

Nitrogen analogs of TEX – A computational study

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Abstract

TEX, a well-known nitramine type explosive, has been subjected to centric perturbations by replacing its etheric (acetal) oxygens with nitrogen atoms one by one. The structural features, stabilities and IR and UV-VIS spectra of new structures formed are investigated. For this purpose, density functional theory has been employed at the B3LYP/6-31G (d,p) and B3LYP/6-311G(d) levels. In general the calculations revealed that the oxygen–nitrogen replacement resulted in more energetic but less sensitive structures than TEX. Copyright © 2014, China Ordnance Society. Production and hosting by Elsevier B.V. All rights reserved.

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1. Introduction

TEX (4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazawurtzitane) (see Fig. 1) has attracted attention in recent years as one of the novel energetic materials [1]. It was first synthesized by Boyer and coworkers [2]. Their synthesis started with form amide and glyoxal and in a two-step synthesis involving a piperazine derivative as an intermediary product, TEX is obtained. It is a nitramine and additionally contains two embedded five-membered cyclic dietheric (also can be considered as acetal) structures resembling to 1,3-dioxalane.

TEX is much less sensitive to impact and friction stimuli as compared to the well known explosives, RDX and HMX. Moreover, it has high density (1.99 g/cm^3), excellent thermal stability ($m.p > 240 \text{ }^\circ\text{C}$) as well as its high detonation velocity (VOD: 8665 m/s) and pressure (370 kbar) [1–7].

In the literature, based on density functional theory (DFT), various computational works have piled up on TEX molecule in order to predict some of its properties, such as the crystal density [8], bond dissociation energies and impact sensitivity [9], detonation velocity [10], sensitivity and performance

relation [11]. One of the studies was about the influence of RDX and HMX on the thermal stability of TEX [12]. DFT calculations were employed in various modeling work which involve TEX and other explosives [13–15]. The density functional theory at the B3LYP/6-31 + G(d,p) level of theory was employed to calculate the heat of reactions of free dinitramidic acid ($\text{HN}(\text{NO}_2)_2$) with derivatives of 2,4-(R)-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}] dodecane (R = H, F, CH_3 , NO_2 (TEX)) [16]. Also, the heat of formation (HOF) for a caged wurtzitane analog compound, 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane (TEX) was obtained by density functional theory (B3LYP method with 6-31 + G(d,p) basis set) [17].

In the present work, centric perturbations [18] have been performed on the etheric (acetal) oxygen atoms present in the structure of TEX by replacing them with nitrogen atoms (considering isomeric structures) in order to get more nitrogenous materials which are thought to be candidates for explosives.

2. Methods of calculation

All the theoretical methods were applied using the restricted level of theory because all the structures are closed shell systems (no radicals) [19]. The initial optimizations of

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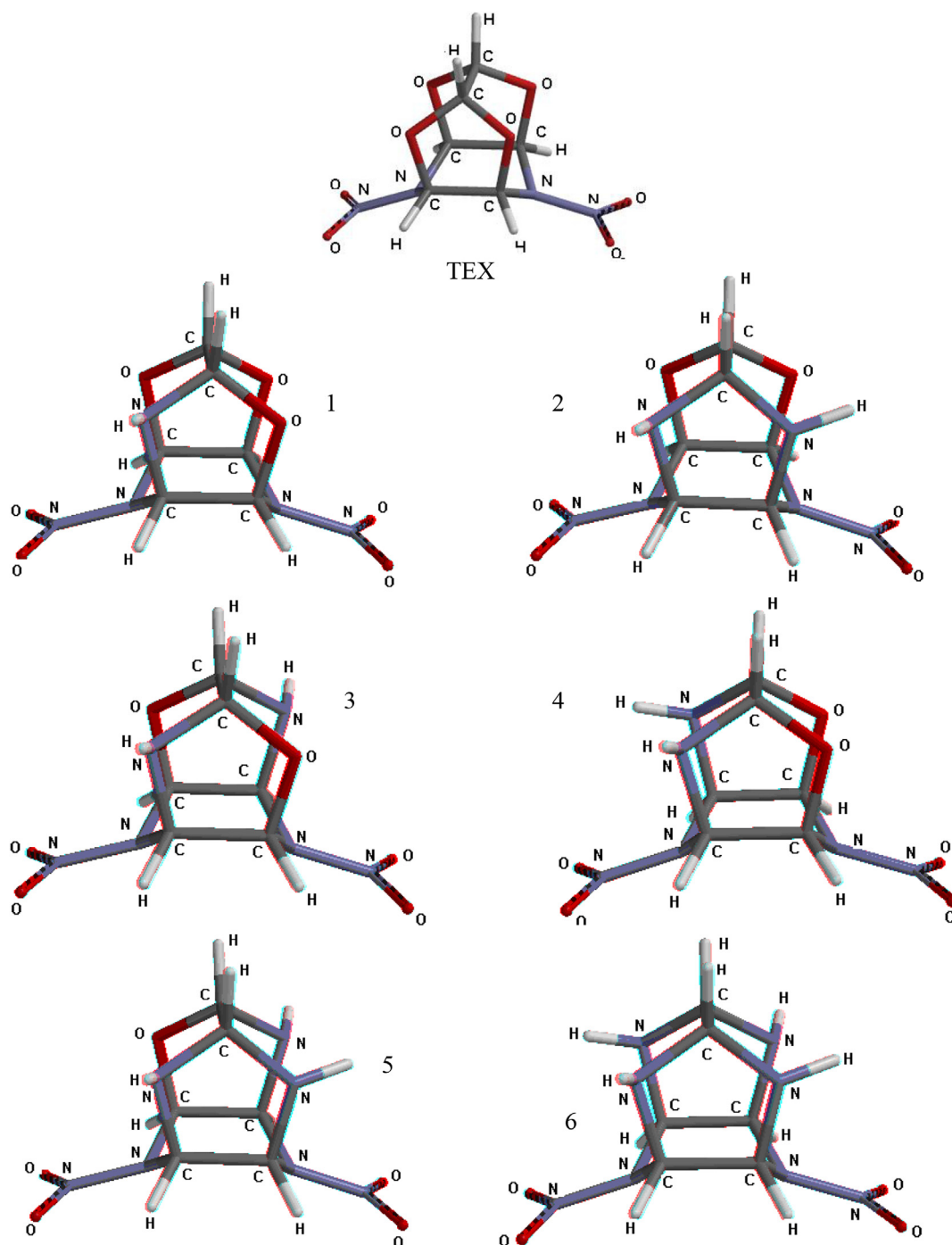


Fig. 1. Structures of the present concern.

the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF-MO) method [19,20]. Then, further structure optimizations were achieved by using STO and RHF levels of theory (6-31G (d,p)) and then within the framework of Density Functional Theory (DFT, B3LYP) [20–22] at the levels of 6-31G(d,p) and 6-311G(d). All the presently considered structures are dealt in their singlet states (restricted type calculations have been done). Note that 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 [23]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [24] and Lee, Yang, Parr (LYP) correlation correction functional [25].

The normal mode analysis (at the same theoretical levels as the optimizations) for each structure yielded no imaginary frequencies, which indicates that each compound has at least a local minimum on the potential energy surface. The total

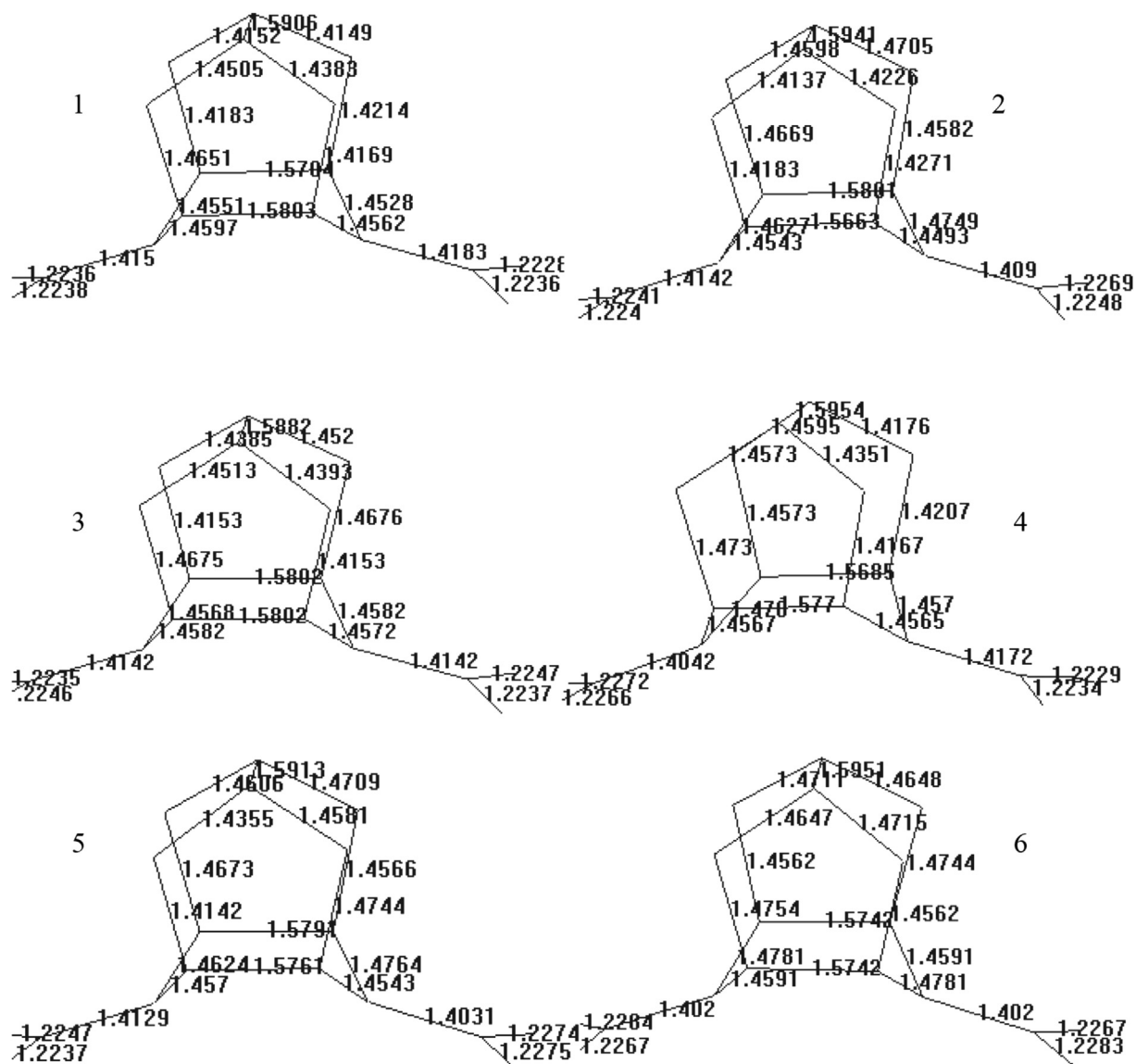


Fig. 2. Bond lengths of the hydrogen depleted structures (B3LYP/6-31G(d,p), see Fig. 1 for the atoms in the structures).

electronic energies were corrected for zero point vibrational energies (ZPVE or ZPE). Aqueous energies are calculated by the computer program based on Cramer–Truhlar SM54 solvation method for water [26–28]. All these computations were performed by using Spartan 06 package program at standard conditions of 298.15 K and 1.00 atm [29].

Table 1
Various properties of the structures considered.

No	Dipole moment/debye	Area/ 10^{-20} m ²	Volume/ 10^{-30} m ³
1	2.95	202.81	185.86
2	3.40	206.35	189.03
3	3.14	206.33	188.04
4	4.01	206.12	189.02
5	3.98	209.66	192.08
6	4.35	212.88	195.31

3. Results and discussion

3.1. Structural features

Fig. 1 shows the structures of present concern which are obtained by the replacement of etheric (acetal) oxygens of TEX one by one with nitrogen atom. Consequently, the nitrogen and hydrogen numbers increase through structures 1–6. However, 2–4 are isomeric structures in which only the locations of nitrogen atoms (each contains two more nitrogen

Table 2
Nitramine bond lengths (10^{-10} m, B3LYP/6-31G(d,p)).

TEX	1	2	3	4	5	6
1.421	1.415	1.409	1.414	1.404	1.403	1.402
1.421	1.419	1.414	1.414	1.417	1.412	1.402

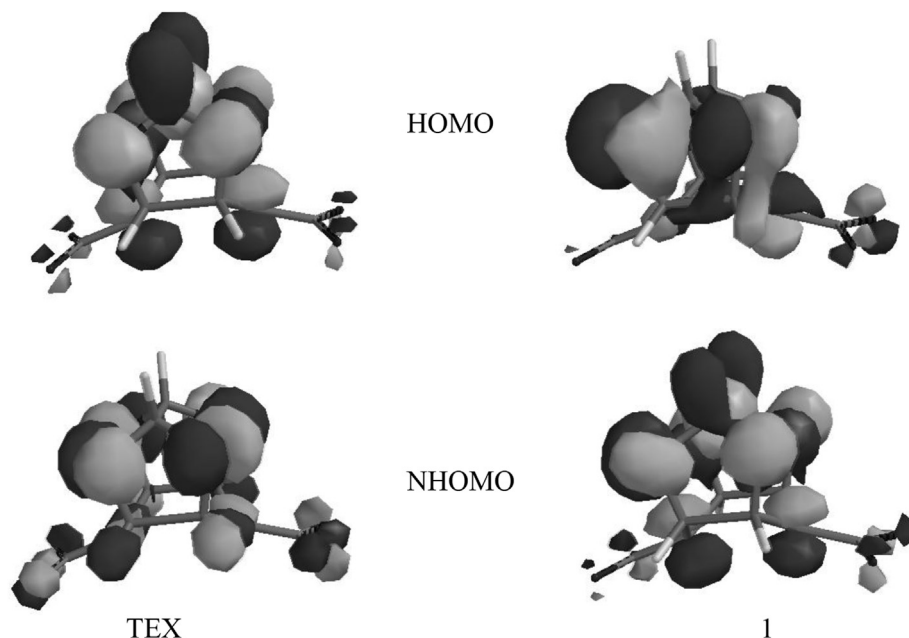


Fig. 3. HOMO and NHOMO of TEX and 1.

atoms compared to TEX) differ. In 2 both of the oxygen–nitrogen replacements are in the same pentagonal moiety. In 3 and 4 the replacements are in different pentagons but the nitrogen atoms are symmetrical in 4 (with respect to vertical symmetry plane). Whereas in 3 the nitrogen atoms occupy opposite corners in different pentagons. In 5 and 6 one and two of the 5-membered rings is/are amination(s), respectively.

Fig. 2 shows the bond lengths of structures. Table 1 includes some properties of the structures presently concerned. Structure 6 has the highest dipole moment, area and volume among the compounds, whereas 1 has the lowest. These properties of the isomeric structures 2–4 fluctuate in value depending on position of the nitrogen atoms and their symmetrical or unsymmetrical occurrences in the structures.

Table 2 displays the nitramine bond lengths in TEX and structures 1–6. Both of the N–NO₂ bond lengths are pair wise equal in TEX, 3 and 6. The values for TEX are longer than the nitramine bond lengths of the present perturbed structures which implies that the N–NO₂ bond dissociation energy of TEX should be less than the respective energies of structures 1–6. Hence, they should be less sensitive than TEX. Note that

N–N bond length in N,N-dimethylnitramine and TEX are $1.382 \cdot 10^{-10}$ m [30] and $1.41 \cdot 10^{-10}$ m [7], respectively. Variation of the nitramine bond lengths, even in the isomeric cases, should be due to varying degree of conjugation involved in N–NO₂ moiety. It is dictated by structural variations and field effects present in the structures. Fig. 3 shows the HOMO and NHOMO (HOMO-1) of TEX and structure-1. In the later case better conjugation is observed for the nitramine bond.

3.2. Energetics

Tables 3a and 3b show the zero point energy and the relative corrected total energy values of the structures in the vacuum and in water at the levels of B3LYP/6-31G(d,p) and B3LYP/6-311G(d) levels, respectively. Although the number of nitrogen and oxygen atoms are different, the stability order is $1 > 3 > 2 > 4 > 5 > 6$ in the vacuum at the both levels of calculations. Hence, with the exception of 3 (or 2), the oxygen–nitrogen replacement regularly decreases the stability. Note 2–4 are isomers having two oxygen–nitrogen replacements. Whereas in water the order is $1 > 3 > 4 > 2 > 5 > 6$ (at the both

Table 3a

Various relative energies (kJ/mol) of the structures considered (B3LYP/6-31G(d,p)).

No	ZPE	$E_{\text{corrected}}/(\text{kJ} \cdot \text{mol}^{-1})$	$E_{\text{aq corrected}}(\text{kJ} \cdot \text{mol}^{-1})$
1	464.71587	0	0
2	498.51011	52189.763	52194.58
3	498.93727	52189.521	52180.87
4	498.26109	52190.285	52192.48
5	533.01387	104378.358	104366.25
6	566.30943	156563.643	156555.64

$E_{\text{corrected}}$ of 1 in vacuum and water are -2711423.55 and -2711472.54 kJ/mol, respectively.

Table 3b

Various relative energies (kJ/mol) of the structures considered (B3LYP/6-311(d)).

No	ZPE	$E_{\text{corrected}}/(\text{kJ} \cdot \text{mol}^{-1})$	$E_{\text{aq corrected}}/(\text{kJ} \cdot \text{mol}^{-1})$
1	464.3117	0	0
2	498.1839	52215.49	52213.28
3	498.4697	52215.17	52198.52
4	497.8568	52215.81	52210.48
5	532.8793	104429.71	104417.56
6	566.1618	156640.38	104450.84

$E_{\text{corrected}}$ of 1 in vacuum and water are -2712088.54 and -2712135.61 kJ/mol, respectively.

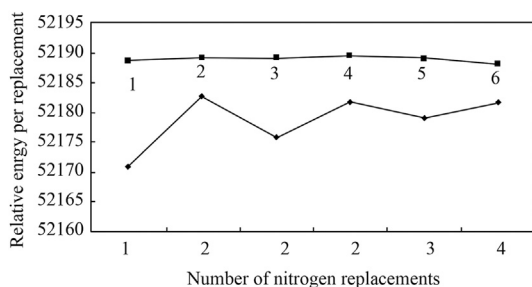


Fig. 4. Relative energy per oxygen–nitrogen replacement (kJ/mol). Upper curve stands for aqueous conditions. Structure numbers are on the graph. Based on B3LYP/6-31G(d,p) level of calculations.

levels). It seems, in water, with the exception of 2, stability decreases regularly as the number of oxygen–nitrogen replacement increases. Of the isomeric structures (2–4), 3 has the maximum stability in the vacuum and in aqueous conditions. All these results indicate that the effect of oxygen–nitrogen replacements is also position dependent. However, inspection of the total energies of the structures reveals that generally as the number of nitrogen atoms increases the stability decreases in this particular cage system (see Fig. 4 too).

Fig. 4 shows the variation of relative energy (with respect to TEX, see Fig. 3) per oxygen–nitrogen replacement. From the figure it is evident that all the present structures are more energetic than TEX and in vacuum, and as the number of nitrogen atoms increases the stability decreases. Generally the trend of relative energy increases having local maximas (structures 2, 4,6) and local minimas (3 and 5). Since 2–4 are isomeric structures, the most stable structure (3) among them is obtained when the replacement takes place in the different rings and on the opposite corners. In the aqueous conditions the model (SM 54 [26,27]) predicts that the oxygen–nitrogen replacement do not cause appreciable energy changes in contrast to the vacuum conditions.

3.3. Spectra

Structures 1–6 show similar calculated IR spectra (B3LYP/6-31G(d,p)) with some changes in the fingerprint region (a few typical examples are shown in the supplement). The calculated (B3LYP/6-31G(d,p)) UV-VIS spectra of TEX as well as the structures 1–6 also can be found in the supplement. In all the cases absorptions span in the UV region (extending at most to 350 nm).

Table 4 shows the λ_{max} values of the structures whereas the HOMO, LUMO energies and the interfrontier energy gaps (the HOMO- LUMO energy difference, $\Delta\epsilon$) are displayed in Table 5. The data in the table reveal that the first centric perturbation, leading to 1, results in the deepest HOMO and LUMO

Table 4
 λ_{max} (nm) values of the structures considered (B3LYP/6-31G(d,p)).

1	2	3	4	5	6
270.86	285.22	271.33	282.89	289.39	305.74
			271.02		290.11

Table 5
HOMO, LUMO energies (kJ/mol) and interfrontier energy gaps ($\Delta\epsilon$) (B3LYP/6-31G(d,p)).

	1	2	3	4	5	6
HOMO	−740.93	−683.55	−706.19	−685.23	−662.09	−630.06
LUMO	−200.53	−195.82	−183.70	−194.14	−179.20	−172.96
$\Delta\epsilon$	540.40	487.73	522.49	491.09	482.89	457.11

$$\Delta\epsilon = \epsilon_{LUMO} - \epsilon_{HOMO}.$$

(frontier molecular orbitals, FMO) levels. The second perturbation (structure-2) in the same ring causes elevation of the FMO levels. The second perturbation in different rings and on opposite corners (structure-3) lowers the HOMO but raises the LUMO. Whereas the second centric perturbation in different rings but in the symmetrical positions (structure-4) raises the HOMO but lowers the LUMO. The third and fourth perturbations cause steady elevation of FMOs.

4. Conclusion

Including the isomeric structures, six nitrogen analogs of TEX have been subjected to computational treatment. The structures considered are found to be more energetic than TEX. However, the bond dissociation energies of the nitramine bonds of them are expected to be less sensitive or comparable to TEX based on the respective bond lengths. Their electronic spectra happens in the UV region and similar to TEX but having some bathochromic shift.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dt.2014.07.001>.

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