.1790445 a.u.

ZPVE = 189.1967 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.689909	-1.210211	-0.061338
2	7	N	-0.399797	-1.150225	-0.056447
3	6	C	0.187309	0.008707	-0.000627
4	6	C	-0.477720	1.204457	0.054840
5	6	C	-1.845067	1.047700	0.053913
6	7	N	-2.409864	-0.144639	-0.004246
7	7	N	1.666625	-0.012120	0.000179
8	8	O	2.204964	-1.046750	0.125996
9	8	O	2.187692	1.049539	-0.124485
10	1	H	0.020550	2.150302	0.093522
11	1	H	-2.518318	1.882563	0.098601

5-nitro-1,2,3-triazine (3B)

E = -482.1809840 a.u.

ZPVE = 189.7722 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.436339	-0.000002	0.000003
2	7	N	1.815469	-1.130079	-0.000001
3	6	C	0.496173	-1.168077	-0.000002
4	6	C	-0.221270	-0.000001	0.000000
5	6	C	0.496175	1.168078	0.000002
6	7	N	1.815468	1.130080	0.000004
7	7	N	-1.678654	0.000000	-0.000002
8	8	O	-2.213178	-1.055839	-0.000003
9	8	O	-2.213177	1.055840	-0.000001
10	1	H	0.032007	-2.134099	-0.000004
11	1	H	0.032007	2.134098	0.000005

4,5-dinitro-1,2,3-triazine (3C)

E = -685.6688801 a.u.

ZPVE = 198.2145 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.023706	-1.623690	0.002946
2	7	N	0.735770	-1.756749	0.019184
3	6	C	-0.031062	-0.708396	0.009457
4	6	C	0.482200	0.565998	-0.018176
5	6	C	1.849407	0.631026	-0.027818
6	7	N	2.582699	-0.471653	-0.017429
7	7	N	-1.463517	-1.022507	0.091195
8	7	N	-0.322932	1.778522	-0.086338
9	8	O	-1.946081	-1.508659	-0.862998
10	8	O	-1.432122	1.652441	-0.469064
11	8	O	-1.969745	-0.780254	1.129943
12	8	O	0.214784	2.783232	0.227386
13	1	H	2.371963	1.566685	-0.049824

4,6-dinitro-1,2,3-triazine (3D)

E = -685.6794235 a.u.

ZPVE = 197.5041 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.000008	2.081115	-0.000003
2	7	N	-1.120864	1.444511	-0.006299
3	6	C	-1.129462	0.143286	-0.006999
4	6	C	-0.000002	-0.634633	-0.000016
5	6	C	1.129456	0.143287	0.006981
6	7	N	1.120848	1.444514	0.006283
7	7	N	-2.459775	-0.502201	-0.016161
8	7	N	2.459776	-0.502194	0.016168
9	8	O	-3.399103	0.177976	0.154040
10	8	O	-2.445727	-1.676018	-0.194890
11	8	O	2.445747	-1.676013	0.194883
12	8	O	3.399108	0.177986	-0.153996
13	1	H	-0.000002	-1.703306	-0.000015

4,5,6-trinitro-1,2,3-triazine (3E)

E = -889.1532050 a.u.

ZPVE = 206.5886 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000002	2.549294	0.000000
2	7	N	1.119481	1.915570	0.009577
3	6	C	1.140128	0.613248	0.011763
4	6	C	0.000001	-0.147915	-0.000010
5	6	C	-1.140126	0.613250	-0.011785
6	7	N	-1.119479	1.915571	-0.009584
7	7	N	2.480445	0.016095	0.098629
8	7	N	-0.000001	-1.609505	-0.000004
9	7	N	-2.480445	0.016098	-0.098624
10	8	O	-2.604844	-0.793941	-0.952462
11	8	O	3.283072	0.407346	-0.660257
12	8	O	0.654657	-2.119249	-0.835305
13	8	O	2.604828	-0.793939	0.952475
14	8	O	-0.654659	-2.119240	0.835302
15	8	O	-3.283059	0.407353	0.660275

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at HF/6-311+G(d,p) Level**

2-nitro-1,3,5-triazine (1A) E = -482.2736592 a.u. ZPVE = 193.4044 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.008673	1.110215	1.707398
2	7	N	0.000000	1.170891	0.387388
3	6	C	0.000000	0.000000	-0.171576
4	7	N	0.000000	-1.170891	0.387388
5	6	C	-0.008673	-1.110215	1.707398
6	7	N	0.000000	0.000000	2.412893
7	7	N	0.000000	0.000000	-1.648239
8	8	O	0.988266	-0.381601	-2.169784
9	8	O	-0.988266	0.381601	-2.169784
10	1	H	0.021665	2.042854	2.240610
11	1	H	-0.021665	-2.042854	2.240610

2,4-dinitro-1,3,5-triazine (1B) E = -685.7773992 a.u. ZPVE = 201.3806 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.076588	0.169703	-0.033336
2	7	N	0.000000	-0.557666	0.059693
3	6	C	1.076588	0.169702	-0.033336
4	7	N	1.168657	1.449522	-0.222557
5	6	C	0.000000	2.053737	-0.326467
6	7	N	-1.168657	1.449522	-0.222556
7	7	N	-2.351883	-0.559344	0.090674
8	7	N	2.351883	-0.559345	0.090674
9	8	O	2.603177	-1.311940	-0.781627
10	8	O	2.993658	-0.314957	1.049793
11	8	O	-2.603180	-1.311935	-0.781630
12	8	O	-2.993656	-0.314960	1.049796
13	1	H	0.000000	3.112667	-0.503320

2,4,6-trinitro-1,3,5-triazine (1C) E = -889.2748030 a.u. ZPVE = 209.1468 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	N	-1.071379	-0.640359	-0.000011
2	7	N	-1.178561	0.656878	-0.000013
3	6	N	-0.018879	1.248021	-0.000010
4	7	C	1.158153	0.692225	-0.000001
5	6	N	1.090258	-0.607660	-0.000001
6	7	O	0.020407	-1.349101	-0.000002
7	7	O	-2.336773	-1.396681	-0.000008
8	7	C	-0.041176	2.722045	-0.000006
9	7	N	2.377948	-1.325363	0.000018
10	8	O	0.495807	3.240957	0.911242
11	8	O	-0.593609	3.224483	-0.911251
12	8	C	-3.054650	-1.191109	0.911247
13	8	N	-2.495688	-2.126310	-0.911260
14	8	O	2.558848	-2.049847	0.911276
15	8	O	3.089293	-1.098177	-0.911228

3-nitro-1,2,4-triazine (2A)

E = -482.2178882 a.u.

ZPVE = 190.4123 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.397330	1.156884	0.256755
2	6	C	1.698427	1.110945	0.255693
3	6	C	2.357454	-0.092009	-0.022462
4	7	N	1.686811	-1.180950	-0.271168
5	7	N	0.378354	-1.138862	-0.245808
6	6	C	-0.169333	0.001305	0.005653
7	7	N	-1.644257	0.003617	0.000669
8	8	O	-2.159584	0.774585	-0.732741
9	8	O	-2.179515	-0.756928	0.727772
10	1	H	2.237799	2.016298	0.467663
11	1	H	3.428041	-0.163820	-0.044357

6-nitro-1,2,4-triazine (2B)

E = -482.2209196 a.u.

ZPVE = 190.3426 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.807209	1.150074	0.000001
2	6	C	-0.506446	1.190146	0.000001
3	6	C	0.189622	-0.018495	0.000000
4	7	N	-0.397998	-1.166139	-0.000001
5	7	N	-1.700212	-1.201355	-0.000001
6	6	C	-2.347806	-0.061502	0.000000
7	7	N	1.661395	-0.021591	0.000000
8	8	O	2.219280	-1.055048	0.000002
9	8	O	2.170652	1.055422	-0.000002
10	1	H	-0.004594	2.137379	0.000002
11	1	H	-3.418909	-0.128180	0.000000

5-nitro-1,2,4-triazine (2C)

E = -482.2201869 a.u.

ZPVE = 190.1651 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.400204	-1.166298	0.000038
2	6	C	-0.189679	-0.027835	0.000002
3	6	C	0.499604	1.179356	-0.000038
4	7	N	1.806919	1.150594	-0.000042
5	7	N	2.428310	0.005124	-0.000003
6	6	C	1.726536	-1.098510	0.000036
7	7	N	-1.672703	-0.027668	0.000002
8	8	O	-2.222103	-1.065948	-0.000114
9	8	O	-2.183347	1.045819	0.000117
10	1	H	0.012995	2.132059	-0.000067
11	1	H	2.272737	-2.021351	0.000072

3,6-dinitro-1,2,4-triazine (2D)

E = -685.7242872 a.u.

ZPVE = 198.6080 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.710172	1.198646	-0.151580
2	6	C	-0.591676	1.206084	-0.163504
3	6	C	-1.256281	-0.013229	-0.000660
4	7	N	-0.640000	-1.134547	0.146989
5	7	N	0.664875	-1.136589	0.133279
6	6	C	1.244910	0.011073	-0.007319
7	7	N	-2.728322	-0.051735	0.009943
8	7	N	2.716987	-0.028333	0.004390
9	8	O	3.239996	0.586677	0.865973
10	8	O	3.231346	-0.662596	-0.846379
11	8	O	-3.255161	-1.081248	0.204820
12	8	O	-3.257905	0.996058	-0.184575
13	1	H	-1.113912	2.133216	-0.290957

3,5-dinitro-1,2,4-triazine (2E)

E = -685.7231507 a.u.

ZPVE = 198.5783 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.004224	-0.554963	-0.018200
2	6	C	-1.082483	0.127318	-0.008872
3	6	C	-1.092958	1.519094	0.057819
4	7	N	0.047594	2.155254	0.094179
5	7	N	1.163103	1.478557	0.064891
6	6	C	1.082708	0.190489	0.018681
7	7	N	-2.357955	-0.620465	-0.069263
8	7	N	2.366078	-0.534004	0.017097
9	8	O	3.166758	-0.185596	-0.775431
10	8	O	2.468511	-1.398852	0.814748
11	8	O	-2.307058	-1.760117	-0.342808
12	8	O	-3.329466	0.021243	0.165032
13	1	H	-1.994864	2.094510	0.080978

5,6-dinitro-1,2,4-triazine (2F)

E = -685.7167200 a.u.

ZPVE = 199.2796 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.194854	-1.501334	0.036759
2	6	C	0.180394	-0.725163	0.019857
3	6	C	0.351268	0.660589	-0.026322
4	7	N	1.528209	1.174795	-0.047531
5	7	N	2.575964	0.392747	-0.023829
6	6	C	2.383699	-0.895621	0.009661
7	7	N	-1.140616	-1.363797	0.143892
8	7	N	-0.774718	1.593431	-0.139204
9	8	O	-0.716780	2.593365	0.472724
10	8	O	-1.641760	1.238217	-0.867969
11	8	O	-1.415535	-2.178774	-0.655412
12	8	O	-1.780246	-1.001752	1.071675
13	1	H	3.256566	-1.518184	0.022077

3,5,6-trinitro-1,2,4-triazine (2G)

E = -889.2139568 a.u.

ZPVE = 207.1075 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.847071	0.815602	-0.004254
2	6	C	0.405601	0.559542	-0.013173
3	6	C	0.852120	-0.767930	0.007497
4	7	N	0.017106	-1.742993	0.029782
5	7	N	-1.267773	-1.490357	0.024308
6	6	C	-1.619761	-0.252332	0.006285
7	7	N	1.317916	1.712694	0.047453
8	7	N	2.272812	-1.124187	-0.080337
9	7	O	-3.070185	0.006142	0.018593
10	8	O	-3.707813	-0.556109	-0.796594
11	8	O	-3.445442	0.754866	0.849816
12	8	O	2.655711	-1.991289	0.609640
13	8	O	2.888188	-0.490994	-0.871848
14	8	O	2.073525	1.690352	0.956913
15	8	O	1.187408	2.533926	-0.779485

4-nitro-1,2,3-triazine (3A)

E = -482.1887060 a.u.

ZPVE = 188.5103 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.690415	-1.210505	-0.061152
2	7	N	-0.400504	-1.150450	-0.056063
3	6	C	0.185970	0.008838	-0.000897
4	6	C	-0.478397	1.205135	0.054807
5	6	C	-1.846215	1.047470	0.053939
6	7	N	-2.410580	-0.145218	-0.004502
7	7	N	1.667134	-0.012515	-0.000176
8	8	O	2.207767	-1.046487	0.125918
9	8	O	2.188986	1.049931	-0.124247
10	1	H	0.018031	2.152234	0.094063
11	1	H	-2.519637	1.882371	0.098727

5-nitro-1,2,3-triazine (3B)

E = -482.1902358 a.u.

ZPVE = 188.6426 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.436882	-0.000001	0.000002
2	7	N	1.816380	-1.129911	-0.000001
3	6	C	0.496609	-1.168620	-0.000002
4	6	C	-0.220614	-0.000001	-0.000001
5	6	C	0.496611	1.168621	0.000002
6	7	N	1.816379	1.129913	0.000004
7	7	N	-1.679007	0.000000	-0.000001
8	8	O	-2.214834	-1.056032	-0.000002
9	8	O	-2.214833	1.056032	-0.000001
10	1	H	0.033633	-2.135510	-0.000004
11	1	H	0.033632	2.135509	0.000005

4,5-dinitro-1,2,3-triazine (3C)

E = -685.6838530 a.u.

ZPVE = 197.3826 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.097811	-1.530926	0.002875
2	7	N	0.817273	-1.724199	0.023296
3	6	C	0.003735	-0.711958	0.008179
4	6	C	0.456729	0.585267	-0.024715
5	6	C	1.819341	0.713987	-0.032694
6	7	N	2.602391	-0.354741	-0.021066
7	7	N	-1.415587	-1.086170	0.102188
8	7	N	-0.404547	1.759400	-0.096407
9	8	O	-1.878643	-1.632600	-0.828999
10	8	O	-1.487131	1.593184	-0.536921
11	8	O	-1.935018	-0.820236	1.130039
12	8	O	0.068318	2.779680	0.270301
13	1	H	2.299575	1.672450	-0.056178

4,6-dinitro-1,2,3-triazine (3D)

E = -685.6939953 a.u.

ZPVE = 196.4405 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000001	2.081564	-0.000003
2	7	N	1.120873	1.445054	0.005291
3	6	C	1.129306	0.143988	0.007448
4	6	C	0.000000	-0.634916	0.000001
5	6	C	-1.129306	0.143989	-0.007448
6	7	N	-1.120873	1.445054	-0.005295
7	7	N	2.461223	-0.501708	0.017305
8	7	N	-2.461223	-0.501708	-0.017304
9	8	O	3.401761	0.175424	-0.162218
10	8	O	2.448292	-1.674936	0.205478
11	8	O	-2.448293	-1.674934	-0.205484
12	8	O	-3.401760	0.175423	0.162228
13	1	H	0.000000	-1.703969	0.000002

4,5,6-trinitro-1,2,3-triazine (3E)

E = -889.1738767 a.u.

ZPVE = 205.5158 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.549394	0.000000
2	7	N	-1.120077	1.916806	-0.011621
3	6	C	-1.140205	0.614052	-0.012265
4	6	C	0.000000	-0.147218	-0.000002
5	6	C	1.140206	0.614052	0.012262
6	7	N	1.120078	1.916806	0.011621
7	7	N	-2.481783	0.016239	-0.099309
8	7	N	0.000000	-1.609474	-0.000001
9	7	N	2.481783	0.016238	0.099310
10	8	O	2.625402	-0.747427	0.992413
11	8	O	-3.267084	0.360731	0.700256
12	8	O	-0.685246	-2.121266	0.810260
13	8	O	-2.625406	-0.747425	-0.992412
14	8	O	0.685246	-2.121268	-0.810260
15	8	O	3.267087	0.360732	-0.700252

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at HF/cc-pVDZ Level**

2-nitro-1,3,5-triazine (1A) E = -482.1926574 a.u. ZPVE = 194.6474 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.012407	1.110551	1.708771
2	7	N	0.000000	1.173796	0.386916
3	6	C	0.000000	0.000000	-0.174947
4	7	N	0.000000	-1.173796	0.386916
5	6	C	-0.012407	-1.110551	1.708771
6	7	N	0.000000	0.000000	2.418760
7	7	N	0.000000	0.000000	-1.649856
8	8	O	0.825249	-0.665627	-2.171560
9	8	O	-0.825249	0.665627	-2.171560
10	1	H	0.030856	2.049258	2.245121
11	1	H	-0.030856	-2.049258	2.245121

2,4-dinitro-1,3,5-triazine (1B) E = -685.6586131 a.u. ZPVE = 203.1892 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.080090	0.167861	-0.037706
2	7	N	0.000000	-0.559110	0.060937
3	6	C	1.080092	0.167862	-0.037706
4	7	N	1.171558	1.448501	-0.246786
5	6	C	0.000000	2.049104	-0.364822
6	7	N	-1.171556	1.448501	-0.246787
7	7	N	-2.354344	-0.558208	0.101623
8	7	N	2.354343	-0.558208	0.101623
9	8	O	2.468767	-1.531490	-0.555549
10	8	O	3.133103	-0.091629	0.856338
11	8	O	-2.468767	-1.531495	-0.555543
12	8	O	-3.133105	-0.091625	0.856333
13	1	H	0.000000	3.110620	-0.565503

2,4,6-trinitro-1,3,5-triazine (1C) E = -889.1185620 a.u. ZPVE = 211.3891 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	N	1.021222	-0.724116	-0.000001
2	7	N	1.228674	0.564108	0.000000
3	6	N	0.116492	1.246463	0.000000
4	7	C	-1.102869	0.782009	-0.000002
5	6	N	-1.137715	-0.522346	-0.000004
6	7	O	-0.125805	-1.346117	-0.000003
7	7	O	2.222279	-1.575748	0.000002
8	7	C	0.253498	2.712424	0.000004
9	7	N	-2.475777	-1.136676	-0.000004
10	8	O	-0.421396	3.287991	-0.776691
11	8	O	1.023354	3.152963	0.776701
12	8	C	3.058184	-1.279053	-0.776690
13	8	N	2.218869	-2.462735	0.776696
14	8	O	-2.636784	-2.008934	-0.776701
15	8	O	-3.242225	-0.690233	0.776693

3-nitro-1,2,4-triazine (2A)

E = -482.1378909 a.u.

ZPVE = 191.6404 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.396475	1.166587	0.225916
2	6	C	1.701075	1.117896	0.226437
3	6	C	2.359252	-0.092613	-0.020351
4	7	N	1.687308	-1.191266	-0.241667
5	7	N	0.379235	-1.147345	-0.215097
6	6	C	-0.172927	0.002506	0.006560
7	7	N	-1.645615	0.004304	0.001496
8	8	O	-2.160362	0.913546	-0.553337
9	8	O	-2.180500	-0.896007	0.547741
10	1	H	2.244147	2.034057	0.415658
11	1	H	3.436528	-0.167077	-0.041291

6-nitro-1,2,4-triazine (2B)

E = -482.1417453 a.u.

ZPVE = 191.9733 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.809655	1.153646	0.000000
2	6	C	-0.504978	1.191257	0.000000
3	6	C	0.193062	-0.016970	0.000000
4	7	N	-0.395874	-1.169375	0.000000
5	7	N	-1.698545	-1.204271	0.000000
6	6	C	-2.346886	-0.061547	0.000000
7	7	N	1.660630	-0.020443	0.000000
8	8	O	2.214970	-1.057334	0.000001
9	8	O	2.170169	1.056490	-0.000001
10	1	H	0.000542	2.144031	0.000001
11	1	H	-3.424737	-0.130617	0.000000

5-nitro-1,2,4-triazine (2C)

E = -482.1411405 a.u.

ZPVE = 191.8235 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.396483	-1.170336	0.000021
2	6	C	-0.194366	-0.026442	0.000000
3	6	C	0.499230	1.179501	-0.000019
4	7	N	1.809768	1.152381	-0.000016
5	7	N	2.430010	0.005273	0.000006
6	6	C	1.724163	-1.099518	0.000023
7	7	N	-1.672009	-0.026280	-0.000004
8	8	O	-2.218531	-1.067520	-0.000026
9	8	O	-2.182479	1.047678	0.000014
10	1	H	0.009714	2.138184	-0.000036
11	1	H	2.274447	-2.027947	0.000045

3,6-dinitro-1,2,4-triazine (2D)

E = -685.6069798 a.u.

ZPVE = 200.5248 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.711109	1.200336	-0.166078
2	6	C	-0.594336	1.205315	-0.179014
3	6	C	-1.260125	-0.011221	-0.001202
4	7	N	-0.641626	-1.135021	0.161774
5	7	N	0.662843	-1.136335	0.145763
6	6	C	1.247951	0.012227	-0.008752
7	7	N	-2.728272	-0.050610	0.010887
8	7	N	2.718082	-0.028473	0.003900
9	8	O	3.246889	0.787898	0.674738
10	8	O	3.225647	-0.866781	-0.653238
11	8	O	-3.251054	-1.086796	0.188580
12	8	O	-3.258433	1.000269	-0.165215
13	1	H	-1.120283	2.136078	-0.318827

3,5-dinitro-1,2,4-triazine (2E)

E = -685.6060131 a.u.

ZPVE = 200.4460 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.001156	-0.558526	0.020279
2	6	C	1.086231	0.131612	0.005302
3	6	C	1.087475	1.523451	-0.073691
4	7	N	-0.058387	2.156900	-0.117910
5	7	N	-1.169944	1.474531	-0.078302
6	6	C	-1.085824	0.182275	-0.018982
7	7	N	2.361521	-0.608463	0.069271
8	7	N	-2.364615	-0.545792	-0.004839
9	8	O	-3.235400	-0.066704	0.631200
10	8	O	-2.393837	-1.543039	-0.637663
11	8	O	2.306711	-1.765936	0.258466
12	8	O	3.336147	0.055505	-0.076156
13	1	H	1.991806	2.106809	-0.102023

5,6-dinitro-1,2,4-triazine (2F)

E = -685.5988228 a.u.

ZPVE = 200.8934 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.127295	-1.552434	0.030782
2	6	C	0.142281	-0.729962	0.018528
3	6	C	0.372934	0.647253	-0.022099
4	7	N	1.575722	1.112854	-0.040065
5	7	N	2.589236	0.287734	-0.018502
6	6	C	2.340115	-0.994941	0.007780
7	7	N	-1.196893	-1.318319	0.142095
8	7	N	-0.706143	1.628096	-0.138193
9	8	O	-0.575734	2.648733	0.429220
10	8	O	-1.611891	1.287772	-0.826743
11	8	O	-1.492771	-2.132976	-0.652179
12	8	O	-1.825681	-0.926363	1.065346
13	1	H	3.192121	-1.656941	0.016781

3,5,6-trinitro-1,2,4-triazine (2G)

E = -889.0580536 a.u.

ZPVE = 209.1341 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.845439	0.818692	-0.005347
2	6	C	0.412271	0.560933	-0.013476
3	6	C	0.857358	-0.766369	0.010690
4	7	N	0.018004	-1.744502	0.037228
5	7	N	-1.265752	-1.491633	0.030232
6	6	C	-1.620878	-0.249200	0.007559
7	7	N	1.317112	1.714515	0.047296
8	7	N	2.272606	-1.128049	-0.081540
9	7	O	-3.069204	0.008467	0.016829
10	8	O	-3.728465	-0.698297	-0.657633
11	8	O	-3.421056	0.899884	0.706280
12	8	O	2.643087	-2.025375	0.578113
13	8	O	2.895105	-0.470535	-0.848022
14	8	O	2.086310	1.683630	0.945657
15	8	O	1.164543	2.546365	-0.767085

4-nitro-1,2,3-triazine (3A)

E = -482.1098838 a.u.

ZPVE = 189.8683 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.689952	-1.213491	0.000000
2	7	N	0.399272	-1.153962	0.000000
3	6	C	-0.190374	0.009625	0.000000
4	6	C	0.477130	1.208467	0.000000
5	6	C	1.847851	1.049604	0.000000
6	7	N	2.413006	-0.146096	-0.000001
7	7	N	-1.667357	-0.011629	0.000000
8	8	O	-2.205340	-1.056037	0.000000
9	8	O	-2.188977	1.058206	-0.000001
10	1	H	-0.022774	2.161756	0.000001
11	1	H	2.525554	1.890959	0.000000

5-nitro-1,2,3-triazine (3B)

E = -482.1119909 a.u.

ZPVE = 190.6420 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.438563	-0.000001	0.000004
2	7	N	1.818277	-1.131944	0.000000
3	6	C	0.496405	-1.169572	-0.000002
4	6	C	-0.224700	-0.000001	-0.000001
5	6	C	0.496407	1.169573	0.000002
6	7	N	1.818276	1.131946	0.000005
7	7	N	-1.680186	0.000000	-0.000003
8	8	O	-2.214512	-1.057513	-0.000004
9	8	O	-2.214511	1.057514	-0.000001
10	1	H	0.029507	-2.141907	-0.000004
11	1	H	0.029506	2.141907	0.000005

4,5-dinitro-1,2,3-triazine (3C)

E = -685.5671539 a.u.

ZPVE = 199.0711 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.931698	-1.731904	0.002539
2	7	N	0.638806	-1.794918	0.013821
3	6	C	-0.073033	-0.702053	0.006675
4	6	C	0.510604	0.543832	-0.012514
5	6	C	1.883927	0.530755	-0.019960
6	7	N	2.556917	-0.611171	-0.012498
7	7	N	-1.517502	-0.945755	0.064748
8	7	N	-0.225469	1.798790	-0.061382
9	8	O	-2.022722	-1.302029	-0.936555
10	8	O	-1.375376	1.724529	-0.322859
11	8	O	-2.010118	-0.789731	1.126346
12	8	O	0.398171	2.781888	0.150632
13	1	H	2.460230	1.442255	-0.036302

4,6-dinitro-1,2,3-triazine (3D)

E = -685.5777194 a.u.

ZPVE = 198.3857 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.082284	-0.000001
2	7	N	1.122708	1.446313	-0.000003
3	6	C	1.132576	0.141628	-0.000003
4	6	C	0.000000	-0.637252	0.000000
5	6	C	-1.132575	0.141628	0.000003
6	7	N	-1.122708	1.446313	0.000002
7	7	N	2.461220	-0.502453	-0.000007
8	7	N	-2.461220	-0.502453	0.000007
9	8	O	3.406487	0.193698	0.000068
10	8	O	2.442198	-1.690796	-0.000086
11	8	O	-2.442198	-1.690797	0.000084
12	8	O	-3.406487	0.193698	-0.000065
13	1	H	0.000000	-1.712475	0.000000

4,5,6-trinitro-1,2,3-triazine (3E)

E = -889.0187028 a.u.

ZPVE = 207.5517 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000001	2.552705	0.000000
2	7	N	1.121083	1.919233	0.009959
3	6	C	1.142224	0.613492	0.012392
4	6	C	0.000000	-0.149763	-0.000001
5	6	C	-1.142224	0.613493	-0.012393
6	7	N	-1.121083	1.919233	-0.009959
7	7	N	2.479954	0.015912	0.098828
8	7	N	0.000000	-1.610390	0.000000
9	7	N	-2.479954	0.015913	-0.098828
10	8	O	-2.591532	-0.823917	-0.927110
11	8	O	3.294057	0.433797	-0.635922
12	8	O	0.638468	-2.119353	-0.850011
13	8	O	2.591530	-0.823919	0.927109
14	8	O	-0.638469	-2.119352	0.850011
15	8	O	-3.294055	0.433796	0.635924

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at B3LYP/6-31G(d,p) Level**

2-nitro-1,3,5-triazine (1A) E = -484.8533307 a.u. ZPVE = 177.0649 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.737093	-1.101520	-0.223518
2	7	N	-0.398945	-1.170978	-0.216929
3	6	C	0.172376	0.000000	0.000000
4	7	N	-0.398945	1.170978	0.216929
5	6	C	-1.737093	1.101520	0.223518
6	7	N	-2.459505	0.000000	0.000000
7	7	N	1.674336	0.000000	0.000000
8	8	O	2.215331	0.955118	-0.538369
9	8	O	2.215331	-0.955118	0.538369
10	1	H	-2.276510	-2.023720	-0.424093
11	1	H	-2.276509	2.023720	0.424094

2,4-dinitro-1,3,5-triazine (1B) E = -689.3323909 a.u. ZPVE = 181.6955 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.095156	0.173492	-0.043794
2	7	N	-0.000001	-0.566844	0.034532
3	6	C	1.095155	0.173489	-0.043795
4	7	N	1.188390	1.476943	-0.236980
5	6	C	0.000003	2.081543	-0.357825
6	7	N	-1.188386	1.476946	-0.236978
7	7	N	-2.391617	-0.565588	0.100986
8	7	N	2.391616	-0.565595	0.100988
9	8	O	2.461513	-1.643308	-0.468952
10	8	O	3.248178	-0.013623	0.774899
11	8	O	-2.461532	-1.643280	-0.468993
12	8	O	-3.248162	-0.013637	0.774936
13	1	H	0.000004	3.148609	-0.560469

2,4,6-trinitro-1,3,5-triazine (1C) E = -893.8052072 a.u. ZPVE = 184.6963 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.684920	-1.186347	0.000000
2	7	N	-0.684920	1.186347	0.000000
3	7	N	1.369905	0.000000	0.000000
4	6	C	0.634847	1.099540	0.000000
5	7	N	1.394022	2.414436	0.000000
6	8	O	2.610102	2.326714	0.000000
7	8	O	0.710051	3.423750	0.000000
8	6	C	-1.269651	0.000000	0.000000
9	7	N	-2.788057	0.000000	0.000000
10	8	O	-3.320190	1.096939	0.000000
11	8	O	-3.320190	-1.096939	0.000000
12	6	C	0.634847	-1.099540	0.000000
13	7	N	1.394022	-2.414436	0.000000
14	8	O	2.610102	-2.326714	0.000000
15	8	O	0.710051	-3.423750	0.000000

3-nitro-1,2,4-triazine (2A)

E = -484.8094460 a.u.

ZPVE = 174.0301 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.400735	1.183945	0.221032
2	6	C	1.729280	1.130805	0.226501
3	6	C	2.390960	-0.079806	-0.017268
4	7	N	1.722253	-1.212000	-0.244599
5	7	N	0.387329	-1.174005	-0.213250
6	6	C	-0.170757	0.005808	0.007306
7	7	N	-1.666710	0.005616	0.001965
8	8	O	-2.201860	0.971335	-0.525786
9	8	O	-2.216429	-0.954846	0.521364
10	1	H	2.270362	2.054262	0.417541
11	1	H	3.473800	-0.151916	-0.037448

6-nitro-1,2,4-triazine (2B)

E = -484.8124049 a.u.

ZPVE = 174.2424 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.833357	1.175101	0.000038
2	6	C	0.505052	1.198350	0.000035
3	6	C	-0.188025	-0.015766	0.000000
4	7	N	0.401250	-1.195592	-0.000036
5	7	N	1.733855	-1.223256	-0.000039
6	6	C	2.379179	-0.050371	0.000000
7	7	N	-1.678363	-0.018843	0.000000
8	8	O	-2.252236	-1.093310	0.000075
9	8	O	-2.205169	1.094241	-0.000076
10	1	H	-0.012066	2.151932	0.000061
11	1	H	3.463374	-0.114533	-0.000001

5-nitro-1,2,4-triazine (2C)

E = -484.813589 a.u.

ZPVE = 174.2483 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.404290	-1.191806	0.000017
2	6	C	0.191597	-0.024951	0.000000
3	6	C	-0.503154	1.184659	-0.000015
4	7	N	-1.839654	1.176572	-0.000018
5	7	N	-2.474666	0.004409	-0.000001
6	6	C	-1.744278	-1.115016	0.000016
7	7	N	1.691646	-0.024167	0.000000
8	8	O	2.259465	-1.101971	-0.000036
9	8	O	2.218772	1.086971	0.000036
10	1	H	-0.003310	2.145191	-0.000027
11	1	H	-2.298827	-2.048393	0.000031

3,6-dinitro-1,2,4-triazine (2D)

E = -689.2904014 a.u.

ZPVE = 178.9543 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.720474	1.215587	-0.168445
2	6	C	-0.608118	1.208941	-0.186544
3	6	C	-1.273754	-0.009115	-0.002363
4	7	N	-0.656111	-1.162475	0.171026
5	7	N	0.675717	-1.163822	0.147390
6	6	C	1.264381	0.015250	-0.010391
7	7	N	-2.763631	-0.045298	0.010935
8	7	N	2.755732	-0.023711	0.004031
9	8	O	3.303026	0.839133	0.675246
10	8	O	3.280789	-0.909749	-0.652698
11	8	O	-3.307987	-1.117634	0.196576
12	8	O	-3.310615	1.041553	-0.172223
13	1	H	-1.142014	2.141153	-0.333980

3,5-dinitro-1,2,4-triazine (2E)

E = -689.2913090 a.u.

ZPVE = 178.8831 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.004400	-0.566865	0.017636
2	6	C	1.100145	0.139518	0.001484
3	6	C	1.104411	1.533758	-0.089452
4	7	N	-0.054769	2.197692	-0.141162
5	7	N	-1.193086	1.505889	-0.086610
6	6	C	-1.097161	0.186037	-0.020479
7	7	N	2.393748	-0.614454	0.074743
8	7	N	-2.396559	-0.552489	0.001361
9	8	O	-3.292934	-0.052424	0.663256
10	8	O	-2.431084	-1.585751	-0.650775
11	8	O	2.334068	-1.819504	0.231630
12	8	O	3.405280	0.075538	-0.030017
13	1	H	2.018451	2.112830	-0.123853

5,6-dinitro-1,2,4-triazine (2F)

E = -689.2857030 a.u.

ZPVE = 179.1276 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.263434	-1.492948	0.038449
2	6	C	0.203480	-0.724108	0.025945
3	6	C	0.334171	0.668355	-0.029316
4	7	N	1.519688	1.246392	-0.046957
5	7	N	2.609612	0.481073	-0.014125
6	6	C	2.438912	-0.843122	0.012759
7	7	N	-1.113528	-1.406211	0.156145
8	7	N	-0.829446	1.577963	-0.154302
9	8	O	-0.799693	2.615506	0.481813
10	8	O	-1.706387	1.188210	-0.920328
11	8	O	-1.327672	-2.339101	-0.595998
12	8	O	-1.835053	-0.965493	1.043031
13	1	H	3.342730	-1.443604	0.021046

3,5,6-trinitro-1,2,4-triazine (2G)

E = -893.7597500 a.u.

ZPVE = 183.3697 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.864759	0.829575	-0.011159
2	6	C	-0.417886	0.560787	0.005637
3	6	C	-0.864263	-0.768453	-0.003142
4	7	N	-0.016633	-1.780169	-0.024617
5	7	N	1.290426	-1.523679	-0.017545
6	6	C	1.644316	-0.247224	-0.010488
7	7	N	-1.341475	1.726074	-0.048366
8	7	N	-2.298527	-1.131770	0.085000
9	7	O	3.114619	0.011788	-0.022328
10	8	O	3.792998	-0.709343	0.691233
11	8	O	3.483993	0.920288	-0.750746
12	8	O	-2.689702	-2.031347	-0.633979
13	8	O	-2.936584	-0.483864	0.908535
14	8	O	-2.190521	1.661369	-0.928327
15	8	O	-1.143332	2.618723	0.753415

4-nitro-1,2,3-triazine (3A)

E = -484.7869375 a.u.

ZPVE = 171.9990 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.732371	-1.234844	-0.000046
2	7	N	0.402614	-1.179206	-0.000044
3	6	C	-0.187587	0.003137	0.000006
4	6	C	0.481373	1.213177	0.000050
5	6	C	1.862890	1.072051	0.000036
6	7	N	2.461235	-0.128978	-0.000006
7	7	N	-1.688391	-0.010550	0.000000
8	8	O	-2.249919	-1.090504	0.000094
9	8	O	-2.223635	1.097133	-0.000099
10	1	H	-0.036641	2.163124	0.000094
11	1	H	2.530220	1.928698	0.000065

5-nitro-1,2,3-triazine (3B)

E = -484.7875523 a.u.

ZPVE = 172417.8 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.484288	0.000000	0.000002
2	7	N	1.839328	-1.159876	-0.000001
3	6	C	0.498803	-1.181604	-0.000004
4	6	C	-0.220767	0.000000	-0.000002
5	6	C	0.498804	1.181604	0.000002
6	7	N	1.839328	1.159876	0.000004
7	7	N	-1.693960	0.000000	0.000000
8	8	O	-2.248363	-1.094404	0.000002
9	8	O	-2.248363	1.094404	-0.000003
10	1	H	0.014935	-2.152369	-0.000005
11	1	H	0.014934	2.152369	0.000006

4,5-dinitro-1,2,3-triazine (3C)

E = -689.2586503 a.u.

ZPVE = 176.8121 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.010147	-1.723344	0.005528
2	7	N	0.687384	-1.816512	0.015110
3	6	C	-0.054871	-0.714397	0.007298
4	6	C	0.509543	0.550848	-0.013763
5	6	C	1.894476	0.579093	-0.019318
6	7	N	2.619247	-0.548734	-0.009780
7	7	N	-1.513874	-0.977069	0.054777
8	7	N	-0.265479	1.803949	-0.053786
9	8	O	-2.030218	-1.316617	-0.995450
10	8	O	-1.466973	1.699424	-0.266454
11	8	O	-2.028169	-0.871397	1.157409
12	8	O	0.363790	2.841044	0.117828
13	1	H	2.435687	1.519070	-0.034907

4,6-dinitro-1,2,3-triazine (3D)

E = -689.2679399 a.u.

ZPVE = 176.8149 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	0.000000	2.134871
2	7	N	0.000000	1.153066	1.476624
3	6	C	0.000000	1.144646	0.153779
4	6	C	0.000000	0.000000	-0.624647
5	6	C	0.000000	-1.144646	0.153779
6	7	N	0.000000	-1.153066	1.476624
7	7	N	0.000000	2.488261	-0.516260
8	7	N	0.000000	-2.488261	-0.516260
9	8	O	-0.000024	3.474533	0.195557
10	8	O	0.000025	2.457238	-1.744364
11	8	O	-0.000025	-2.457238	-1.744364
12	8	O	0.000024	-3.474533	0.195557
13	1	H	0.000000	0.000000	-1.705751

4,5,6-trinitro-1,2,3-triazine (3E)

E = -893.7283698 a.u.

ZPVE = 181.4116 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.000007	2.615671	0.000007
2	7	N	1.149332	1.958533	0.018498
3	6	C	1.156266	0.634192	0.020698
4	6	C	0.000001	-0.132062	0.000002
5	6	C	-1.156270	0.634186	-0.020696
6	7	N	-1.149341	1.958527	-0.018488
7	7	N	2.504897	0.005452	0.100180
8	7	N	0.000007	-1.610684	0.000006
9	7	N	-2.504898	0.005441	-0.100187
10	8	O	-2.582676	-0.946272	-0.869315
11	8	O	3.382363	0.499857	-0.580366
12	8	O	0.573956	-2.137875	-0.937950
13	8	O	2.582686	-0.946251	0.869320
14	8	O	-0.573941	-2.137875	0.937961
15	8	O	-3.382376	0.499857	0.580335

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at B3LYP/6-31+G(d,p) Level**

2-nitro-1,3,5-triazine (1A) E = -484.8750564 a.u. ZPVE = 176.5257 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.009528	1.126184	1.733847
2	7	N	0.000000	1.191775	0.394689
3	6	C	0.000000	0.000000	-0.174622
4	7	N	0.000000	-1.191775	0.394689
5	6	C	-0.009528	-1.126184	1.733847
6	7	N	0.000000	0.000000	2.453316
7	7	N	0.000000	0.000000	-1.667406
8	8	O	1.060358	-0.283453	-2.208245
9	8	O	-1.060358	0.283453	-2.208245
10	1	H	0.023850	2.069134	2.273245
11	1	H	-0.023850	-2.069134	2.273245

2,4-dinitro-1,3,5-triazine (1B) E = -689.3518122 a.u. ZPVE = 187.4056 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.093885	0.173552	-0.019374
2	7	N	-0.000004	-0.572052	0.028201
3	6	C	1.093882	0.173545	-0.019372
4	7	N	1.188380	1.487299	-0.120871
5	6	C	0.000004	2.102390	-0.178166
6	7	N	-1.188376	1.487306	-0.120872
7	7	N	-2.382525	-0.569488	0.049489
8	7	N	2.382519	-0.569500	0.049491
9	8	O	2.766651	-1.073993	-0.995487
10	8	O	2.926088	-0.596356	1.144163
11	8	O	-2.766653	-1.073997	-0.995486
12	8	O	-2.926083	-0.596359	1.144166
13	1	H	0.000007	3.183748	-0.275445

2,4,6-trinitro-1,3,5-triazine (1C) E = -893.8430262 a.u. ZPVE = 183.7326 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.684369	-1.185339	0.000000
2	7	N	-0.684369	1.185339	0.000000
3	7	N	1.368702	0.000000	0.000000
4	6	C	0.634728	1.099387	0.000000
5	7	N	1.395796	2.417464	0.000000
6	8	O	2.612865	2.331620	0.000000
7	8	O	0.713139	3.428699	0.000000
8	6	C	-1.269504	0.000000	0.000000
9	7	N	-2.791602	0.000000	0.000000
10	8	O	-3.325967	1.096809	0.000000
11	8	O	-3.325967	-1.096809	0.000000
12	6	C	0.634728	-1.099387	0.000000
13	7	N	1.395796	-2.417464	0.000000
14	8	O	2.612865	-2.331620	0.000000
15	8	O	0.713139	-3.428699	0.000000

3-nitro-1,2,4-triazine (2A)

E = -484.8309580 a.u.

ZPVE = 173.5217 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.398537	1.176849	0.262359
2	6	C	1.727984	1.123500	0.262806
3	6	C	2.388680	-0.080688	-0.019303
4	7	N	1.716977	-1.203517	-0.282179
5	7	N	0.383497	-1.165442	-0.255434
6	6	C	-0.171611	0.007332	0.006307
7	7	N	-1.661581	0.005515	0.001433
8	8	O	-2.198472	0.692265	-0.858776
9	8	O	-2.210473	-0.677262	0.855876
10	1	H	2.268169	2.040847	0.481779
11	1	H	3.471067	-0.155572	-0.040701

6-nitro-1,2,4-triazine (2B)

E = -484.8329824 a.u.

ZPVE = 173.5801 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.835870	1.172947	-0.000004
2	6	C	0.507103	1.200225	0.000001
3	6	C	-0.186951	-0.014867	-0.000001
4	7	N	0.402917	-1.194066	0.000002
5	7	N	1.733869	-1.223395	0.000000
6	6	C	2.383301	-0.051845	-0.000028
7	7	N	-1.680318	-0.019596	0.000002
8	8	O	-2.209122	1.094147	0.000017
9	8	O	-2.257124	-1.093097	0.000001
10	1	H	-0.003977	2.156883	-0.000002
11	1	H	3.466863	-0.117598	0.000028

5-nitro-1,2,4-triazine (2C)

E = -484.8342796 a.u.

ZPVE = 173.7201 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.407018	-1.189808	0.000017
2	6	C	0.189753	-0.024088	0.000002
3	6	C	-0.504415	1.186962	-0.000018
4	7	N	-1.841714	1.174857	-0.000019
5	7	N	-2.475951	0.004674	0.000000
6	6	C	-1.747131	-1.116745	0.000011
7	7	N	1.693836	-0.025117	-0.000001
8	8	O	2.263888	-1.102413	-0.000047
9	8	O	2.223463	1.086163	0.000051
10	1	H	-0.010783	2.150682	-0.000033
11	1	H	-2.301348	-2.049699	0.000040

3,6-dinitro-1,2,4-triazine (2D)

E = -689.3207533 a.u.

ZPVE = 178.0728 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.724171	1.224582	-0.099660
2	6	C	-0.605444	1.220906	-0.108124
3	6	C	-1.270562	-0.008120	-0.000765
4	7	N	-0.651425	-1.168869	0.099958
5	7	N	0.678907	-1.169587	0.089731
6	6	C	1.265723	0.017264	-0.004590
7	7	N	-2.762761	-0.048356	0.005799
8	7	N	2.750637	-0.024336	0.002538
9	8	O	3.289576	0.308726	1.048729
10	8	O	3.284946	-0.381261	-1.037602
11	8	O	-3.309249	-1.129327	0.128427
12	8	O	-3.312801	1.047147	-0.116342
13	1	H	-1.134783	2.163378	-0.193377

3,5-dinitro-1,2,4-triazine (2E)

E = -689.3214574 a.u.

ZPVE = 178.1029 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.011447	-0.566999	0.018127
2	6	C	1.100186	0.128748	0.002645
3	6	C	1.117016	1.524373	-0.073024
4	7	N	-0.038619	2.196942	-0.115735
5	7	N	-1.182121	1.517423	-0.073963
6	6	C	-1.095636	0.195952	-0.016838
7	7	N	2.388059	-0.642331	0.062950
8	7	N	-2.397889	-0.524188	-0.000837
9	8	O	-3.108407	-0.336056	0.976174
10	8	O	-2.626615	-1.234206	-0.970525
11	8	O	2.318180	-1.848624	0.211653
12	8	O	3.408339	0.036194	-0.043473
13	1	H	2.032750	2.101162	-0.101120

5,6-dinitro-1,2,4-triazine (2F)

E = -689.3162257 a.u.

ZPVE = 178.3090 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.282686	-1.478544	0.060853
2	6	C	0.214872	-0.721814	0.033494
3	6	C	0.329968	0.671272	-0.037493
4	7	N	1.509676	1.260368	-0.072111
5	7	N	2.605997	0.507728	-0.033527
6	6	C	2.452213	-0.818372	0.024072
7	7	N	-1.098708	-1.416626	0.153140
8	7	N	-0.846417	1.568255	-0.149389
9	8	O	-0.854387	2.571622	0.541484
10	8	O	-1.699870	1.203033	-0.954969
11	8	O	-1.331543	-2.300756	-0.651680
12	8	O	-1.803874	-1.032254	1.080168
13	1	H	3.362448	-1.407944	0.046774

3,5,6-trinitro-1,2,4-triazine (2G)

E = -893.7995232 a.u.

ZPVE = 182.2582 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.867895	0.830116	0.024755
2	6	C	0.414784	0.560406	0.003706
3	6	C	0.860037	-0.769190	-0.014931
4	7	N	0.011141	-1.779765	-0.021161
5	7	N	-1.294006	-1.524147	-0.019448
6	6	C	-1.645784	-0.246828	0.004396
7	7	N	1.340548	1.725178	0.072748
8	7	N	2.297265	-1.129434	-0.093503
9	7	O	-3.110128	0.008306	0.023585
10	8	O	-3.725042	-0.317767	-0.980250
11	8	O	-3.544621	0.520190	1.045257
12	8	O	2.691550	-2.015723	0.641584
13	8	O	2.940420	-0.487753	-0.920049
14	8	O	2.129205	1.695954	1.010155
15	8	O	1.206899	2.582834	-0.780178

4-nitro-1,2,3-triazine (3A)

E = -484.8074339 a.u.

ZPVE = 171.4309 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.732372	-1.235604	-0.000047
2	7	N	0.403742	-1.177831	-0.000043
3	6	C	-0.186162	0.004584	-0.000002
4	6	C	0.484373	1.214616	0.000037
5	6	C	1.866889	1.071112	0.000038
6	7	N	2.462404	-0.131729	-0.000003
7	7	N	-1.690278	-0.011000	0.000001
8	8	O	-2.254548	-1.090063	0.000076
9	8	O	-2.227610	1.097280	-0.000068
10	1	H	-0.027930	2.168206	0.000065
11	1	H	2.536925	1.925339	0.000072

5-nitro-1,2,3-triazine (3B)

E = -484.8078617 a.u.

ZPVE = 171.7354 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-2.485792	-0.000001	-0.000001
2	7	N	-1.841419	-1.158716	0.000001
3	6	C	-0.500011	-1.182923	0.000002
4	6	C	0.219499	-0.000001	0.000000
5	6	C	-0.500012	1.182922	-0.000003
6	7	N	-1.841418	1.158717	-0.000003
7	7	N	1.695562	0.000000	0.000002
8	8	O	2.252412	-1.094289	0.000002
9	8	O	2.252411	1.094289	-0.000001
10	1	H	-0.021988	-2.156412	0.000005
11	1	H	-0.021986	2.156411	-0.000004

4,5-dinitro-1,2,3-triazine (3C)

E = -689.2890088 a.u.

ZPVE = 176.2829 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.896687	-1.844178	0.000001
2	7	N	-0.572471	-1.853085	0.000002
3	6	C	0.099862	-0.706292	0.000000
4	6	C	-0.542938	0.522111	-0.000002
5	6	C	-1.928266	0.461314	-0.000003
6	7	N	-2.578776	-0.711610	-0.000002
7	7	N	1.573636	-0.890707	0.000004
8	7	N	0.149432	1.827554	-0.000004
9	8	O	2.097054	-0.984153	1.099076
10	8	O	1.374056	1.803018	-0.000023
11	8	O	2.097057	-0.984186	-1.099063
12	8	O	-0.563832	2.825245	0.000013
13	1	H	-2.532555	1.361980	-0.000006

4,6-dinitro-1,2,3-triazine (3D)

E = -689.2969509 a.u.

ZPVE = 175.9551 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.134346	-0.000003
2	7	N	-1.152250	1.476519	0.000000
3	6	C	-1.145006	0.154008	0.000003
4	6	C	0.000000	-0.625709	0.000002
5	6	C	1.145006	0.154008	0.000000
6	7	N	1.152250	1.476519	-0.000003
7	7	N	-2.492760	-0.515186	0.000003
8	7	N	2.492760	-0.515186	-0.000002
9	8	O	-3.480522	0.195500	-0.000018
10	8	O	-2.464071	-1.744589	0.000024
11	8	O	2.464072	-1.744589	-0.000029
12	8	O	3.480522	0.195501	0.000024
13	1	H	0.000000	-1.707512	0.000002

4,5,6-trinitro-1,2,3-triazine (3E)

E = -893.7674034 a.u.

ZPVE = 180.3495 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.000001	2.609358	-0.000155
2	7	N	-1.149674	1.955718	-0.025117
3	6	C	-1.156835	0.629786	-0.023708
4	6	C	0.000000	-0.134280	0.000008
5	6	C	1.156835	0.629790	0.023633
6	7	N	1.149673	1.955722	0.024885
7	7	N	-2.506560	0.006917	-0.105926
8	7	N	0.000000	-1.612554	0.000096
9	7	N	2.506559	0.006931	0.105925
10	8	O	2.658558	-0.773966	1.038994
11	8	O	-3.316061	0.344048	0.737502
12	8	O	-0.697962	-2.145325	0.849828
13	8	O	-2.658556	-0.774093	-1.038900
14	8	O	0.697963	-2.145426	-0.849572
15	8	O	3.316059	0.343959	-0.737546

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at B3LYP/6-311G(d,p) Level**

2-nitro-1,3,5-triazine (1A) E = -484.9747780 a.u. ZPVE = 176.2830 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	1.734976	-1.095441	0.244838
2	7	N	0.399095	-1.162914	0.238514
3	6	C	-0.170180	0.000000	-0.000001
4	7	N	0.399095	1.162913	-0.238516
5	6	C	1.734975	1.095441	-0.244838
6	7	N	2.454301	0.000000	0.000001
7	7	N	-1.675493	0.000000	0.000000
8	8	O	-2.211467	0.891744	0.628379
9	8	O	-2.211469	-0.891743	-0.628378
10	1	H	2.272941	-2.012043	0.463202
11	1	H	2.272942	2.012042	-0.463202

2,4-dinitro-1,3,5-triazine (1B) E = -689.5118983 a.u. ZPVE = 181.0198 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.092108	0.173456	-0.046140
2	7	N	0.000001	-0.563850	0.041279
3	6	C	1.092107	0.173463	-0.046139
4	7	N	1.185128	1.470164	-0.255211
5	6	C	-0.000009	2.073877	-0.383901
6	7	N	-1.185140	1.470156	-0.255214
7	7	N	-2.390269	-0.564861	0.108349
8	7	N	2.390273	-0.564847	0.108349
9	8	O	2.517760	-1.563667	-0.569688
10	8	O	3.180605	-0.085600	0.896157
11	8	O	-2.517714	-1.563728	-0.569629
12	8	O	-3.180636	-0.085572	0.896097
13	1	H	-0.000013	3.136432	-0.599287

2,4,6-trinitro-1,3,5-triazine (1C) E = -894.0415612 a.u. ZPVE = 184.0981 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.682371	1.181993	0.000000
2	7	N	-0.682371	-1.181993	0.000000
3	7	N	1.364954	0.000000	0.000000
4	6	C	0.633187	-1.096606	0.000000
5	7	N	1.397084	-2.419921	0.000000
6	8	O	2.605267	-2.330585	0.000000
7	8	O	0.715525	-3.421508	0.000000
8	6	C	-1.266202	0.000000	0.000000
9	7	N	-2.794212	0.000000	0.000000
10	8	O	-3.320931	-1.090957	0.000000
11	8	O	-3.320931	1.090957	0.000000
12	6	C	0.633187	1.096606	0.000000
13	7	N	1.397084	2.419921	0.000000
14	8	O	2.605267	2.330584	0.000000
15	8	O	0.715526	3.421508	0.000000

3-nitro-1,2,4-triazine (2A)

E = -484.9298265 a.u.

ZPVE = 173.2964 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.401808	1.175568	0.241915
2	6	C	1.727500	1.124045	0.247905
3	6	C	2.387194	-0.080333	-0.018485
4	7	N	1.718930	-1.203913	-0.266901
5	7	N	0.387000	-1.165567	-0.234034
6	6	C	-0.168185	0.005366	0.007380
7	7	N	-1.668341	0.005619	0.001924
8	8	O	-2.197564	0.917359	-0.605241
9	8	O	-2.213526	-0.900403	0.600718
10	1	H	2.265874	2.043199	0.456053
11	1	H	3.468022	-0.155257	-0.040992

6-nitro-1,2,4-triazine (2B)

E = -484.9321587 a.u.

ZPVE = 173.2584 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.832452	1.171198	-0.009723
2	6	C	-0.507682	1.197348	-0.009042
3	6	C	0.183810	-0.015155	0.000033
4	7	N	-0.403070	-1.189488	0.009164
5	7	N	-1.733142	-1.219889	0.010003
6	6	C	-2.378181	-0.051870	0.000136
7	7	N	1.683736	-0.019698	0.000031
8	8	O	2.250235	-1.088524	-0.019410
9	8	O	2.207280	1.087271	0.019680
10	1	H	0.007069	2.150068	-0.015680
11	1	H	-3.460368	-0.116841	0.000432

5-nitro-1,2,4-triazine (2C)

E = -484.933534 a.u.

ZPVE = 173.2897 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.406670	-1.185642	0.000011
2	6	C	0.187526	-0.024187	0.000001
3	6	C	-0.506260	1.183355	-0.000009
4	7	N	-1.839018	1.173156	-0.000012
5	7	N	-2.472311	0.003471	-0.000001
6	6	C	-1.745094	-1.112777	0.000010
7	7	N	1.697471	-0.024815	0.000000
8	8	O	2.257545	-1.097534	-0.000023
9	8	O	2.221677	1.080046	0.000022
10	1	H	-0.009614	2.143476	-0.000015
11	1	H	-2.297497	-2.045115	0.000018

3,6-dinitro-1,2,4-triazine (2D)

E = -689.4680245 a.u.

ZPVE = 178.0909 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.720170	1.214176	-0.152382
2	6	C	-0.605163	1.210094	-0.172901
3	6	C	-1.268563	-0.008868	-0.002997
4	7	N	-0.653127	-1.158834	0.155299
5	7	N	0.676383	-1.161120	0.130534
6	6	C	1.262025	0.014959	-0.010226
7	7	N	-2.767581	-0.046910	0.011279
8	7	N	2.756801	-0.024014	0.004421
9	8	O	3.295095	0.737514	0.783603
10	8	O	3.280781	-0.808095	-0.760243
11	8	O	-3.304410	-1.103782	0.246586
12	8	O	-3.311641	1.023971	-0.222056
13	1	H	-1.136903	2.142934	-0.310446

3,5-dinitro-1,2,4-triazine (2E)

E = -689.4689592 a.u.

ZPVE = 178.0343 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.005687	-0.561115	0.016207
2	6	C	1.096708	0.139706	0.004084
3	6	C	1.103283	1.532007	-0.080802
4	7	N	-0.052187	2.194974	-0.127292
5	7	N	-1.188878	1.505386	-0.077306
6	6	C	-1.095086	0.190899	-0.019822
7	7	N	2.395659	-0.622980	0.075996
8	7	N	-2.398442	-0.548080	-0.006564
9	8	O	-3.248900	-0.123767	0.748579
10	8	O	-2.470492	-1.499792	-0.758683
11	8	O	2.330966	-1.811037	0.288558
12	8	O	3.401143	0.051663	-0.087600
13	1	H	2.015591	2.110492	-0.114893

5,6-dinitro-1,2,4-triazine (2F)

E = -689.4634242 a.u.

ZPVE = 178.3295 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.266563	-1.484365	0.045387
2	6	C	0.208549	-0.722498	0.027554
3	6	C	0.335741	0.667930	-0.029558
4	7	N	1.514486	1.245589	-0.054413
5	7	N	2.605669	0.485525	-0.021122
6	6	C	2.440310	-0.834160	0.016723
7	7	N	-1.112689	-1.411985	0.153046
8	7	N	-0.835807	1.579371	-0.150483
9	8	O	-0.817408	2.596517	0.503363
10	8	O	-1.695849	1.201750	-0.930643
11	8	O	-1.329855	-2.320573	-0.615020
12	8	O	-1.821773	-0.994604	1.051598
13	1	H	3.343929	-1.431310	0.030389

3,5,6-trinitro-1,2,4-triazine (2G)

E = -893.9952482 a.u.

ZPVE = 182.6057 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.863182	0.825096	0.012465
2	6	C	0.414853	0.558692	-0.007302
3	6	C	0.859948	-0.768698	0.001914
4	7	N	0.016075	-1.775545	0.016639
5	7	N	-1.289307	-1.520055	0.007394
6	6	C	-1.641067	-0.249528	0.008214
7	7	N	1.341074	1.730095	0.044333
8	7	N	2.301599	-1.133482	-0.079129
9	7	O	-3.114809	0.010653	0.024398
10	8	O	-3.775884	-0.617838	-0.774982
11	8	O	-3.491607	0.825512	0.842183
12	8	O	2.689473	-2.015344	0.649775
13	8	O	2.934815	-0.499772	-0.907248
14	8	O	2.160503	1.685031	0.943442
15	8	O	1.164881	2.597394	-0.778128

4-nitro-1,2,3-triazine (3A)

E = -484.9060238 a.u.

ZPVE = 170.9137 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.732033	-1.231997	-0.000074
2	7	N	-0.404234	-1.174267	-0.000067
3	6	C	0.183840	0.002876	-0.000002
4	6	C	-0.484896	1.210289	0.000060
5	6	C	-1.863542	1.069534	0.000066
6	7	N	-2.458741	-0.130271	-0.000001
7	7	N	1.694214	-0.010862	0.000001
8	8	O	2.249431	-1.084805	0.000141
9	8	O	2.224745	1.091469	-0.000138
10	1	H	0.031584	2.159215	0.000100
11	1	H	-2.531847	1.923063	0.000124

5-nitro-1,2,3-triazine (3B)

E = -484.9063261 a.u.

ZPVE = 171.3206 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.481856	-0.000001	0.000001
2	7	N	1.838381	-1.156603	-0.000002
3	6	C	0.500768	-1.179468	-0.000002
4	6	C	-0.216817	-0.000001	0.000001
5	6	C	0.500768	1.179468	0.000003
6	7	N	1.838380	1.156604	0.000003
7	7	N	-1.698371	0.000000	-0.000002
8	8	O	-2.248013	-1.088535	-0.000002
9	8	O	-2.248013	1.088535	0.000000
10	1	H	0.019085	-2.149224	-0.000005
11	1	H	0.019084	2.149223	0.000004

4,5-dinitro-1,2,3-triazine (3C)

E = -689.4351410 a.u.

ZPVE = 175.8973 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.084974	-1.629340	0.009751
2	7	N	0.769549	-1.780439	0.028227
3	6	C	-0.018693	-0.718473	0.012342
4	6	C	0.485876	0.568960	-0.020737
5	6	C	1.864467	0.660491	-0.036606
6	7	N	2.637090	-0.432299	-0.022285
7	7	N	-1.470610	-1.043881	0.082782
8	7	N	-0.349194	1.790904	-0.079081
9	8	O	-1.962524	-1.507746	-0.921056
10	8	O	-1.506276	1.640845	-0.425382
11	8	O	-1.991436	-0.848071	1.162897
12	8	O	0.203178	2.837260	0.208330
13	1	H	2.363895	1.621220	-0.064056

4,6-dinitro-1,2,3-triazine (3D)

E = -689.4441414 a.u.

ZPVE = 175.5831 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.131812	0.000015
2	7	N	-1.149682	1.474062	0.000008
3	6	C	-1.142288	0.156105	0.000001
4	6	C	0.000000	-0.620842	0.000000
5	6	C	1.142287	0.156105	0.000003
6	7	N	1.149682	1.474062	0.000010
7	7	N	-2.494650	-0.517855	-0.000007
8	7	N	2.494650	-0.517855	-0.000001
9	8	O	-3.472497	0.191540	0.000001
10	8	O	-2.462202	-1.738878	-0.000021
11	8	O	2.462202	-1.738878	0.000048
12	8	O	3.472497	0.191540	-0.000053
13	1	H	0.000000	-1.700368	-0.000002

4,5,6-trinitro-1,2,3-triazine (3E)

E = -893.9622941 a.u.

ZPVE = 180.4656 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.609815	0.000000
2	7	N	-1.146194	1.953915	-0.020425
3	6	C	-1.153725	0.633732	-0.020426
4	6	C	0.000000	-0.129991	0.000000
5	6	C	1.153725	0.633732	0.020425
6	7	N	1.146194	1.953915	0.020424
7	7	N	-2.509088	0.004953	-0.101099
8	7	N	0.000000	-1.614411	0.000000
9	7	N	2.509088	0.004953	0.101100
10	8	O	2.604784	-0.894051	0.918481
11	8	O	-3.361134	0.456011	0.625970
12	8	O	-0.600306	-2.138012	0.913861
13	8	O	-2.604786	-0.894050	-0.918481
14	8	O	0.600306	-2.138012	-0.913862
15	8	O	3.361136	0.456011	-0.625967

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at B3LYP/6-311+G(d,p) Level**

2-nitro-1,3,5-triazine (1A) E = -484.9890015 a.u. ZPVE = 175.9529 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	1.733122	-1.097129	0.242554
2	7	N	0.396831	-1.162990	0.241736
3	6	C	-0.170893	0.000000	0.000000
4	7	N	0.396831	1.162990	-0.241737
5	6	C	1.733122	1.097129	-0.242554
6	7	N	2.450483	0.000000	0.000000
7	7	N	-1.670837	0.000000	0.000000
8	8	O	-2.208010	0.628018	0.892148
9	8	O	-2.208010	-0.628018	-0.892147
10	1	H	2.271446	-2.014866	0.455436
11	1	H	2.271447	2.014866	-0.455434

2,4-dinitro-1,3,5-triazine (1B) E = -689.5330020 a.u. ZPVE = 180.3845 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.091226	0.173453	-0.037142
2	7	N	0.000000	-0.566134	0.047513
3	6	C	1.091226	0.173452	-0.037144
4	7	N	1.185193	1.473736	-0.222594
5	6	C	0.000000	2.081902	-0.330163
6	7	N	-1.185193	1.473736	-0.222593
7	7	N	-2.385905	-0.565903	0.092301
8	7	N	2.385906	-0.565903	0.092301
9	8	O	2.665378	-1.315031	-0.821978
10	8	O	3.027473	-0.339367	1.098890
11	8	O	-2.665374	-1.315034	-0.821978
12	8	O	-3.027476	-0.339366	1.098887
13	1	H	0.000000	3.150817	-0.512362

2,4,6-trinitro-1,3,5-triazine (1C) E = -894.0676098 a.u. ZPVE = 182.9861 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.682289	-1.181814	0.000000
2	7	N	-0.682289	1.181814	0.000000
3	7	N	1.364726	0.000000	0.000000
4	6	C	0.632974	1.096265	0.000000
5	7	N	1.397892	2.421277	0.000000
6	8	O	2.606883	2.334488	0.000000
7	8	O	0.718253	3.424919	0.000000
8	6	C	-1.265832	0.000000	0.000000
9	7	N	-2.795822	0.000000	0.000000
10	8	O	-3.325226	1.090352	0.000000
11	8	O	-3.325226	-1.090352	0.000000
12	6	C	0.632974	-1.096265	0.000000
13	7	N	1.397892	-2.421277	0.000000
14	8	O	2.606883	-2.334488	0.000000
15	8	O	0.718253	-3.424919	0.000000

3-nitro-1,2,4-triazine (2A)

E = -484.9439297 a.u.

ZPVE = 172.9538 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.400885	1.171680	0.264440
2	6	C	1.726806	1.119734	0.266519
3	6	C	2.385778	-0.080988	-0.019450
4	7	N	1.715625	-1.199042	-0.286091
5	7	N	0.384788	-1.160950	-0.257838
6	6	C	-0.168241	0.006600	0.006448
7	7	N	-1.664694	0.005548	0.001599
8	8	O	-2.196789	0.738371	-0.811616
9	8	O	-2.210128	-0.722359	0.808672
10	1	H	2.266426	2.034695	0.489083
11	1	H	3.466621	-0.155513	-0.041400

6-nitro-1,2,4-triazine (2B)

E = -484.9454224 a.u.

ZPVE = 172.9306 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.831612	1.166224	0.095188
2	6	C	-0.507174	1.194623	0.088977
3	6	C	0.183983	-0.015135	-0.001720
4	7	N	-0.403515	-1.185851	-0.090298
5	7	N	-1.732167	-1.215662	-0.097101
6	6	C	-2.379268	-0.051839	-0.001380
7	7	N	1.682277	-0.020316	-0.001237
8	8	O	2.206746	1.070275	-0.195174
9	8	O	2.251577	-1.071156	0.193469
10	1	H	0.004765	2.146965	0.156977
11	1	H	-3.461481	-0.116570	-0.004474

5-nitro-1,2,4-triazine (2C)

E = -484.9467169 a.u.

ZPVE = 172.6992 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.408768	-1.184318	0.000011
2	6	C	0.186078	-0.023722	-0.000001
3	6	C	-0.506423	1.184805	-0.000012
4	7	N	-1.839699	1.171689	-0.000013
5	7	N	-2.472862	0.004059	-0.000001
6	6	C	-1.746691	-1.113902	0.000012
7	7	N	1.697868	-0.025560	0.000001
8	8	O	2.261075	-1.097332	-0.000033
9	8	O	2.223774	1.079221	0.000036
10	1	H	-0.013130	2.146929	-0.000020
11	1	H	-2.299223	-2.046208	0.000022

3,6-dinitro-1,2,4-triazine (2D)

E = -689.4765824 a.u.

ZPVE = 183.9928 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.721501	1.221029	-0.092410
2	6	C	-0.604241	1.218809	-0.109247
3	6	C	-1.267324	-0.008093	-0.001751
4	7	N	-0.650911	-1.163776	0.098371
5	7	N	0.677414	-1.166091	0.078948
6	6	C	1.262129	0.016481	-0.006598
7	7	N	-2.766478	-0.048793	0.007560
8	7	N	2.754022	-0.024658	0.002779
9	8	O	3.290209	0.453115	0.983592
10	8	O	3.283407	-0.525707	-0.969033
11	8	O	-3.312187	1.019415	-0.238143
12	8	O	-3.306262	-1.102630	0.253175
13	1	H	-1.133552	2.159302	-0.197885

3,5-dinitro-1,2,4-triazine (2E)

E = -689.4892157 a.u.

ZPVE = 177.4042 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.009528	-0.561378	-0.014521
2	6	C	-1.096882	0.133439	-0.004972
3	6	C	-1.111019	1.526757	0.062596
4	7	N	0.042652	2.194552	0.098662
5	7	N	1.182510	1.512774	0.062242
6	6	C	1.093772	0.196520	0.017097
7	7	N	-2.391909	-0.638542	-0.066235
8	7	N	2.399101	-0.531922	0.012067
9	8	O	3.144319	-0.294350	-0.917314
10	8	O	2.583613	-1.291620	0.943241
11	8	O	-2.325449	-1.824037	-0.295990
12	8	O	-3.400436	0.025921	0.122224
13	1	H	-2.024776	2.103998	0.088878

5,6-dinitro-1,2,4-triazine (2F)

E = -689.4840678 a.u.

ZPVE = 177.7088 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.304100	-1.454593	0.060660
2	6	C	0.228837	-0.717925	0.033249
3	6	C	0.322662	0.674241	-0.035694
4	7	N	1.488413	1.278408	-0.070335
5	7	N	2.595213	0.544706	-0.032052
6	6	C	2.462627	-0.778950	0.024872
7	7	N	-1.080119	-1.435116	0.151721
8	7	N	-0.871710	1.557463	-0.148659
9	8	O	-0.901721	2.544093	0.551223
10	8	O	-1.703909	1.191318	-0.964443
11	8	O	-1.288160	-2.329957	-0.635592
12	8	O	-1.795736	-1.048689	1.059818
13	1	H	3.380182	-1.354391	0.048043

3,5,6-trinitro-1,2,4-triazine (2G)

E = -894.0226170 a.u.

ZPVE = 181.7866 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.866295	0.825506	0.021228
2	6	C	0.411901	0.558850	-0.000459
3	6	C	0.857363	-0.768262	-0.009889
4	7	N	0.012742	-1.775219	-0.012175
5	7	N	-1.291191	-1.520879	-0.015100
6	6	C	-1.642584	-0.249408	0.004632
7	7	N	1.341504	1.729167	0.059401
8	7	N	2.300772	-1.130363	-0.085243
9	7	O	-3.113764	0.007605	0.026185
10	8	O	-3.742233	-0.405369	-0.926286
11	8	O	-3.526717	0.605993	0.999564
12	8	O	2.696222	-1.986982	0.670376
13	8	O	2.932767	-0.518116	-0.931006
14	8	O	2.145712	1.691040	0.973135
15	8	O	1.188443	2.588710	-0.776506

4-nitro-1,2,3-triazine (3A)

E = -484.9191751 a.u.

ZPVE = 170.5691 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.731126	-1.231604	-0.047266
2	7	N	-0.404449	-1.172933	-0.042510
3	6	C	0.182643	0.003998	-0.001355
4	6	C	-0.486171	1.210851	0.039096
5	6	C	-1.865113	1.067800	0.041731
6	7	N	-2.458574	-0.132082	-0.001491
7	7	N	1.693762	-0.011265	0.000355
8	8	O	2.251943	-1.080325	0.093318
9	8	O	2.225989	1.087464	-0.091336
10	1	H	0.025500	2.162371	0.066032
11	1	H	-2.534406	1.919816	0.077658

5-nitro-1,2,3-triazine (3B)

E = -484.9190078 a.u.

ZPVE = 170.4786 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-2.482205	-0.000001	-0.000001
2	7	N	-1.839286	-1.155709	0.000002
3	6	C	-0.501213	-1.180153	0.000003
4	6	C	0.216203	-0.000001	0.000001
5	6	C	-0.501214	1.180153	-0.000003
6	7	N	-1.839285	1.155710	-0.000004
7	7	N	1.698395	0.000000	0.000002
8	8	O	2.250009	-1.088357	-0.000001
9	8	O	2.250008	1.088357	0.000001
10	1	H	-0.023061	-2.151853	0.000006
11	1	H	-0.023060	2.151853	-0.000004

4,5-dinitro-1,2,3-triazine (3C)

E = -689.4553045 a.u.

ZPVE = 175.4734 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.195804	-1.481429	0.012334
2	7	N	0.894719	-1.725278	0.040631
3	6	C	0.034876	-0.721476	0.014490
4	6	C	0.446017	0.598343	-0.033086
5	6	C	1.814918	0.787491	-0.051564
6	7	N	2.661029	-0.249850	-0.033182
7	7	N	-1.394121	-1.139704	0.105101
8	7	N	-0.473939	1.756740	-0.098816
9	8	O	-1.851466	-1.711460	-0.858761
10	8	O	-1.578933	1.548216	-0.565344
11	8	O	-1.938273	-0.892909	1.165130
12	8	O	-0.032415	2.820045	0.299762
13	1	H	2.249390	1.779364	-0.087804

4,6-dinitro-1,2,3-triazine (3D)

E = -689.4635626 a.u.

ZPVE = 174.8337 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.130932	-0.000073
2	7	N	-1.149045	1.473538	-0.000046
3	6	C	-1.142076	0.155936	-0.000009
4	6	C	0.000000	-0.622388	0.000006
5	6	C	1.142076	0.155936	-0.000008
6	7	N	1.149045	1.473538	-0.000045
7	7	N	-2.496801	-0.516427	0.000019
8	7	N	2.496801	-0.516427	0.000020
9	8	O	-3.476441	0.191365	0.000125
10	8	O	-2.466625	-1.738273	-0.000068
11	8	O	2.466626	-1.738273	-0.000066
12	8	O	3.476441	0.191365	0.000123
13	1	H	0.000000	-1.702454	0.000023

4,5,6-trinitro-1,2,3-triazine (3E)

E = -893.9893272 a.u.

ZPVE = 179.7285 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.000005	2.606839	-0.000002
2	7	N	1.146494	1.953500	0.023926
3	6	C	1.153969	0.632245	0.022226
4	6	C	0.000000	-0.130664	0.000000
5	6	C	-1.153971	0.632241	-0.022227
6	7	N	-1.146502	1.953496	-0.023927
7	7	N	2.509652	0.005924	0.103993
8	7	N	0.000004	-1.614973	0.000002
9	7	N	-2.509653	0.005916	-0.103995
10	8	O	-2.647407	-0.798637	-1.009040
11	8	O	3.324690	0.367623	-0.711419
12	8	O	0.667775	-2.142628	-0.865221
13	8	O	2.647419	-0.798600	1.009062
14	8	O	-0.667764	-2.142629	0.865226
15	8	O	-3.324703	0.367640	0.711394

**Cartesian Coordinates of Ground State Geometries of Nitrotriazine
Derivatives at B3LYP/cc-pVDZ Level**

2-nitro-1,3,5-triazine (1A) E = -484.8877448 a.u. ZPVE = 176.4998 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	1.737329	1.102608	-0.217117
2	7	N	0.398096	1.174008	-0.209805
3	6	C	-0.172175	0.000000	-0.000001
4	7	N	0.398096	-1.174008	0.209804
5	6	C	1.737329	-1.102608	0.217117
6	7	N	2.462277	0.000000	0.000000
7	7	N	-1.678237	0.000000	0.000000
8	8	O	-2.214823	-0.961691	-0.520133
9	8	O	-2.214822	0.961692	0.520134
10	1	H	2.280318	2.032295	-0.413872
11	1	H	2.280318	-2.032295	0.413871

2,4-dinitro-1,3,5-triazine (1B) E = -689.3889353 a.u. ZPVE = 181.4802 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.095094	0.173935	-0.043229
2	7	N	-0.000004	-0.568808	0.031885
3	6	C	1.095094	0.173927	-0.043226
4	7	N	1.190337	1.478960	-0.232065
5	6	C	0.000007	2.082637	-0.351629
6	7	N	-1.190325	1.478971	-0.232069
7	7	N	-2.394874	-0.567657	0.099627
8	7	N	2.394872	-0.567682	0.099633
9	8	O	2.456228	-1.646792	-0.458475
10	8	O	3.252572	-0.010550	0.759246
11	8	O	-2.456313	-1.646677	-0.458647
12	8	O	-3.252499	-0.010606	0.759408
13	1	H	0.000014	3.157516	-0.552834

2,4,6-trinitro-1,3,5-triazine (1C) E = -893.8842268 a.u. ZPVE = 185.0550 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.685868	-1.187983	0.000000
2	7	N	-0.685868	1.187983	0.000000
3	7	N	1.371827	0.000000	0.000000
4	6	C	0.634836	1.099506	0.000000
5	7	N	1.396291	2.418406	0.000000
6	8	O	2.607402	2.328081	0.000000
7	8	O	0.712528	3.422098	0.000000
8	6	C	-1.269613	0.000000	0.000000
9	7	N	-2.792611	0.000000	0.000000
10	8	O	-3.319979	1.093956	0.000000
11	8	O	-3.319979	-1.093956	0.000000
12	6	C	0.634836	-1.099506	0.000000
13	7	N	1.396291	-2.418406	0.000000
14	8	O	2.607402	-2.328080	0.000000
15	8	O	0.712528	-3.422098	0.000000

3-nitro-1,2,4-triazine (2A)

E = -484.8445574 a.u.

ZPVE = 173.5765 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.399118	1.187535	0.217132
2	6	C	1.729220	1.132403	0.223269
3	6	C	2.389942	-0.080838	-0.016780
4	7	N	1.720809	-1.214494	-0.241556
5	7	N	0.388120	-1.175130	-0.209688
6	6	C	-0.169838	0.006464	0.007431
7	7	N	-1.669701	0.005317	0.002178
8	8	O	-2.200492	0.971078	-0.518967
9	8	O	-2.214302	-0.955736	0.514541
10	1	H	2.274116	2.062389	0.412668
11	1	H	3.479866	-0.155897	-0.037240

6-nitro-1,2,4-triazine (2B)

E = -484.8474012 a.u.

ZPVE = 173.8388 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.836963	1.177258	0.000001
2	6	C	0.507123	1.199323	0.000001
3	6	C	-0.186919	-0.015344	0.000000
4	7	N	0.401428	-1.196535	-0.000001
5	7	N	1.732379	-1.224849	-0.000001
6	6	C	2.378401	-0.051518	0.000000
7	7	N	-1.683299	-0.018312	0.000000
8	8	O	-2.250547	-1.090652	0.000002
9	8	O	-2.206908	1.091019	-0.000002
10	1	H	-0.014091	2.158492	0.000001
11	1	H	3.469806	-0.119126	0.000000

5-nitro-1,2,4-triazine (2C)

E = -484.8486630 a.u.

ZPVE = 173.8348 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.402854	-1.194009	-0.000001
2	6	C	-0.191785	-0.025034	0.000003
3	6	C	0.506331	1.183951	0.000003
4	7	N	1.843802	1.176137	0.000002
5	7	N	2.476298	0.004857	-0.000002
6	6	C	1.744028	-1.114462	-0.000003
7	7	N	-1.697357	-0.023089	0.000000
8	8	O	-2.259179	-1.098527	0.000005
9	8	O	-2.220549	1.084612	-0.000008
10	1	H	0.003938	2.151034	0.000013
11	1	H	2.303265	-2.053712	-0.000006

3,6-dinitro-1,2,4-triazine (2D)

E = -689.3472688 a.u.

ZPVE = 178.8250 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.723222	1.219813	-0.162673
2	6	C	-0.606849	1.211094	-0.181857
3	6	C	-1.272468	-0.008731	-0.002682
4	7	N	-0.655054	-1.163583	0.167130
5	7	N	0.675185	-1.164262	0.142596
6	6	C	1.263862	0.015977	-0.010196
7	7	N	-2.768322	-0.045645	0.010675
8	7	N	2.758791	-0.024551	0.003606
9	8	O	3.302384	0.835646	0.672783
10	8	O	3.278773	-0.908586	-0.650994
11	8	O	-3.305900	-1.114569	0.203036
12	8	O	-3.312571	1.036087	-0.179100
13	1	H	-1.145524	2.148938	-0.326716

3,5-dinitro-1,2,4-triazine (2E)

E = -689.3482235 a.u.

ZPVE = 178.7519 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.004190	-0.569445	0.017301
2	6	C	1.099983	0.140166	0.001209
3	6	C	1.100431	1.535397	-0.090082
4	7	N	-0.059747	2.199214	-0.142363
5	7	N	-1.194950	1.505974	-0.086626
6	6	C	-1.096965	0.185635	-0.020024
7	7	N	2.399504	-0.614821	0.074674
8	7	N	-2.399264	-0.555507	0.002429
9	8	O	-3.291600	-0.054833	0.660490
10	8	O	-2.429537	-1.585592	-0.646162
11	8	O	2.336829	-1.815594	0.225182
12	8	O	3.405585	0.075469	-0.024419
13	1	H	2.019604	2.119305	-0.125256

5,6-dinitro-1,2,4-triazine (2F)

E = -689.3422223 a.u.

ZPVE = 178.8585 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.228043	-1.523907	0.041046
2	6	C	0.185921	-0.728475	0.024965
3	6	C	0.350412	0.661310	-0.027730
4	7	N	1.549302	1.212441	-0.050216
5	7	N	2.620041	0.423044	-0.017598
6	6	C	2.417556	-0.897191	0.014962
7	7	N	-1.148809	-1.384497	0.153246
8	7	N	-0.795200	1.601692	-0.151200
9	8	O	-0.731038	2.639883	0.471812
10	8	O	-1.685357	1.224813	-0.901056
11	8	O	-1.385415	-2.294916	-0.611889
12	8	O	-1.849622	-0.944065	1.050283
13	1	H	3.314482	-1.521001	0.026668

3,5,6-trinitro-1,2,4-triazine (2G)

E = -893.8383680 a.u.

ZPVE = 183.3851 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.864822	0.832910	0.011844
2	6	C	0.418782	0.560826	-0.008140
3	6	C	0.862680	-0.770009	0.003684
4	7	N	0.014302	-1.781736	0.020329
5	7	N	-1.291076	-1.523938	0.010823
6	6	C	-1.642960	-0.246586	0.008810
7	7	N	1.343675	1.730014	0.046072
8	7	N	2.301438	-1.136551	-0.081460
9	7	O	-3.116784	0.013662	0.023236
10	8	O	-3.791974	-0.701954	-0.690680
11	8	O	-3.480588	0.915855	0.754519
12	8	O	2.683035	-2.043298	0.625229
13	8	O	2.941398	-0.479147	-0.889215
14	8	O	2.174043	1.675431	0.937858
15	8	O	1.156819	2.607374	-0.767964

4-nitro-1,2,3-triazine (3A)

E = -484.8224942 a.u.

ZPVE = 171.5445 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	1.732487	-1.234204	-0.000018
2	7	N	0.403424	-1.179384	-0.000016
3	6	C	-0.187665	0.003478	0.000000
4	6	C	0.482569	1.215033	0.000014
5	6	C	1.865695	1.071709	0.000016
6	7	N	2.462707	-0.131356	-0.000001
7	7	N	-1.693934	-0.010472	0.000000
8	8	O	-2.249008	-1.088177	0.000035
9	8	O	-2.225593	1.093689	-0.000034
10	1	H	-0.039360	2.170355	0.000024
11	1	H	2.539790	1.932136	0.000030

5-nitro-1,2,3-triazine (3B)

E = -484.8229237 a.u.

ZPVE = 171.9756 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	2.485652	-0.000001	0.000001
2	7	N	1.842881	-1.159610	-0.000002
3	6	C	0.501152	-1.181848	-0.000002
4	6	C	-0.221448	0.000000	0.000000
5	6	C	0.501153	1.181847	0.000003
6	7	N	1.842880	1.159611	0.000003
7	7	N	-1.700999	0.000000	-0.000002
8	8	O	-2.250456	-1.091323	-0.000003
9	8	O	-2.250456	1.091323	0.000001
10	1	H	0.014636	-2.159084	-0.000004
11	1	H	0.014635	2.159084	0.000004

4,5-dinitro-1,2,3-triazine (3C)

E = -689.3159584 a.u.

ZPVE = 176.7524 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-1.959948	-1.778456	0.000019
2	7	N	-0.636801	-1.834414	0.000050
3	6	C	0.075950	-0.710871	0.000021
4	6	C	-0.524537	0.539553	-0.000037
5	6	C	-1.911496	0.525086	-0.000066
6	7	N	-2.604413	-0.623875	-0.000038
7	7	N	1.544077	-0.940757	0.000165
8	7	N	0.216121	1.821652	-0.000161
9	8	O	2.058086	-1.046785	1.095973
10	8	O	1.433617	1.745840	-0.000809
11	8	O	2.058132	-1.048112	-1.095482
12	8	O	-0.458550	2.838211	0.000363
13	1	H	-2.483050	1.455101	-0.000119

4,6-dinitro-1,2,3-triazine (3D)

E = -689.3252549 a.u.

ZPVE = 176.5404 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	0.000000	2.134018	0.000001
2	7	N	-1.153022	1.478019	0.000001
3	6	C	-1.145771	0.154018	0.000000
4	6	C	0.000000	-0.625591	0.000000
5	6	C	1.145771	0.154018	0.000000
6	7	N	1.153022	1.478019	0.000000
7	7	N	-2.494454	-0.518251	0.000000
8	7	N	2.494454	-0.518251	-0.000001
9	8	O	-3.474153	0.194291	-0.000005
10	8	O	-2.461872	-1.741568	0.000006
11	8	O	2.461872	-1.741568	-0.000005
12	8	O	3.474153	0.194291	0.000003
13	1	H	0.000000	-1.713123	0.000000

4,5,6-trinitro-1,2,3-triazine (3E)

E = -893.8072866 a.u.

ZPVE = 181.4358 kJ/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	N	-0.000002	2.615686	0.000003
2	7	N	1.148794	1.960228	0.019818
3	6	C	1.156317	0.634762	0.019427
4	6	C	0.000000	-0.134318	0.000000
5	6	C	-1.156319	0.634761	-0.019427
6	7	N	-1.148797	1.960227	-0.019814
7	7	N	2.510135	0.005991	0.097751
8	7	N	0.000002	-1.617801	0.000001
9	7	N	-2.510136	0.005987	-0.097754
10	8	O	-2.582870	-0.953064	-0.851088
11	8	O	3.385469	0.511003	-0.568783
12	8	O	0.554158	-2.140659	-0.945845
13	8	O	2.582874	-0.953055	0.851092
14	8	O	-0.554151	-2.140659	0.945849
15	8	O	-3.385475	0.511003	0.568771