



A DFT study on TNGU isomers and aluminized *cis*-TNGU composites



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ABSTRACT

Cis- and *trans*-1,3,4,6-tetranitroglycouril (TNGU, Sorguyl) have been considered for density functional treatment at the levels of B3LYP/6-31G(d,p) and B3LYP/cc-PVDZ. *Cis*-TNGU has been found to be more stable than its *trans* isomer. Then, mono and dialuminized (*cis*-TNGU + Al and *cis*-TNGU+2Al) have been subjected to theoretical treatment at the level of B3LYP/6-31 + G(d). The spin states of the aluminized *cis*-TNGU composites have been considered as well. Although, *cis*-TNGU + Al (doublet) is found to be structurally stable, *cis*-TNGU+2Al singlet and triplet composites undergo certain bond cleavages. Structural and some quantum chemical properties, IR-UV spectra etc. have been presented.

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1. Introduction

Among the various high energy density materials (HEDMs), heterocyclic nitrogen compounds have attracted significant attention, such as the well-known explosives 1,3,4,6-tetranitroglycouril (TNGU, Sorguyl, see Fig. 1) [1], hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) [2,3], and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) [4,5] and the newer compounds *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD) [6], 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) [7] and *cis*-2,4,6,8-tetranitro-1H,5H-2,4,6,8-tetraazabicyclo[3.3.0]octane (Bicycle-HMX) [8,9]. They are all explosives with high positive HOFs and excellent detonation properties.

The inspection of properties of nitrourea compounds suggests that they would make excellent candidates as both insensitive and highly energetic materials, as well as they serve as precursors of other energetic compounds: (1) the urea moiety inherently has a high molecular density, suggesting that the mono and dinitrourea derivatives of it should also have attractive molecular densities. Indeed, this conjecture was supported by the work [10] at Picatinny Arsenal where glycoluril was first nitrated using 100% HNO₃ and P₂O₅ at 50°C to yield TNGU, which has one of the highest densities of known organic materials (2.04 g/cm³). 1,4-Dinitroglycouril (DNGU), the analog of TNGU, also has an

attractive crystal density of 1.992 g/cm³ [11].

Although there are many types of HEDMs, each one has different advantages and disadvantages with respect to its stability and detonation properties. For example, TNGU (Fig. 1), whose density and detonation properties are superior to many popular explosives, such as RDX and HMX. This molecule has four nitro groups for improved density and detonation properties [12].

The synthesis of TNGU has been achieved by many researches via different routes [13–17]. An improved synthetic method was presented for TNGU via the in situ decomposition of a nitrimino group with elimination of nitrogen without the use of dinitrogen pentoxide [14].

Some studies about morphology of TNGU have been published [11,18,19]. Sherrill et al., described a new method for the preparation of TNGU in which imidazo-[4,5-d]-imidazoles are nitrated with the elimination of N₂O to generate TNGU. This method of TNGU synthesis yields a material which is less sensitive than material produced with some alternative routes. Additionally, a new spherical morphology of TNGU was described. This morphology exhibits an even higher resistance to external insult even than material synthesized with the new method [19]. Its usage in preparation of some eco-friendly propellant compositions was published by Lim and Byun [19]. The stability of TNGU was investigated by many researchers [20–22]. Relations between properties and electronic structure of cyclic nitroureas including TNGU was studied by Xi et al., [21].

TNGU was also the subject of many calculations [23–26]. A simple correlation for predicting detonation velocity of ideal and

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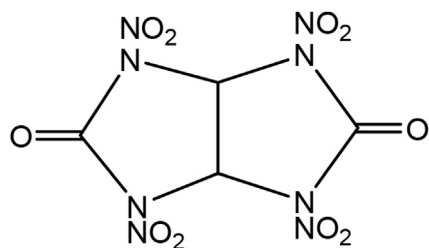


Fig. 1. Hydrogen depleted structure of TNGU.

non-ideal explosives including TNGU was given by Keshavarz [24]. A brief thermodynamic calculation of the thermo chemical properties of monopropellants, composite propellants, and metalized solid composite propellants considering TNGU and others (binder, Al or Al/Mg and AP) was given [24].

In the present study, firstly *cis* and *trans* isomers of TNGU have been investigated quantum chemically. Then, the aluminized *cis*-TNGU composites having different spin states are subjected to quantum chemical treatment.

2. Method of calculation

Geometry optimizations of all the structures leading to energy minima were initially achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [27,28] at the restricted level [29,30]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, geometry optimizations were managed within the framework of density functional theory (DFT) using B3LYP functional [31,32] at the level of 6–31G(d,p) and cc-PVDZ for *cis*- and *trans*-TNGU. Note that cc-PVDZ is a correlation consisted and refers to the fact that the basis set is designed so that functions which contribute similar amounts of correlation energy are included at the same stage, independently of the function type [33] and the set includes polarization functions [34]. Whereas for the aluminized *cis*-TNGU composites (*cis*-TNGU + $n\text{Al}$, $n:1,2$) B3LYP/6-31 + G(d) (unrestricted) [29] level of calculations were adopted. 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 [32,35]. Note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [36] and Lee, Yang, Parr (LYP) correlation correction functional [37]. The vibrational analyses were also done at the same

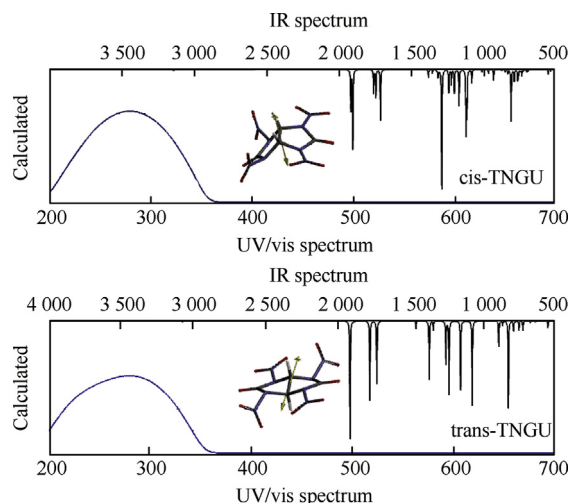


Fig. 3. The calculated IR (upper scale) and UV-VIS (lower scale) spectra of *cis*- and *trans*-TNGU (B3LYP/6-31G(d,p)).

Table 1
Various energies of *cis*- and *trans*-TNGU.

	E	ZPE	E_c
<i>cis</i> -TNGU*	–3527011.22	337.49	–3526673.73
<i>trans</i> -TNGU*	–3526902.58	336.58	–3526566.00
<i>cis</i> -TNGU**	–3527325.94	336.84	–3526989.09
<i>trans</i> -TNGU**	–3527219.21	335.95	–3526883.26

At level of *B3LYP/6-31G(d,p), **B3LYP/cc-PVDZ. Energies in kJ/mol.

level of calculations which had been performed for the optimizations. The total electronic energies (E) are corrected for the zero point vibrational energy (ZPE) to yield E_c values. 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. All these calculations were done by using the Spartan 06 package program [38].

3. Results and discussion

TNGU having four nitramine groups and two carbonyls does not

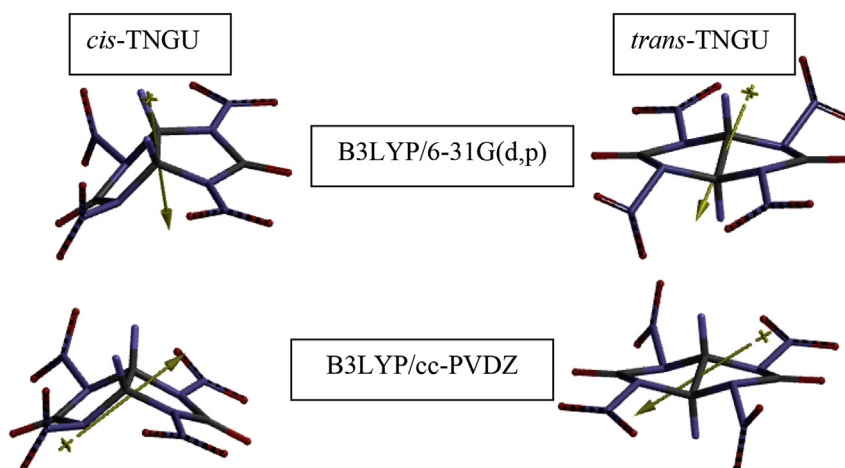


Fig. 2. Optimized structures of *cis*- and *trans*-TNGU.

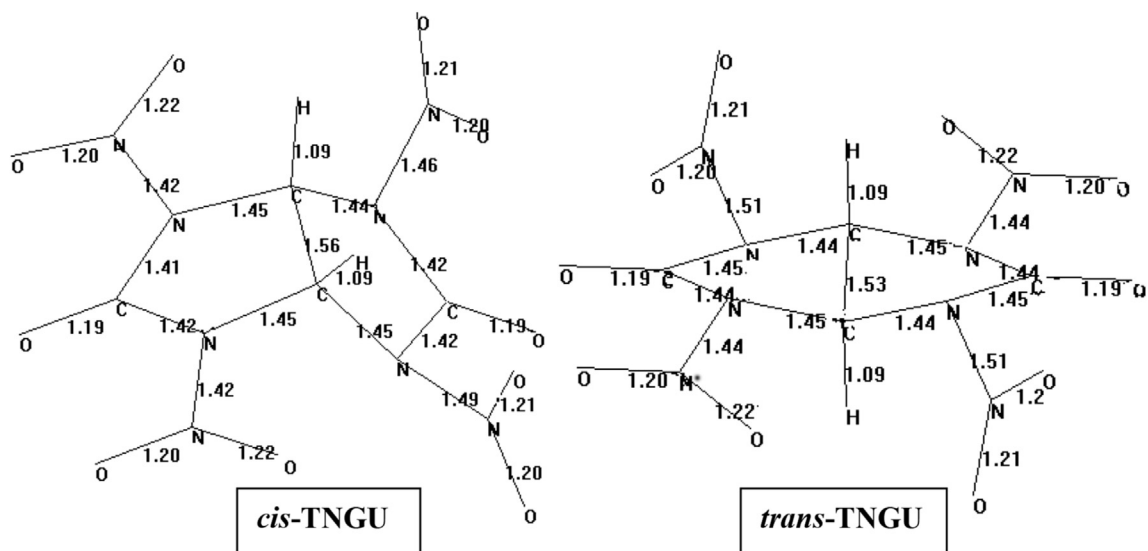


Fig. 4. Bond lengths (Å) in *cis*- and *trans*-TNGU (B3LYP/6-31G(d,p)).

Table 2
Some properties of *cis*- and *trans*-TNGU.

	Pt Group	Area Å ²	Volume Å ³	Polarizability Å ³	Dipole moment (Debye)
<i>cis</i> -TNGU*	C1	247.24	210.83	57.13	3.14
<i>trans</i> -TNGU*	C1	247.95	210.83	57.08	0.01
<i>cis</i> -TNGU**	C1	247.10	210.73	57.11	14.52
<i>trans</i> -TNGU**	C1	247.63	210.72	57.06	0.92

Based on optimized structure at the level of *B3LYP/6-31G(d,p), **B3LYP/cc-PVDZ.

Table 3
HOMO, LUMO energies, FMO energy gaps ($\Delta\epsilon$) and μ and η values of *cis*- and *trans*-TNGU.

	HOMO	LUMO	$\Delta\epsilon$	μ	η
<i>cis</i> -TNGU*	-869.88	-321.04	548.84	595.46	274.42
<i>trans</i> -TNGU*	-889.71	-320.03	569.68	604.87	284.84
<i>cis</i> -TNGU**	-862.49	-309.55	552.95	586.02	276.47
<i>trans</i> -TNGU**	-882.38	-307.74	574.64	595.06	287.32

At the level of *B3LYP/6-31G(d,p), **B3LYP/cc-PVDZ. Energies in kJ/mol.

have much possibility for constitutional isomerization. However, the bridgehead hydrogens can have different orientations which lead to the *cis*- and *trans*-TNGU structures.

3.1. *Cis*- and *trans*-TNGU

Cis- and *trans*-TNGU differ from each other only with respect to the orientation of hydrogen atoms linked to bridgehead positions (see Fig. 2). In the figure, optimized structures of these isomeric compounds, obtained by employing two different basis sets (6-31G(d,p) and cc-PVDZ) have been displayed. Fig. 3 shows the IR and UV-VIS (Time dependent, TDDFT) spectra of the isomers. Depending on basis set variation, some orientation changes of the nitro groups in space occurs, thus some energy and bond lengths changes take place (see Table 1 and Figs. 2 and 4).

In the calculated IR spectra (in vacuum, unstandardized), the peaks about 1910 cm^{-1} stand for the carbonyl stretchings. The nitro stretchings occur in the range of 1764–1717 cm^{-1} . The bendings of hydrogens happen at 1294 cm^{-1} (*cis*-TNGU) and 1255 cm^{-1} (*trans*-

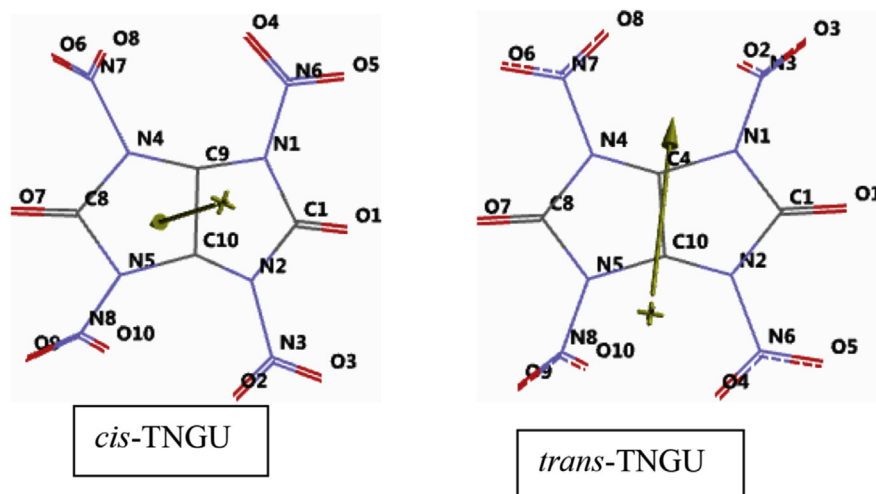


Fig. 5. Numbering of *cis*- and *trans*-TNGU.

Table 4

Mulliken charges on nitro groups linked to N_i and the respective nitramine bond lengths in *cis*-TNGU.

N _i	N	O1	O2	Sum	Nitramine bond length (Å)
B3LYP/6-31G(d,p) level of calculations					
N1	0.692	-0.392	-0.332	-0.032	1.42
N2	0.687	-0.333	-0.389	-0.035	1.42
N4	0.634	-0.282	-0.634	-0.282	1.49
N5	0.655	-0.301	-0.346	0.008	1.46
B3LYP/cc-PVDZ level of calculations					
N1	0.350	-0.228	-0.169	-0.047	1.42
N2	0.355	-0.169	-0.233	-0.047	1.42
N4	0.345	-0.192	-0.153	0	1.47
N5	0.340	-0.145	-0.183	0.012	1.49

Table 5

Mulliken charges on nitro groups linked to N_i and the respective nitramine bond lengths in *trans*-TNGU.

N _i	N	O1	O2	Sum	Nitramine bond length (Å)
B3LYP/6-31G(d,p) level of calculations					
N1	0.619	-0.286	-0.305	0.028	1.51
N2	0.681	-0.325	-0.375	-0.019	1.44
N4	0.680	-0.375	-0.325	-0.020	1.44
N5	0.619	-0.305	-0.286	0.028	1.51
B3LYP/cc-PVDZ level of calculations					
N1	0.332	-0.143	-0.169	0.020	1.52
N2	0.354	-0.166	-0.223	-0.035	1.44
N4	0.354	-0.223	-0.166	-0.035	1.44
N5	0.332	-0.169	-0.143	0.020	1.52

TNGU). Both of the isomers absorb in the same UV region, but the *trans* isomer has somewhat flattened spectrum. Due to the competing actions of nitro and lactam carbonyl groups to attract the lone-pair of nitrogen of the lactam moiety, a rather small chromophore group exists in the structure (limited conjugation). Therefore, the light absorption occurs only in the UV-region.

Table 1 tabulates the total electronic energy (E), zero point vibrational energy (ZPE) and the corrected total energy (E_c). The calculations (performed using two different basis sets) have revealed that in each case, *cis*-TNGU is more stable than its *trans*-isomer (at 298 K). The stability is probably due to existence of

better charge–charge, charge–dipole and dipole–dipole interactions of the nitro groups or nitramine moieties present in the *cis*-TNGU.

Fig. 4 exhibits bond length data which reveals that *cis* and *trans* isomers have rather comparable bond lengths. Table 2 displays some properties of TNGU isomers. *Cis*-isomer is characterized with a higher dipole moment than the *trans*. The B3LYP/cc-PVDZ level of calculations yield appreciably high dipole moment for the *cis*-isomer.

The heats of formation values (at the standard conditions) obtained by using T1 method of calculation [39,40] (The T1 method is a little bit less accurate than the expensive G3(MP2) method) are 91.33 kJ/mol and 186.26 kJ/mol, respectively for the *cis*- and *trans*-forms. However, Smirnov et al., reported the value of ΔH_f° for TNGU (without mentioning its *cisness* or *transness*) as 75.3 kJ/kg (density: 2.03 g/cm³) which corresponds to 24.25 kJ/mol [41].

According to the following formula [42],

$$I_{sp}(\text{seconds}) = 265 \sqrt{\frac{\Delta H_f(\text{kcal/mol})}{MW(\text{g/mol})}}$$

I_{sp} values of *cis* and *trans* TNGU are obtained as 69.01 s and 98.56 s, respectively for the *cis*- and *trans*-isomers.

Table 3 includes the HOMO, LUMO energies and the inter-frontier molecular orbital energy gaps (FMO energy gap, $\Delta\epsilon$) of the TNGU isomers of present concern. At each level of calculations the HOMO energy of *cis*-TNGU is higher than the *trans*-isomer. Whereas, the LUMO energy of *cis*-isomer is lower than the *trans* at each level of calculations. Consequently, $\Delta\epsilon$ values for *cis*-TNGU is less than the *trans*-TNGU. It is known that the impact sensitivity of explosives increases as the HOMO–LUMO energy gap decreases [43]. Hence, *cis*-TNGU is expected to be more sensitive to impact than its *trans*-isomer should be. Table 3 also includes μ (electronegativity) and η (hardness) values of these isomers which are defined as [44–46],

$$\mu = -(\text{HOMO} + \text{LUMO})/2$$

$$\eta = -(\text{HOMO} - \text{LUMO})/2$$

According to the both level of calculations, *trans*-TNGU is more electronegative and harder than its *cis* isomer.

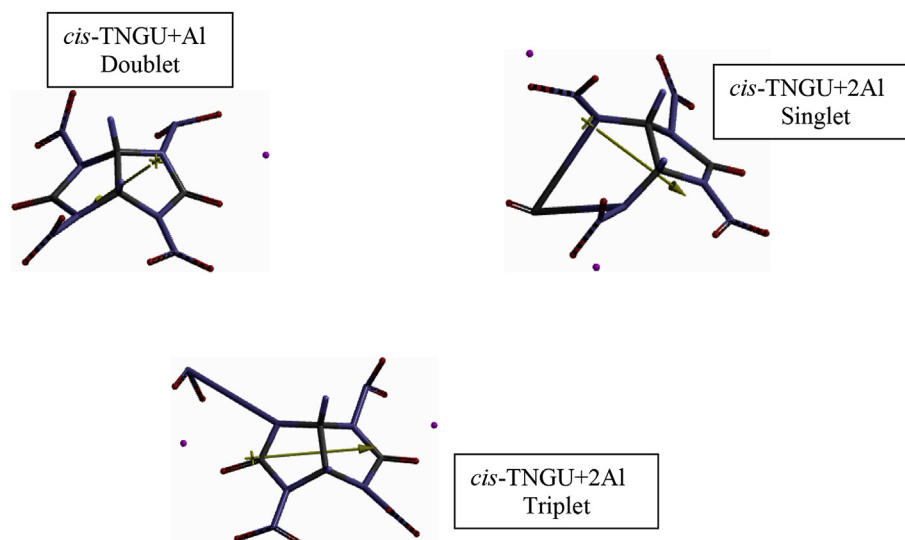


Fig. 6. Optimized structures of aluminized *cis*-TNGU (B3LYP/6-31 + G(d)).

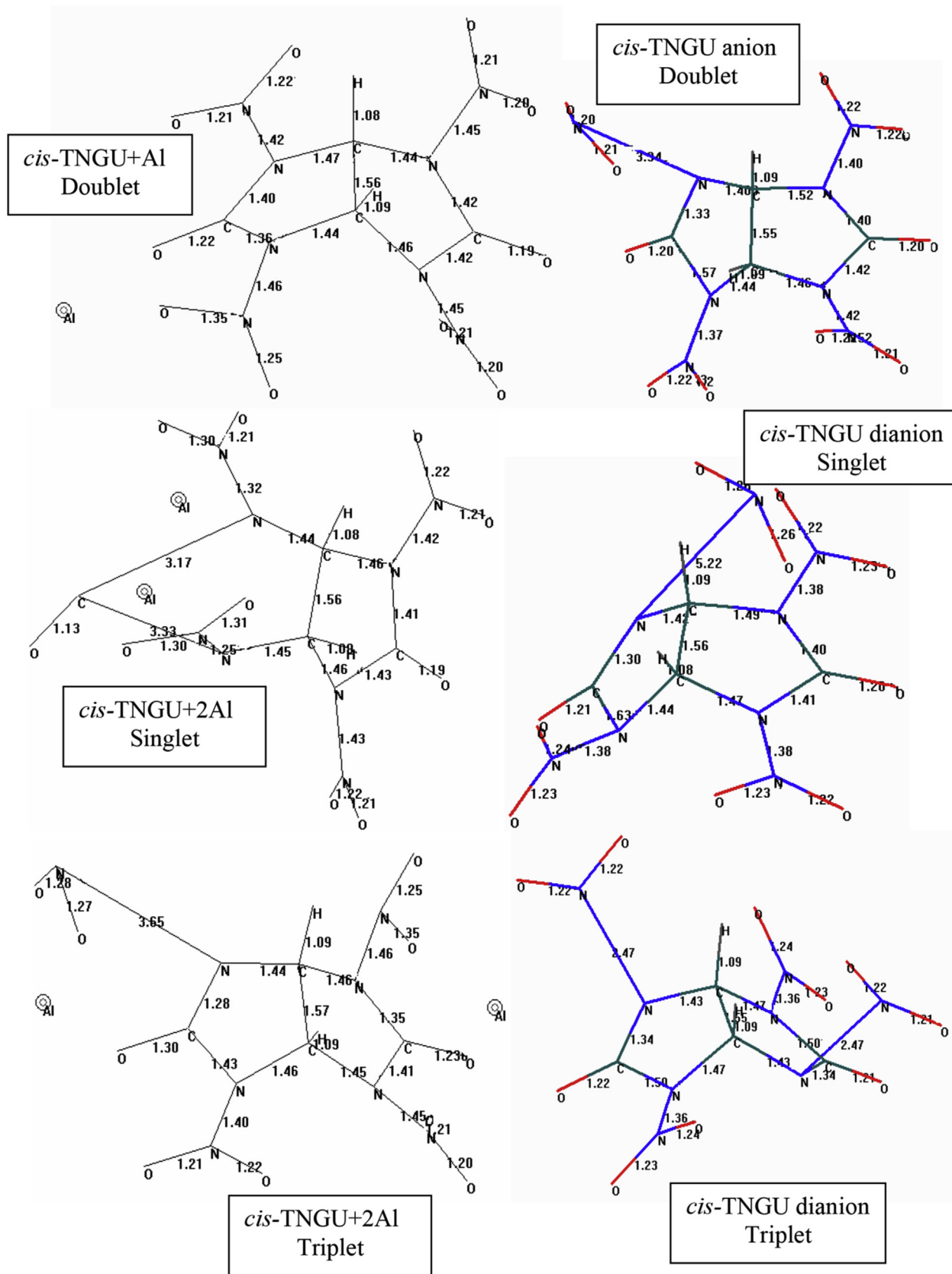


Fig. 7. Bond lengths in *cis*-TNGU anions and aluminized *cis*-TNGU composites (B3LYP/6-31 + G(d)).

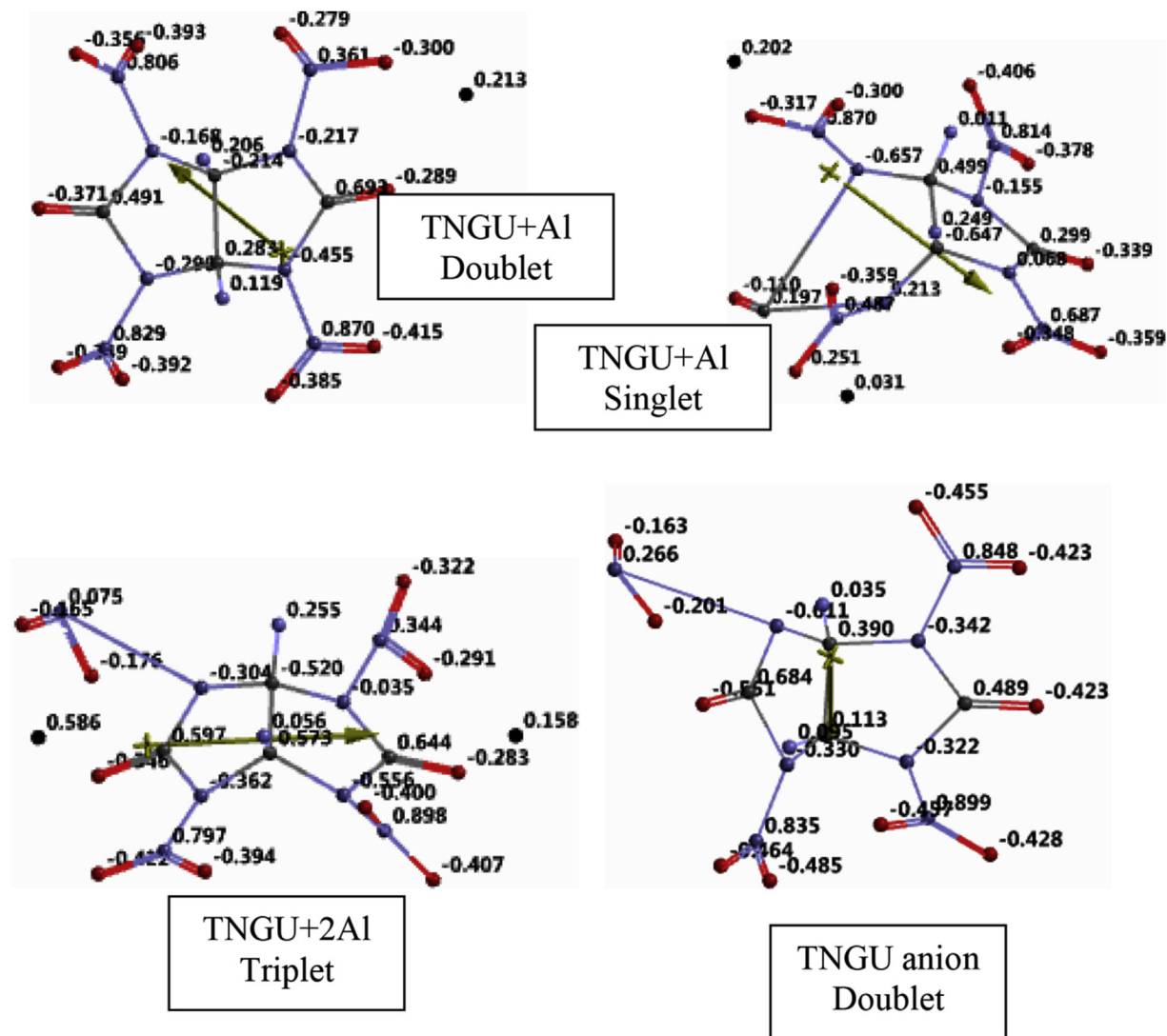


Fig. 8. Electrostatic charges (ESP) on TNGU anion and aluminized *cis*-TNGU composites (B3LYP/6-31 + G(d)).

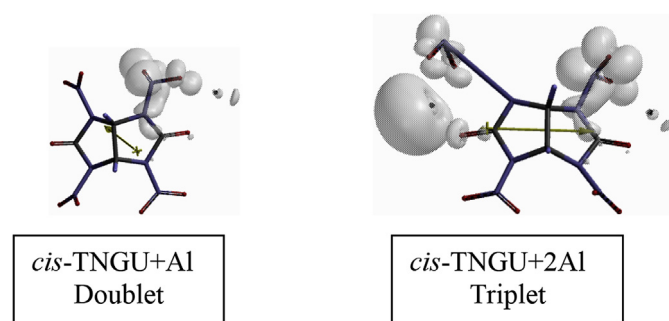


Fig. 9. Spin density maps of open-shell aluminized TNGU composites (B3LYP/6-31 + G(d)).

Zhang et al., proposed a method of correlation to predict the impact sensitivities of nitro compounds based on nitro group charges (Mulliken) [47]. The more negative charge the nitro group possesses it is less likely to split from the backbone (R-NO₂). In systems conjugated with the nitro group, some electron population can be transferred to NO₂ moiety via mesomerism and

Table 6

Various energies of aluminized *cis*-TNGU.

	<i>E</i>	ZPE	<i>E_c</i>
<i>cis</i> -TNGU + Al (Doublet)	-4163727.52	333.71	-4163393.81
<i>cis</i> -TNGU+2Al (Singlet)	-4800400.76	328.83	-4800071.93
<i>cis</i> -TNGU+2Al (Triplet)	-4800532.08	331.37	-4800200.71

At the level of B3LYP/6-31 + G(d), Energies in kJ/mol.

consequently the bond order between the NO₂ and its neighbor atom in the backbone increases. Meanwhile the bond length is expected to shorten. However, that relationship is not so explicitly occurring all the time. Fig. 5 shows the numbering of atoms in *cis* and *trans* TNGU. Tables 4 and 5 show the Mulliken charges on NO₂ atoms and the respective N-NO₂ bond lengths in *cis*- and *trans*-TNGU, respectively.

According to the data in Table 4, the nitro group linked to N5 atom is more likely to be split off from *cis*-TNGU structure (both level of calculations predict the same). Note that the corresponding nitramine bonds is the longest among all. As for the *trans*-TNGU case, the nitro groups linked to N1 and N5 atoms are more likely candidates to split off than the others. The corresponding bond

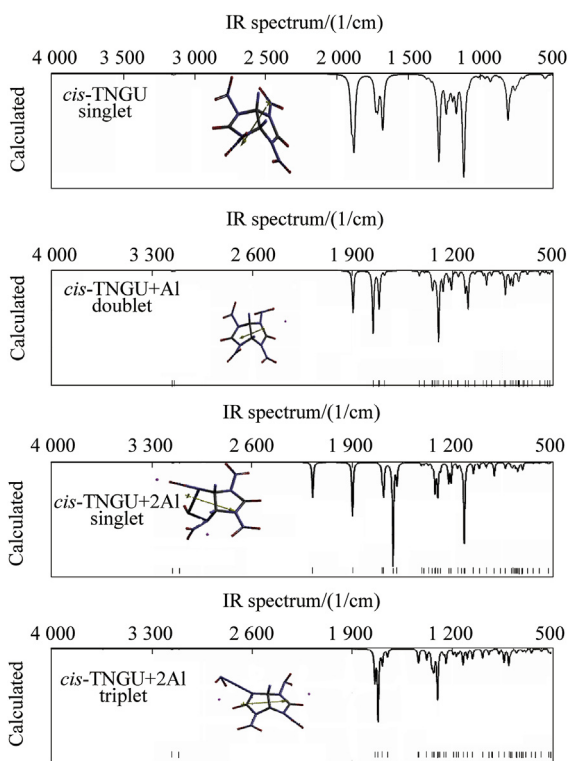


Fig. 10. IR spectra of *cis*-TNGU and *cis*-TNGU + *n*Al composites (B3LYP/6-31 + G(d)).

Table 7

HOMO, LUMO energies, FMO energy gaps ($\Delta\epsilon$) and μ and η values of aluminized *cis*-TNGU composites.

	HOMO	LUMO	$\Delta\epsilon$	μ	η
<i>cis</i> -TNGU	-907.64	-369.29	538.35	638.465	269.175
<i>cis</i> -TNGU + Al Doublet	-623.19	-357.02	266.18	490.105	133.085
<i>cis</i> -TNGU+2Al Singlet	-631.99	-324.97	307.02	478.48	153.51
<i>cis</i> -TNGU+2Al Triplet	-574.69	-391.22	183.47	482.955	91.735

At the level of B3LYP/6-31 + G(d), Energies in kJ/mol.

lengths are comparatively longer too.

Relying on higher stability of the *cis*-isomer, the aluminized composites of it has been further focus of investigation presently.

3.2. Aluminized *cis*-TNGU

Being aluminum powder a combustible high energy material, it is widely employed as a component of explosive and propellant formulations to increase the explosive/propellant performance.

In the present study, *cis*-TNGU, which is the more stable isomer compared to the *trans* form, has been considered to be investigated for the interaction with aluminum. The composite systems having one and two atoms of aluminum per molecule of *cis*-TNGU have been subjected to density functional treatment at the level of B3LYP/6-31 + G(d). Hence, *cis*-TNGU + Al and *cis*-TNGU+2Al type composite systems are investigated. Note that aluminum has $1s^22s^22p^63s^23p^1$ electronic configuration. Thus, *cis*-TNGU + Al system is a doublet, having an unpaired electron. Whereas, *cis*-TNGU+2Al composite might have a singlet state (a closed shell system) or a triplet state having two unpaired electrons with parallel spins (open shell system). Fig. 6 shows the optimized structures of the aluminized *cis*-TNGU composites of the present concern. Fig. 7 exhibits the bond lengths/distances of those systems. The doublet system (*cis*-TNGU + Al) has very reasonable bond

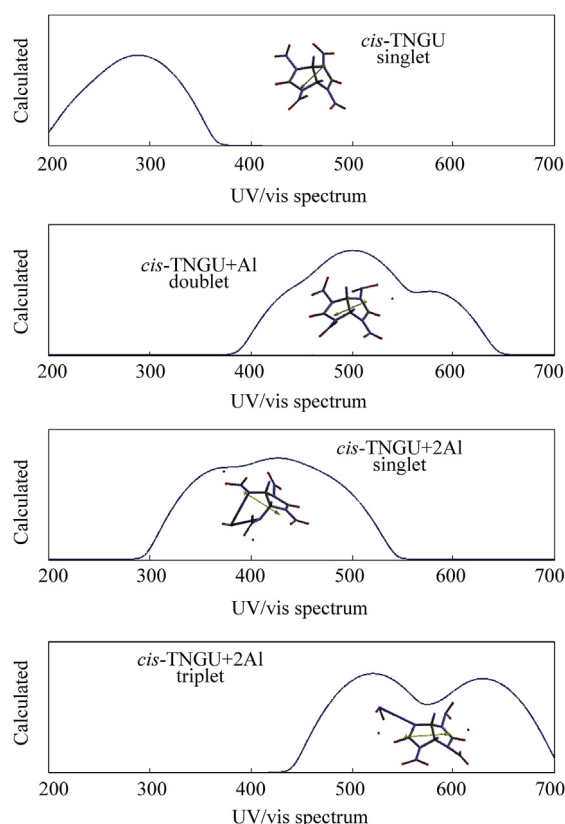


Fig. 11. Time dependent (TDDFT) UV-VIS spectra (B3LYP/6-31 + G(d)) of *cis*-TNGU and its aluminized forms.

lengths. Its aluminum content corresponds to 7.73% Al by weight. On the other hand, the composite system (*cis*-TNGU+2Al) having 14.35% Al are structurally unstable that is *cis*-TNGU moiety undergoes some bond cleavages (see Fig. 6).

Interestingly enough, the singlet system with two aluminum atoms undergoes bond rupture of the ring (see Figs. 6 and 7). There C-N distances are 3.17 Å and 3.33 Å. Whereas the triplet system having two aluminum atoms emanates an NO₂ moiety. Hence, *cis*-TNGU seems to be incompatible with the presence of a second Al atom. Fig. 8 shows the electrostatic charges (ESP) on the atoms of the aluminized *cis*-TNGU composites. Note that ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic field from the entire wavefunction [38]. In the triplet system, the overall charge of the dispelled NO₂ moiety is -0.566 esu. The result indicates that Al atom supplies some electron population to *cis*-TNGU which causes the elimination of the NO₂ group (quasi nitrite ion). Since the calculations reveal that some electron population has been transferred to the organic component from Al atom(s), the anions of *cis*-TNGU are considered for comparison purpose to have a better understanding of the process. Fig. 7 also contains the bond lengths of mono and dianions of *cis*-TNGU. Note that they are not aluminized. The aluminized triplet (TNGU+2Al) system highly resembles the mono anion of *cis*-TNGU (doublet) both of which expel single NO₂ moiety but no resemblance exists to dianions of *cis*-TNGU. So, the aluminum atom should have transferred some electron population, nearly a single electron, to *cis*-TNGU molecule. In the case of *cis*-TNGU+2Al (singlet) composite system, the structure is completely different from the structures of anions of *cis*-TNGU. Hence, it implies that a more complex electron transfer process should have occurred from aluminum atom to the organic system resulting in a

ring opening reaction. In organic chemistry there exist many examples of metal reduction processes and also many examples of nitro compounds acting as oxidizers (eg., Skraup synthesis) [48–50]. All these data reveal that *cis*-TNGU can be incorporated with approximately 7–8% Al safely, but 14% Al content causes bond cleavages in the singlet or triplet states. Of course, in between those limits some much better weight limits can be obtained experimentally.

Fig. 9 shows the spin densities for the open shell composites *cis*-TNGU + Al (doublet) and *cis*-TNGU+2Al (triplet). The aluminum atom in the doublet and one of the aluminum atoms in the triplet composites are characterized with very low spin population, which is an other evidence that those aluminum atoms have transferred some electron population to the organic moiety.

Table 6 shows various energies of the aluminized *cis*-TNGU. They are all stable in terms of overall energy. The corrected total electronic energy of the triplet system (*cis*-TNGU+2Al) stands for a much more stable composite than the singlet (*cis*-TNGU+2Al). Note that both the triplet and the singlet composites are structurally decomposed.

Fig. 10 displays the calculated (in vacuum) IR spectra of the *cis*-TNGU and its aluminized composites. In the figure the peaks about 1887–1896 cm^{-1} stand for the carbonyl stretchings. In the case of *cis*-TNGU + Al composite, the carbonyl nearby the Al atom vibrates at 1756 cm^{-1} . The carbonyl of the broken ring in the case of singlet *cis*-TNGU+2Al composite occurs at 2175 cm^{-1} . Whereas, in the triplet case the carbonyl stretch is at 1740 cm^{-1} . The nitro stretchings are lowered by the effect of presence of Al atom(s).

Table 7 shows the HOMO, LUMO energies and the interfrontier molecular orbital energy gaps as well as the μ and η values for *cis*-TNGU and its aluminized forms. The HOMO energy order is *cis*-TNGU < *cis*-TNGU+2Al (singlet) < *cis*-TNGU + Al (doublet) < *cis*-TNGU+2Al(triplet). Whereas the LUMO energy order is TNGU+2Al (triplet) < *cis*-TNGU < *cis*-TNGU + Al (doublet) < *cis*-TNGU+2Al (singlet). Consequently, the $\Delta\epsilon$ values have the sequence of TNGU+2Al (triplet) < *cis*-TNGU + Al (doublet) < *cis*-TNGU+2Al (singlet) < *cis*-TNGU. The sequence of HOMO energies indicates that the presence of Al atom raises up the HOMO energy level as compared to *cis*-TNGU. This is also true for the LUMO levels with the exception of triplet *cis*-TNGU+2Al case. Such kind of situation

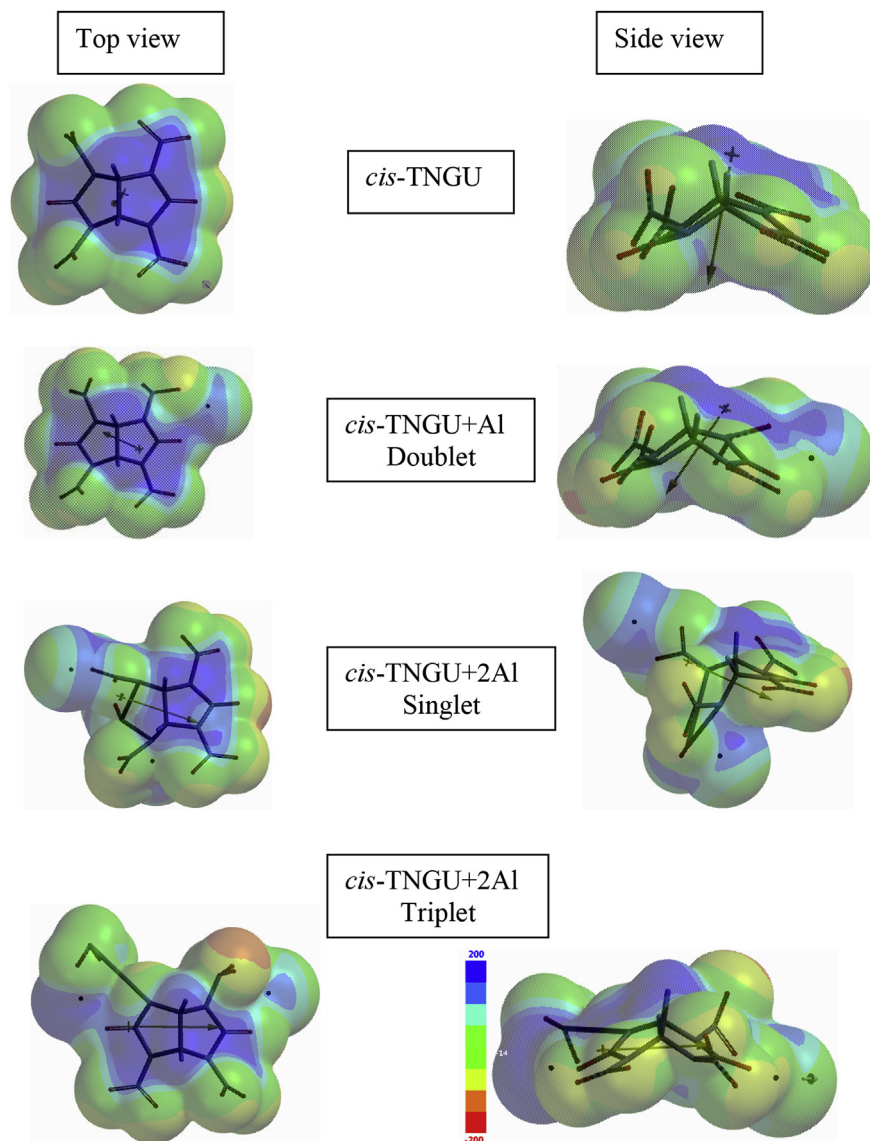


Fig. 12. Electrostatic potential maps of *cis*-TNGU and its aluminized forms (B3LYP/6-31 + G(d)).

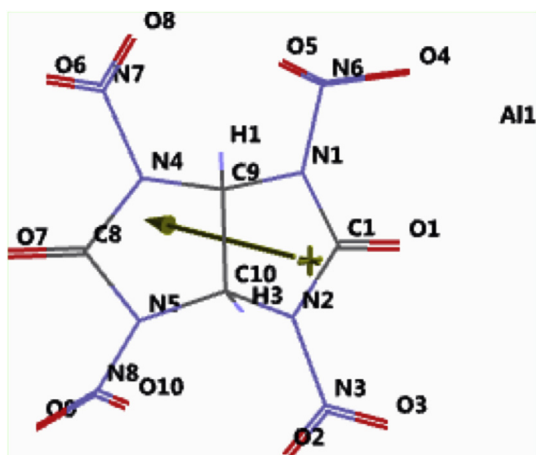


Fig. 13. Numbering of *cis*-TNGU + Al composite system.

Table 8

Mulliken charges on nitro groups linked to Ni and the respective nitramine bond lengths in *cis*-TNGU + Al composite.

N _i	N	O1	O2	Sum	Nitramine bond length (Å)
N1	-0.329	0.054	0.124	-0.151	1.47
N2	-0.396	0.041	-0.063	-0.418	1.42
N4	-0.254	0.058	-0.101	-0.297	1.45
N5	-0.151	0.038	-0.099	-0.212	1.46

B3LYP/6-31G(d,p) level of calculations.

arises whenever electron donating effect exists [51]. Although, some composite systems considered presently are decomposed, *cis*-TNGU + Al (doublet) is an intact system. Therefore, arose of its frontier molecular orbital energy levels compared to *cis*-TNGU can be mainly attributed to electron donation from the aluminum atom. Note that *cis*-TNGU + Al (doublet) is a stable system which is less electronegative and softer as compared to *cis*-TNGU at the same level of calculation.

Fig. 11 shows the time-dependent UV-VIS spectra of the systems of present concern. One observes that the presence of Al atom(s) causes different extents of bathochromic shift in the spectra of these composites. This effect is more pronounced in the triplet *cis*-TNGU+2Al composite. The conformational changes of nitramine groups in the doublet case and both the structural and conformational changes in the cases of singlet and triplet should have created chromophores responsible for the observed bathochromic shifts in the calculated spectra.

Fig. 12 shows the electrostatic potential maps of *cis*-TNGU and its aluminized forms (B3LYP/6-31 + G(d)). In the figure, the electron deficient regions (blue) occur at the central region of the rings.

Of the presently concerned composite structures, *cis*-TNGU + Al is the only stable one. Fig. 13 shows the numbering of *cis*-TNGU + Al composite system and Table 8 lists the Mulliken charges on nitro groups as well as the respective nitramine bond lengths in *cis*-TNGU + Al composite.

Inspection of the data in Table 8 reveals that NO₂ group linked to N1 atom has the least negative charge and the longest nitramine bond length hence it is more susceptible to cleavage.

4. Conclusion

The present DFT treatment, within the limitation of the method, has revealed that *cis*-TNGU is more stable than *trans*-TNGU. As for the aluminized *cis*-TNGU composites (*cis*-TNGU + Al) doublet has

been found to be structurally stable. Whereas, the singlet and triplet of *cis*-TNGU+2Al systems are unstable. The former one undergoes a ring cleavage whereas the triplet system expels a NO₂ moiety. Structurally comparing with *cis*-TNGU mono and dianions and referring to some quantum chemical analyses one concludes that the bond cleavages occur with transfer of some electron population from the aluminum atoms in the TNGU+2Al composites. The present study put some light not only from the quantum chemical aspects at the molecular level but also to the stability of the aluminized *cis*-TNGU composites.

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