

Some Isomers of TNABN - A DFT Treatment

Lemi Türker

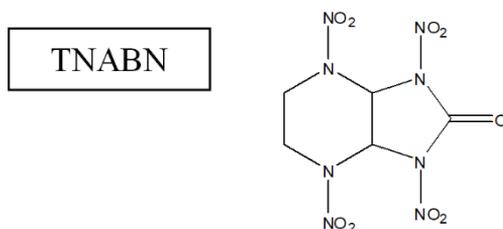
Department of Chemistry, Middle East Technical University, Üniversiteler, Eskişehir Yolu No: 1, 06800 Çankaya/Ankara, Turkey; e-mail: lturker@gmail.com; lturker@metu.edu.tr

Abstract

TNABN is a nitrourea derivative. Isomers presently considered comprise both the configurational and constitutional forms of TNABN (K56, C₅H₆N₈O₉). Density functional theory (DFT) has been employed at the level of RB3LYP/6-31++G(D,P). Within the restrictions of the level of calculations, the work has revealed that all the isomers considered are electronically stable and follow the stability order of *Cis* > *Cis-iso* > *Trans* > *Trans-iso*. Various physicochemical and quantum chemical properties of the isomers were obtained and discussed. The HOMO-LUMO energy separation falls in to the order of *Cis-iso* < *Cis* < *Trans-iso* < *Trans*. Thus, *Cis-iso* isomer should be more susceptible to impact stimulus because there exists a reverse correlation between the impact sensitivity and HOMO-LUMO energy separation value.

1. Introduction

Heterocyclic polyamines containing methylenediamine functionality are usually unstable if unprotected. In contrast, the presence of urea group stabilizes this functionality such as 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (TNABN) (K56, C₅H₆N₈O₉) [1].



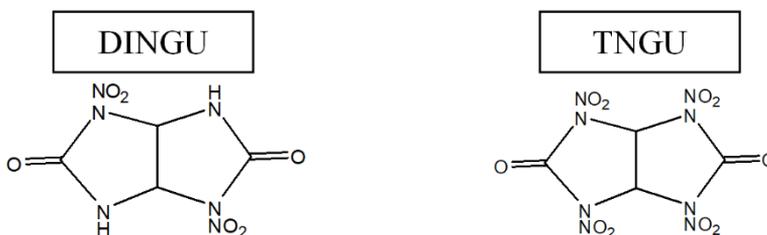
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Graindorge et al., synthesized K56 from the nitration of 2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one dichloride [2].

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 [3] at Picatinny Arsenal where glycoluril was first nitrated using 100% HNO_3 and P_2O_5 at 50°C to yield TNGU, which has one of the highest densities of known organic materials (2.04 g/cm^3). 1,4-Dinitroglycoluril (DINGU), the analog of TNGU (Sorguy), also has an attractive crystal density of 1.992 g/cm^3 [4-6].



The nitration of 2,5,7,9-tetraazabicyclo[4,3,0]nonan-8-one ring system has been investigated [7]. Some trinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one derivatives were also investigated [8,9].

Although there are many types of high energy density materials (HEDMs), each one has different advantages and disadvantages with respect to its stability and detonation properties. For example, TNGU 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 [10,11]. Both TNPDU and TNABN are powerful explosives with high densities and high detonation velocities. These compounds are significantly more resistant to hydrolytic destruction than tetranitroglycoluril (TNGU) [11].

In the present study, some constitutional and configurational isomers of TNABN (K56) were considered within the limitations of density functional theory and the applied bases set.

2. Method of Calculation

The initial geometry optimizations of all the structures leading to energy minima have been achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [12,13] at the restricted level [14,15]. Subsequent optimizations were achieved at Hartree-Fock level employing various basis sets. Then, geometry optimizations were managed within the framework of density functional theory [16,17] at the level of B3LYP/6-31++G(d,p) [14,18]. 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 [17,19]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [20] and Lee, Yang, Parr (LYP) correlation correction functional [21]. The vibrational analyses also have been done. The total electronic energies are corrected for the zero point vibrational energy (ZPE). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N stands for the number of atoms in the system. This has indicated that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations have been done by using the Spartan 06 package program [22].

3. Results and Discussion

The isomers presently considered are consisted of two fused rings having 5- and 6-membered heterocyclic systems. Each isomer contains four nitramine type explorophores. The *cis* and *trans* configurations have been defined based on the relative positions of hydrogens linked to the carbon atoms on the fusion points. When the C=O group occupies a position on the five-membered ring, presently it is called either *Cis* or *Trans* whereas if it is on the six-membered ring the system is called *Cis-iso* or *Trans-iso*. Note that the *Cis* and *Cis-iso* systems (also *Trans* and *Trans-iso*) are constitutional but *Cis* and *Trans* (also *Cis-iso* and *Trans-iso*) are configurational isomers.

Figure 1 shows some presently considered isomers of TNABN and their dipole moment vectors. As seen in the figure the conformation of the nitro groups and consequently the direction of the dipole moment vectors are highly variable. Various effects operating on the dipole moment vectors act in such a way that in the *Trans-iso* case the vector lies along the bond shared by two fused rings.

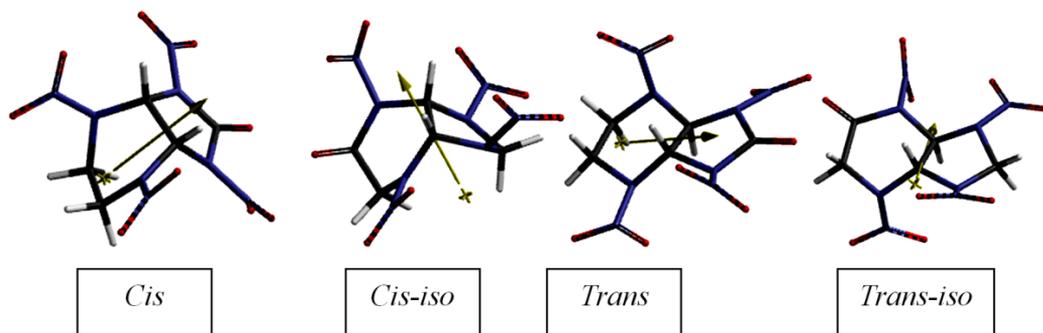


Figure 1. Some isomers of TNABN presently considered.

Table 1 lists some properties of the isomers considered. Most of the properties listed, except the dipole moments and log P values, remain more or less constant from one isomer to other. Some variations are also exhibited in $E(aq)$ values depending on the extent of interactions in aqueous media.

Table 1. Some properties of the isomers considered.

Structures	Area (\AA^2)	Volume (\AA^3)	Ovality	Dipole Moment	Log P	Polarizability	$E(aq)$
<i>Cis</i>	260.82	224.92	1.46	2.46	2.17	58.36	-3436061.77
<i>Cis-iso</i>	259.96	224.96	1.45	3.03	2.53	58.39	-3436045.84
<i>Trans</i>	258.03	224.57	1.44	6.11	2.17	58.25	-3436009.18
<i>Trans-iso</i>	258.15	224.77	1.44	2.58	2.53	58.32	-3435997.91

Dipole moments in debye units. Energies in kJ/mol.

Figure 2 shows the electrostatic potential (ESP) charges on the atoms of the isomers considered. Note that the ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [22].

As seen in Figure 2, the amine nitrogens of the nitramine groups are negatively charged in all the cases. Another point to be emphasized is that the carbon atoms at the fusion points are oppositely charged in the *Cis* and *Cis-iso* cases (which is not the case in *Trans* and *Trans-iso* isomers).

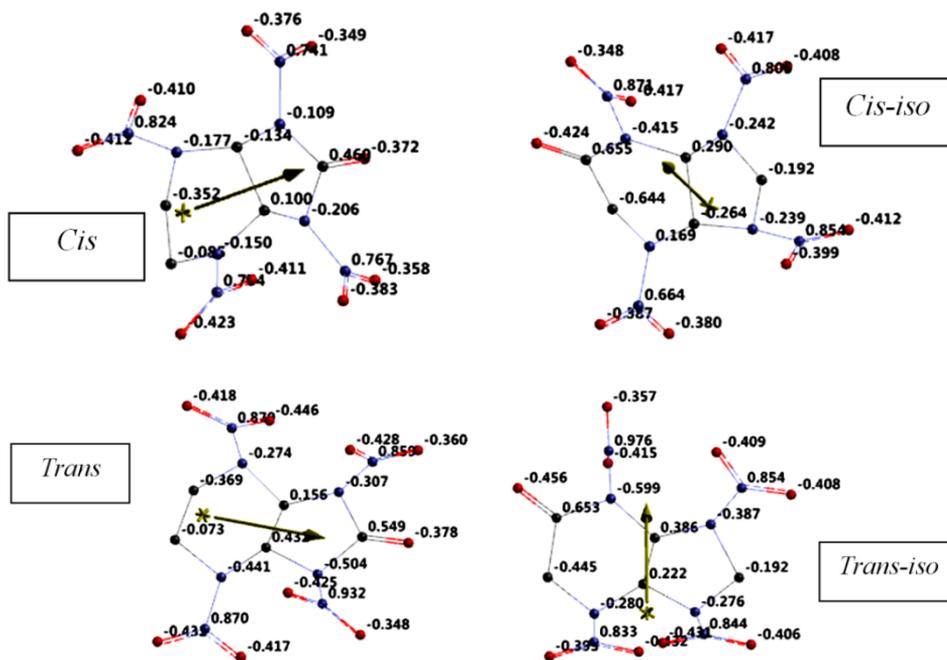


Figure 2. ESP charges on the atoms of the isomers considered (hydrogens depleted).

Figure 3 shows the electrostatic potential maps of the isomers where the blue regions relatively stand for the most positive potential field and red ones, if exists any, the most negative ones.

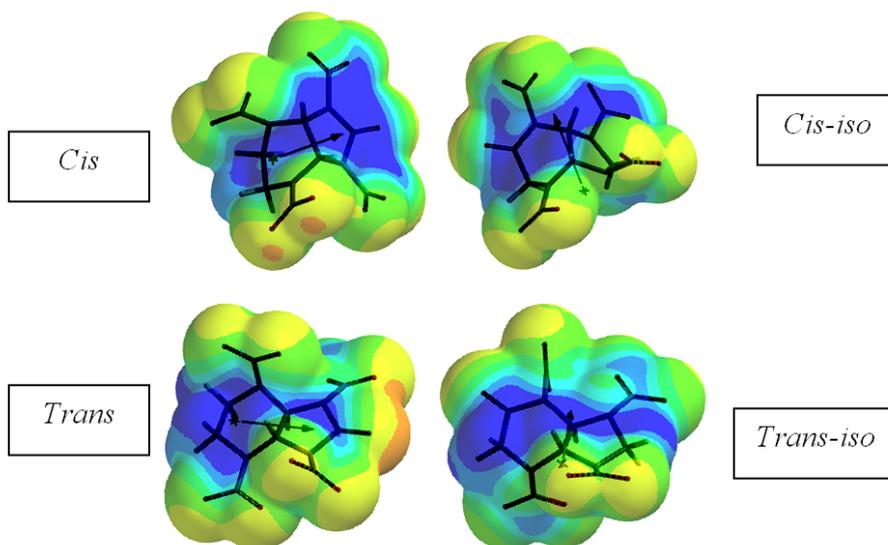


Figure 3. The ESP maps of the isomers considered.

Table 2 shows some energies of the isomers considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. As seen in the table, the corrected electronic energies lead the stability of the isomers which follow the order of *Cis* > *Cis-iso* > *Trans* > *Trans-iso*. Note that the *Iso* isomers in every case are less stable than their respective *Cis* or *Trans* forms. Thus, the keto group in the six-membered ring destabilizes the systems somewhat. The cause of it might be electronic as well as steric rigidity imposed by the presence of keto moiety in the six-membered ring.

Table 2. Some energies of the isomers considered.

Structures	E	ZPE	E_C
<i>Cis</i>	-3436077.92	464.99	-3435612.93
<i>Cis-iso</i>	-3436048.71	464.09	-3435584.62
<i>Trans</i>	-3436011.81	465.40	-3435546.41
<i>Trans-iso</i>	-3435987.70	464.50	-3435523.20

Energies in kJ/mol.

Table 3 shows the C=O frequencies (cm^{-1}) of the isomers considered. As seen in the table the *Iso* forms have lower frequencies than the corresponding normal ones. Note that *Cis* isomer is characterized with a lower frequency as compared to the *Trans* form. Whereas the *Cis-iso* isomer possesses a higher frequency than the *Trans-iso* form has. There should be some combined effects of electronic as well as the ring strain present in the isomers considered. Note that the environment of the C=O group in the five and six-membered rings are different.

Table 3. The C=O frequencies (cm^{-1}) of the isomers considered.

<i>Cis</i>	<i>Cis-iso</i>	<i>Trans</i>	<i>Trans-iso</i>
1894	1834	1897	1808

Figure 4 displays some of the molecular orbital energy levels of the isomers considered.

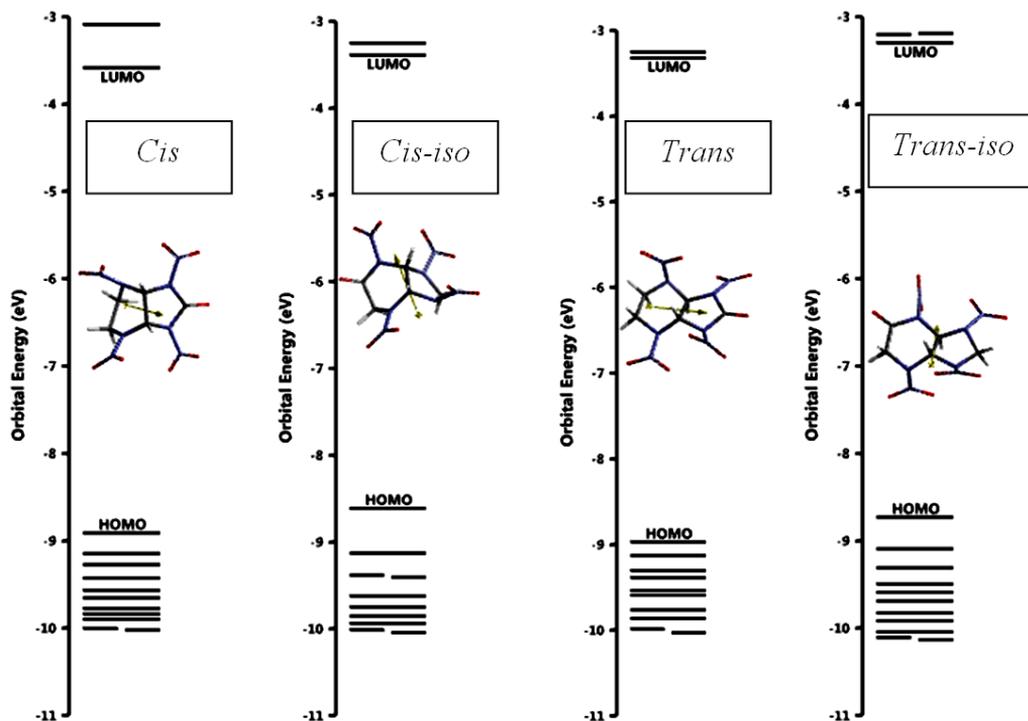


Figure 4. Some of the molecular orbital energy levels of the isomers considered.

As seen in the figure and in Table 4, the HOMO and LUMO energy levels of the *Iso* isomers are somewhat higher than the respective energy levels of the *Cis* and *Trans* isomers. Since electron attracting groups, in general, lowers both the HOMO and LUMO energy levels [23] the present situation can be alternatively interpreted that the C=O moiety in the five-membered ring attracting electrons from the adjacent nitramine groups thus lowering the frontier molecular energy levels as compared to the case where it is in the six-membered ring. Moreover, in the *Iso* isomers the HOMO and the NEXT-HOMO levels are more distinct compared to their normal isomers. Consequently it is expected that the NEXT-HOMO orbital should be less influential on some chemistry of the *Iso* isomers.

Table 4 lists the HOMO, LUMO energies and the interfrontier molecular orbital energy gap ($\Delta\varepsilon = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$) values of the isomers considered. The $\Delta\varepsilon$ values follow the order of *Cis-iso* < *Cis* < *Trans-iso* < *Trans*. Thus, the *Cis-iso* isomer should be more susceptible to impact stimulus because there exists a reverse correlation between the impact sensitivity and $\Delta\varepsilon$ value [24,25].

Table 4. The HOMO, LUMO energies and $\Delta\varepsilon$ values of the isomers considered.

Structures	HOMO	LUMO	$\Delta\varepsilon$
<i>Cis</i>	-859.65	-346.07	513.58
<i>Cis-iso</i>	-830.93	-327.09	503.84
<i>Trans</i>	-865.47	-320.43	545.04
<i>Trans-iso</i>	-842.46	-318.57	523.89

Energies in kJ/mol. $\Delta\varepsilon = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$.

As for the UV-VIS spectra (Time-dependent DFT, TDDFT), all the isomers absorb in the UV region exhibiting a single λ_{max} value.

Figure 5 shows the local ionization potential maps of the isomers presently considered. In the local ionization potential map conventionally red regions on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. On the other hand, regions having blue color represent areas where ionization is relatively difficult.

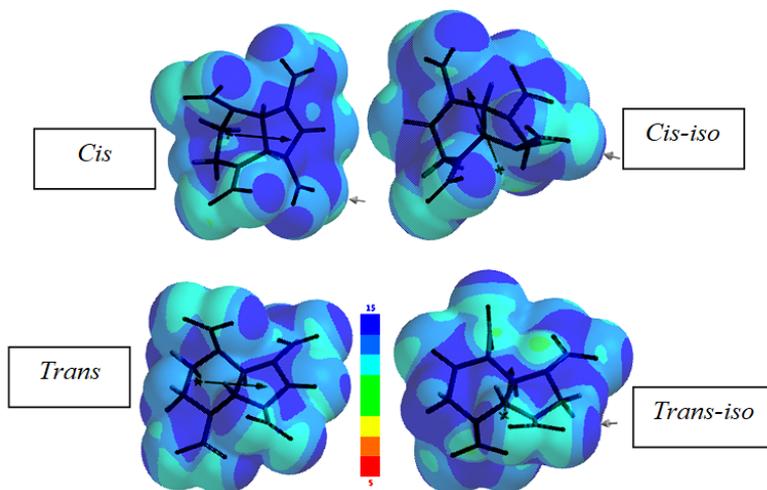
**Figure 5.** The local ionization potential maps of the isomers considered.

Figure 6 shows the LUMO maps of the isomers considered. A LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color stands for the maximum value of the LUMO and the color red, the minimum value.

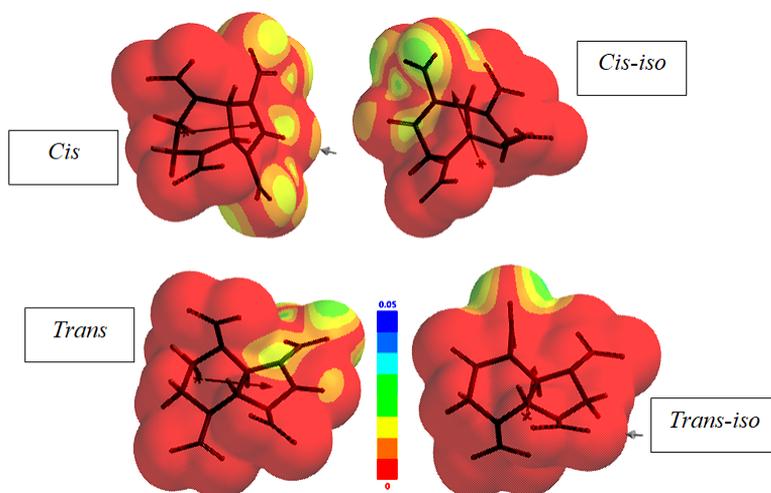


Figure 6. The LUMO maps of the isomers considered.

4. Conclusion

The present DFT treatise, within the constraints of the theory and the basis set employed, reveals that the isomers considered are electronically stable and bond lengths are reasonable. The *Cis* and the *Trans-iso* isomers represent electronically the most and least stable ones, respectively. The carbonyl group in the six-membered ring somewhat destabilizes the system compared to the respective isomer in which that group occupies the five-membered ring. The order of interfrontier molecular orbital energy gap values indicates that the *Cis-iso* isomer should be more, whereas the *Trans* isomer the least susceptible to impact stimulus.

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