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CONSIDERATIONS ON DADNE ISOMERS – A DFT TREATMENT

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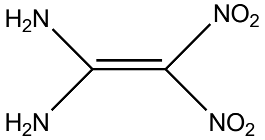
Abstract. Isomers of diaminodinitroethylene (DADNE) are subjected to quantum chemical treatment within the realm of density functional theory at the level of B3LYP/6-311++G(d,p). Mono anions and cations of them are also considered (UB3LYP/6-311++G(d,p)). The possibility of *cis-trans* isomerization is analyzed. Some quantum chemical properties, IR and UV-VIS spectra, some ballistic properties etc. are mentioned.

Keywords: DADNE; FOX-7; DADE; Explosives; DFT calculations; isomers; ions

Introduction

Diaminodinitroethylene has structurally three isomers of which the *geminal* one possesses reputation as FOX-7 (Agrawal, 2010). The others are *cis*- and *trans*-isomers. FOX-7, 1,1-diamino-2,2-dinitroethylene, is also known as DADNE or DADE. It was synthesized in 1998 by members of the Swedish Defense Research Agency (FOI) (Politzer & Murray, 2003; Lochert, 2001) and its explosive potential was thoroughly investigated (Latypow et al., 1998; 1999; Bemm & Östmark, 1998; Östmark et al., 1998; 2001; Bergman et al., 199; Trziński et al., 2006; 2008; 2016; Janzon et al., 2002; Matyushin et al., 2003; Bellamy et al., 2004; Cudziło et al., 2005; Anniyappan et al., 2006; Mishra et al., 2013). It was also synthesized by the nitration of 4,6-dihydroxy-2-methylpyrimidine and then hydrolysis (Latypov et al., 2007).



FOX-7

FOX-7 is a novel high-energy insensitive material possessing good thermal stability and low sensitivity. It exhibits excellent application performance in the field of insensitive ammunitions and solid propellants. Albeit the fact that no structural resemblance exists among FOX-7, RDX and HMX they have the same C/H/N/O ratio but FOX-7 is much less sensitive than RDX (in terms of impact, friction, and electrostatic discharge sensitivities (Klapötke, 2011).

Although molecular composition and structure of FOX-7 is simple, chemical reactivity of it is abundant and surprising, due to the amino and nitro groups it has (including coordination reactions, nucleophilic substitutions, electrophilic addition reactions, salification reaction, acetylate reactions, oxidizing and reduction reactions, etc. (Zhang et al., 2016; Baum et al., 1992).

FOX-7 has many polymorphic forms. It is known that the α-form reversibly turns into β-form by heat treatment (Evers et al., 2006; Crawford et al., 2007). Also, at higher temperature, β-polymorph undergoes an irreversible conversion to γ-phase which decomposes at 504 K (Evers et al., 2006). Its decomposition has been extensively investigated (Gindulytė et al., 1999). Also the effect of high pressure on the crystal structure of FOX-7 has been searched (Dreger et al., 2016).

For application in high performance insensitive munition (IM) compliant explosive recipies, FOX-7 is an attractive ingredient. FOX-7 also possesses the ability of increasing the burning rate in propellants, thus it is of interest for high performance propellants (Agrawal, 2010).

Many FOX-7 based propellant formulations have been studied in order to obtain a reduced or minimum smoke producing composite propellant with inherent IM-properties (Lips & Menke, 2013).

On the other hand, thermo chemical calculations have indicated that PBX's based on FOX-7 and energetic binders could serve as a replacement of Comp-B even at rather low solid loadings. A plastic bound explosive based on FOX-7 and an energetic binder have been prepared (Karlsson et al., 2002).

The effects of nitration and epoxidation on ballistic properties of FOX-7 were also investigated within the realm of density functional theory (DFT) (Türker & Varis, 2013). Various ground state properties of FOX-7 were calculated based on B3LYP/aug-cc-pVDZ predictions (Dorsett, 2000).

Laser ignitibility of FOX-7 was investigated in order to achieve the direct optical ignition of an insensitive explosives. Such a process of course would have safer features for insensitive munitions (IM) or explosive devices (Fang & McLuckie, 2015).

Recently, some novel derivatives of FOX-7 (*geminal* DADNE) and their properties as energetic materials have been reported (Zhou et al., 2017; Gao & Sgreeve, 2016). In the present study, isomers of DADNE have been investigated within the constraints of density functional theory (DFT).

Method of calculation

Structure optimizations leading to energy minima were initially achieved by using MM2 method which is followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method (Stewart, 1989a; 1989b) at the restricted level (Leach, 1997; Fletcher, 1990). Subsequent optimizations were achieved at Hartree-Fock level by using various basis sets. Then, the optimizations were managed within the framework of density functional theory (DFT) using B3LYP functional (Kohn & Sham, 1965; Parr & Yang, 1989) at the level of 6-311++G(d,p). The charged forms of the isomers have been handled at UB3LYP/6-311++G(d,p) level. 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 (Parr & Yang, 1989; Becke, 1988). The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional (Vosko et al., 1980) and Lee, Yang, Parr (LYP) correlation correction functional (Lee et al., 1988). The vibrational analyses were also done at the same 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 (SPARTAN 06, 2006).

Results and discussion

In the structure of *geminal* DADNE (FOX-7) amino and nitro groups are located in such a manner that the whole system is an effective pull-push type molecule. In the *cis* and *trans*-isomers the donor and acceptor groups (NH_2 and NO_2, respectively) are oriented so that carbon-carbon π-skeleton is under the opposing effects of the donor (or attractor) groups. Because of that much less effective pull-push system arises. This qualitative argument originating from the theory of mesomerism would be verified by quantum chemical calculations to visualize the power of *cis* and *trans*-isomers compared to the *geminal* isomer. Note that the insensitive character of the *geminal* isomer to various stimuli is due to somewhat reduced electron demand of NO_2 groups caused by the electron donating effect of amino groups.

Structures

Fig. 1 shows the optimized structures of the isomers considered. Permutatively changing the location of groups, strikingly varies the direction of the dipole moment vector. In the case of *trans*-isomer it is perpendicular to C=C π-system and its magnitude is very small compared to the respective property of the *geminal* and *cis*-isomers. Table 1 shows some properties of the isomers. In the table the heat of formation values (ΔH_f°) calculated by the methods of T1 (Ohlinger et al., 2009; Curtiss et al., 1998) and PM3 are displayed. The T1 method is a little bit less accurate than the expensive G3(MP2) method but most of the cases T1 results are quite close to the experimental values (Türker, 2018) such as -45.45 kcal/mol instead of -37.0 kcal/mole (Meyer et al., 2002) for the experimental value of ethylnitrate. The heat of formation value of FOX-7 has been reported to be -32 Kcal/mol (-133.88 kJ/mol.) by bomb calorimetry (Östmark et al., 1998), whereas T1 and PM3 methods yield +35.30 kJ/mol and -56.22 kJ/mol, respectively.

As seen in Table 1 both of the *cis* and *trans*- isomers are predicted to be endothermic structures, the *trans* being less endothermic.

Fig. 2 shows the bond lengths of these isomers. Note that the comparatively longer carbon-carbon bond exists in the *geminal* isomer. Normally C=C bond is about 1.33 Å (Ferguson, 1969). So, in this isomer, carbon-carbon bond should be in between single and double bond in nature. The IR spectra of the isomers have two different N-H stretching bands in between 3400-3700 cm^{-1} and various nitro stretchings around 1500 cm^{-1} and plenty of bending vibrations, mostly coupled, in the fingerprint region of the spectra.

In Fig. 3, the electrostatic potential (ESP) charges are displayed. 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 wave function (SPARTAN 06, 2006).

Fig. 4 shows the numbering of atoms in the isomers considered. The figure aids Table 2 which tabulates the data of some of the bond and dihedral angles

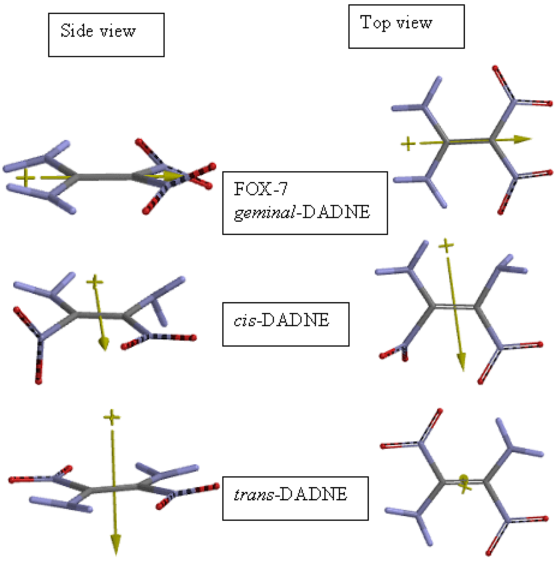


Figure 1. Optimized structures of the present concern B3LYP/6-311++G(d,p)

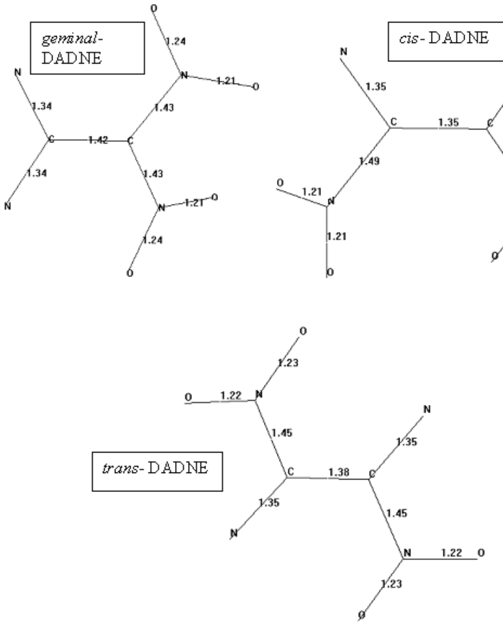


Figure 2. Bond lengths (Å) of the structures considered (B3LYP/6-311++G(d,p))

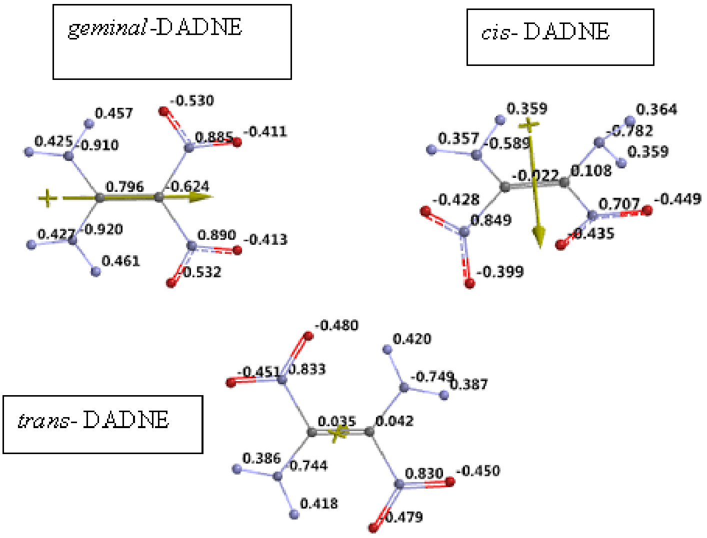


Figure 3. Electrostatic charges (ESP) possessed by the atoms of isomers concerned (in esu unit, B3LYP/6-311++G(d,p))

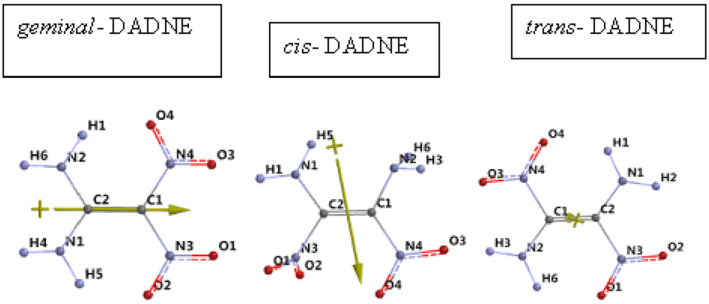


Figure 4. Numbering of the atoms in the isomers considered

Table 1. Various properties of DADNE isomers

Structure	Dipole moment (Debye)	Area (Å^2)	Volume (Å^3)	Polarizability (Å^3)	Heat of formation (kJ/mol)
geminal- DADNE (FOX-7)	8.54	139.18	109.76	49.18	35.30[a] -56.22[b]
cis-DADNE	6.66	146.51	111.99	49.46	78.36[a] 14.62[b]
trans-DADNE	0.51	137.61	109.68	49.65	57.03[a] 11.52[b]

B3LYP/6-311++G(d,p) level of calculations. [a] *Result of T1 calculation.* [b] *PM3. Log P value is -0.31 for all.*

Table 2. Some angles (degrees) of the isomers (B3LYP/6-311++G(d,p))

Angle	*geminal-* DADNE	*cis-* DADNE	*trans-* DADNE
N4C1N3	116.44		
N2C2N1	116.97		
N1C2N3		111.46	112.68
N2C1N4		119.32	112.68
N2C2C1N3	166.34		
N1C2C1N4	166.13	177.01	-6.57
N2C1C2N3		173.66	-6.57
N4C1C2N3		-8.35	174.18
N1C2C1N2		-0.98	172.68
N2C2C1N4	-13.87		
N1C2C1N3	-13.65		

Energies and orbitals

Some energies of the isomers are shown in Table 3 where E and E_c stand for the total electronic energy and its corrected form, respectively. The corrected energy includes the zero- point vibrational energy (ZPE) contribution. According to the data of Table 3, the order of stabilities is **2**<**3**<**1**. The *geminal*-isomer (FOX-7) having perfect pull-push system is more stable than the others.

Fig. 5 displays some of the molecular orbital energy levels of the isomers. The figure clearly shows the influence of positional variations of the same kind of substituents on the molecular orbital energy levels, not only on the HOMO and LUMO but also the inner lying molecular orbitals energies and NEXT HOMO (NHOMO) and NEXT LUMO (NLUMO). The HOMO energy order is **1**<**2**<**3**, namely *geminal*< *cis* < *trans* isomers. Whereas the LUMO energy order is **3**<**2**<**1** (*trans*<*cis*<*geminal*). Consequently, the interfrontier energy gap (ε_{LUMO} - ε_{HOMO}) order becomes **3**<**2**<**1** (*trans*<*cis*<*geminal*). It has been claimed that a reverse correlation exists between the impact sensitivity of an explosive and its HOMO-LUMO energy gap (Ovens, 1984). The order of $\Delta\varepsilon$ values suggests that the impact sensitivities of them should follow the reverse order, namely the *geminal*-isomer is less sensitive to any impact stimulus, whereas the *trans*-isomer is the most sensitive.

Table 3. Various energies of DADNE isomers

No	Structure	E	ZPE	E_c
1	*geminal*- DADNE	-1571382.62	240.682179	-1571141.94
2	*cis*- DADNE	-1571317.89	239.211638	-1571078.68
3	*trans*- DADNE	-1571363.56	238.910152	-1571124.65

B3LYP/6-311++G(d,p) level of calculations. Energies in kJ/mol.

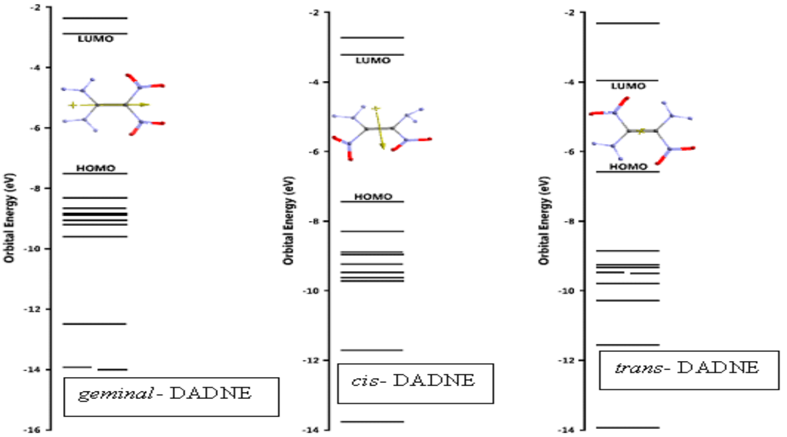


Figure 5. Some of the molecular orbital energy levels of the isomers considered (B3LYP/6-311++G(d,p))

Table 4. The HOMO, LUMO energies and Δε values of DADNE isomers and their **μ** and **η** values

No	Structure	HOMO	LUMO	Δε	μ	η
1	*geminal*-DADNE	-724.244548	-276.638006	447.6065	500.441	223.8033
2	*cis*- DADNE	-718.164216	-311.275342	406.8889	514.72	203.4444
3	*trans*- DADNE	-634.816738	-382.487199	252.3295	508.652	126.1648

B3LYP/6-311++G(d,p) level of calculations. Energies in kJ/mol.

Table 4 shows the HOMO, LUMO energies and the interfrontier molecular orbital energy gaps, namely the LUMO-HOMO energy difference (**Δε).** The table also includes μ (electronegativity) and η (hardness) values of these isomers which are defined as (Person, 1989; 1997; Zhou & Parr, 1990).

$$\mu = -(\mathrm{HOMO}+\mathrm{LUMO})/2 \qquad (1)$$

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

According to the calculations, electronegativity and hardness orders of the isomers are **2**>**3**>**1** and **1**>**2**>**3**, respectively. Note that there exists a parallelism between the order of hardness and the dipole moment order (Table 1). The net dipole moment of a molecule is the vectorial sum of bond dipoles which are dictated by the charge on each side of the bond and the bond length. On the other hand, the HOMO and LUMO energies of the isoconjugate system are lowered by hetero atoms to an extent depending on their positions (see section 3.5 for the isoconjugates of DADNE isomers). So it is very probable that there should exist an implicit function among the dipole moment, μ and η values.

Figure 6 stands for the HOMO and LUMO patterns of the isomers considered. In the case of HOMOs, π-symmetry is greatly apparent. The ethylenic π-bond of the *geminal* isomer is somewhat perturbed towards the nitro substituents. The amino groups of the *geminal* isomer do not contribute to the LUMO. Since in the cases of *cis*- and *trans*-isomers the pull-push effects of the substituents are counter balanced, the ethylenic π-bond is over the carbon atoms symmetrically. Whereas, the LUMOs of *cis*- and *trans*-isomers have π*-symmetry on the carbons.

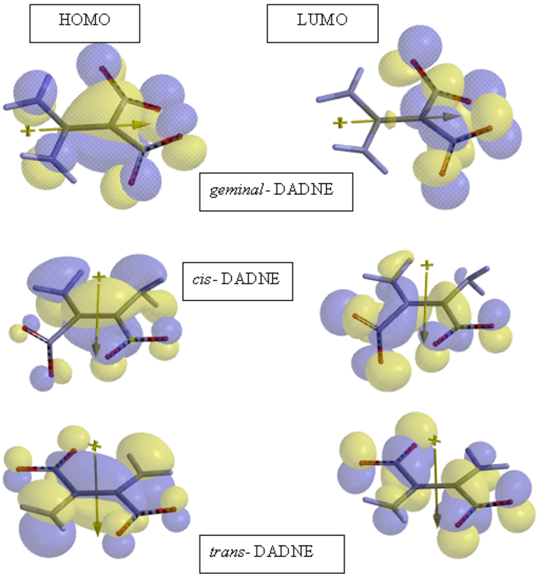


Figure 6. The HOMO and LUMO patterns of the isomers considered (B3LYP/6-311++G(d,p))

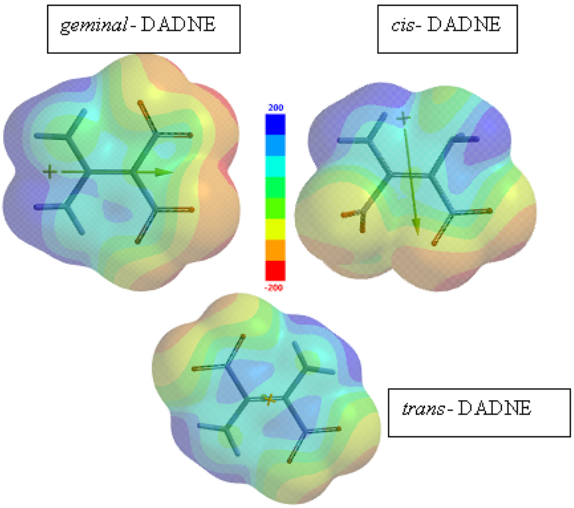


Figure 7. Electrostatic potential maps of the isomers considered (B3LYP/6-311++G(d,p))

Fig. 7 shows the electrostatic potential maps of those isomers. As seen in the figure, the region around the amino groups in the *geminal*-isomer is strongly positive (blue in color), whereas around the nitro groups some strong negative potential (red in color) develops. Those areas are suitable sites for nucleophilic and electrophilic attacks, respectively. This situation of electrostatic potentials arises from the donor-acceptor action of the substituents and it is also strong in the *cis* but less in the *trans*-isomer.

UV-VIS Spectra

Fig. 8 shows the time dependent density functional (TDDFT) UV-VIS spectra of the isomers. Some bathochromic shift is observed as the sequence of *geminal-cis-trans* is followed. In the *geminal* case peaks corresponding to λ_{max-1} and λ_{max-2} are not very distinct. Although, absorption A_1 is greater than A_2 in the *geminal* and *cis*-isomers in the *trans* case $A_2 > A_1$.

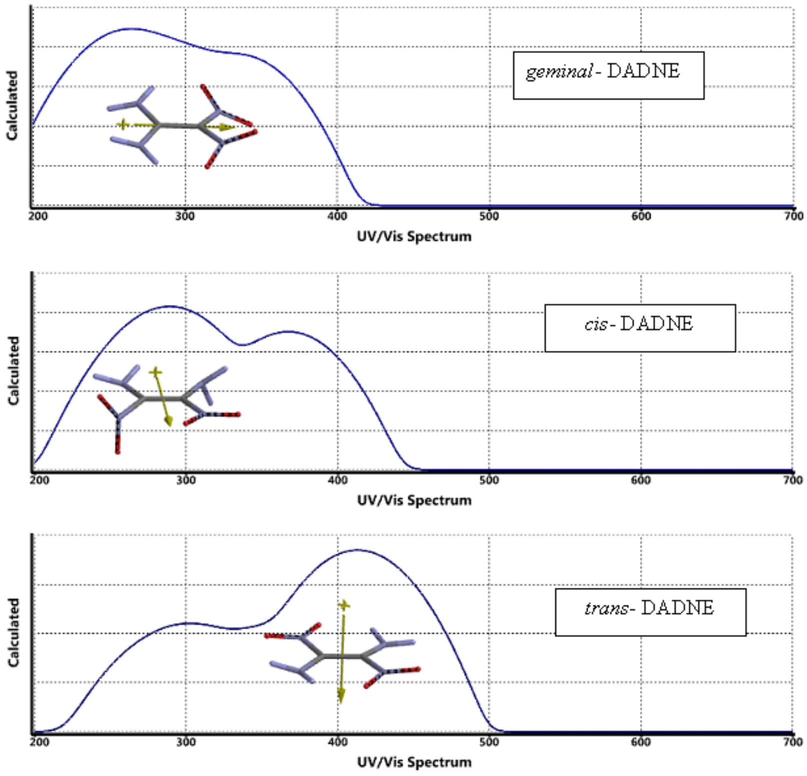


Figure 8. UV-VIS spectra of the isomers (B3LYP/6-311++G(d,p))

Some ballistic properties

Most of the computer codes or empirical techniques cannot predict the ballistic properties desired for isomeric compounds. However, some quantum chemistry based ones can. Eq. (3) is suitable to predict densities (d) (Türker, 2012), where E and M are the total electronic energy and mass, respectively.

$$d = -0.6538(E/M) - 0.8264 \tag{3}$$

Densities are calculated as 1.815 g/cm^3 (upto third digit they are the same but differ at the fifth digit, as FOX-7 >*trans* > *cis*) for all three isomers whereas for *geminal* DADNE (FOX-7) density is reported as 1.878 g.cm^{-3} (crystal density (Östmatk et al., 1998) 1.885 g.cm^{-3} (powder diffraction (Bergman et al., 1999) and 1.86 – 1.87 g.cm^{-3} (helium pycnometry, DSTO laboratories) (Lochert, 2001).

Detonation velocities (D) can be easily estimated by Eq. (4) (Türker, 2010), where N is the number of nitro groups and E and M have the same meaning as they have in Eq. (3).

$$D^2 = -393.6877 - 0.2454(NE/M) - 114.0793(E/M) \tag{4}$$

In both of the formulas E in au units obtained at UB3LYP/6-31(G) level, M in grams, D is in Km/s. Detonation velocities are calculated as 8316.3 m/s, 8315.1 m/s and 8316.0 m/s, for the *geminal* (FOX-7), *cis*-DADNE and *trans*-DADNE, respectively. The reported value for the *geminal* isomer is 8870 m/s (Klapötke, 2011), 7730 m/s (FOX-7/EVA, 92%TND), calculated 9090 m/s (Lochert, 2001). The estimated values imply that these isomers have at least comparable d and D values.

On the other hand, it was reported that specific impulse values of energetic materials are proportional with square root of ΔH_f° /Mw values (Wilson et al., 2001). In that respect, based on PM3 calculations of ΔH_f°, the specific impulse value of *trans*-DADNE should be less than the respective value of its *cis* –isomer.

Geminal-DADNE isoconjugate with a nonKekule' system

The stability order of present isomers is obtained as *geminal*>*trans*>*cis*. Topologically these isomers are isoconjugate with certain alternant hydrocarbon anions shown in Fig. 9. Note that alternant hydrocarbons possess alternatingly labeled stared and unstarred positions (Dewar, 1969). The isoconjugate of *geminal*-DADNE isomer (FOX-7) falls into the class of nonKekule' even alternant hydrocarbons (HC), for which the number of starred (n*) and unstarred (n^0) positions fulfill the requirement that n*- n^0>=2. Note that alternant hydrocarbons are classified as even and odd based on n*- n^0 difference is 0 or 1, respectively. It is also known that an even nonKekule' AH is much less stable than any isomeric Kekule' AH (Dewar, 1969).

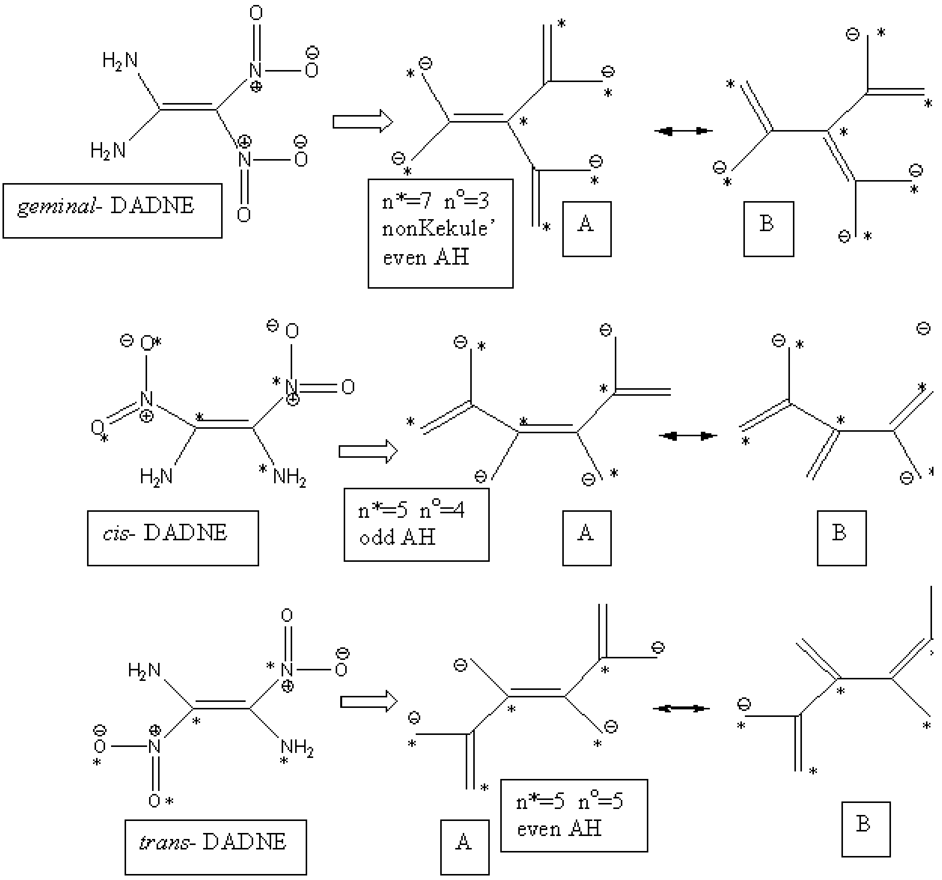


Figure 9. The isoconjugate systems of DADNE isomers

The stability order obtained by the calculations arises from the fact that when certain set of centric perturbations (replacing carbon atoms with heteroatoms) takes place to convert the isoconjugate AH to its real heteroanalog. Meanwhile the molecular orbital energy levels are lowered by heteroatoms. This effect is additive and proportional with $C^2_{ij}\,\delta\alpha$ term, where C_{ij} is the molecular orbital coefficient of atom i in the jth molecular orbital. Whereas, $\delta\alpha$ term is the perturbational effect of a particular heteroatom. Since, the molecular orbital coefficients of the isoconjugate models differ from one structure to other, stabilization effect arising from the topology of heteroatoms exhibit variations for each isomer. As a result, the *geminal* isomer (FOX-7) is an explosive because it possesses explosophoric NO_2 moiety and is a metastable nonKekule system (Türker, 2011) but stabilized by the topology of heteroatoms.

The *cis*- and *trans*- isomers have isoconjugate systems which are odd and even AH property, respectively. So, they should not be metastable inherently. However, the centric perturbations (Dewar, 1969) to engender NO_2 and NH_2 groups may provide some instability to the resultant *cis* and *trans* isomers. However, the centric perturbations at the starred position of the isoconjugate system lowers the HOMO and LUMO in equal extents in even alternant isoconjugate hydrocarbon case but unequally in the case of an odd alternant system (Dewar, 1969). Therefore, the *cis*-isomer is more apt to show the effects of those perturbations compared to the *trans*-isomer.

Isomerization of cis and trans-DADNE

The electron donor character of the amino groups makes the *cis*- and *trans*-isomers to have appreciable contributions from *s-cis* and *s-trans* canonical structures. Then, a conformational/configurational change leading to isomerization is expected (*cis-trans* isomerization of DADNE). Fig. 10 shows some key structures for the isomerization. Table 5 tabulates some energies involved in the isomerization process of the *cis*- and *trans*- DADNE molecules.

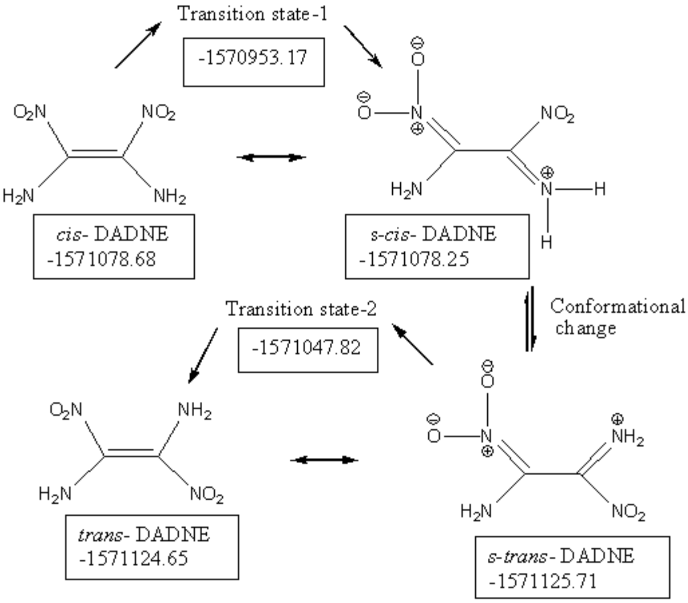


Figure 10. A possible route to the *cis*/*trans* isomerization considered (Energies in kJ/mol. B3LYP/6-311++G(d,p))

Table 5. Various energies of the species involved in the isomerization process.

	ZPE	E	Ec
s-cis- DADNE	239.79	-1571318.04	-1571078.25
s-trans- DADNE	237.45	-1571363.16	-1571125.71
Transition state-1	235.02	-1571188.19	-1570953.17
Transition state-2	234.55	-1571282.37	-1571047.82

Energies in kJ/mol. (B3LYP/6-311++G(d,p)).

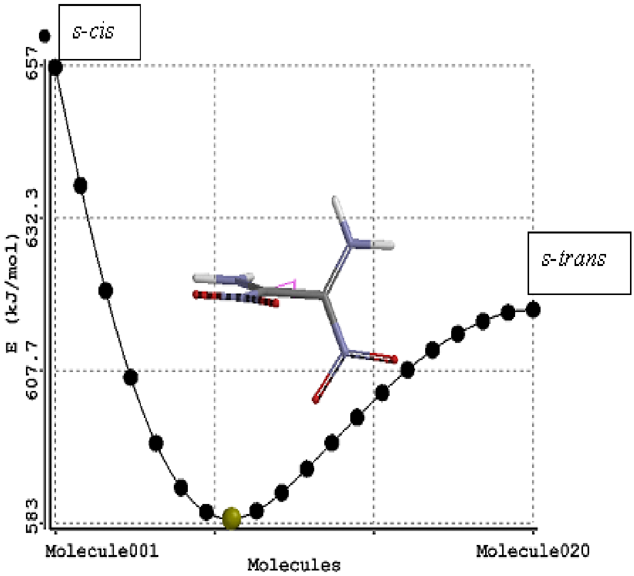


Figure 11. Conformational energy variation for s-*cis*- DADNE to s-*trans*-DADNE conversion

Fig. 11 shows the conformational energy (molecular mechanics) change of *s-cis* to *s-trans* DADNE structures. In the lowest energy state, the nitro (and amino) groups prefer to be in perpendicular planes with the other group of the same kind (Fig.11).

Fig. 12 shows the shift of electrons leading to transition states and bond lengths in the transition state structures are depicted in Fig.13.

Fig. 14 displays the electrostatic charges (ESP) accumulated on atoms in transition states -1 and -2.

Fig. 15 shows the IR spectra of the transition state structures in which most of the bands in between 1700-1000 cm^{-1} are due to nitro stretchings and amino bendings coupled with each other.

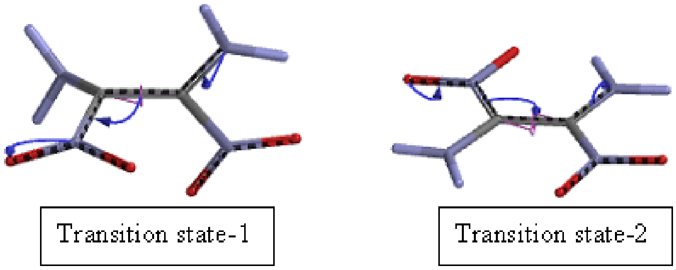


Figure 12. The shift of electrons leading to the transition state geometries (B3LYP/6-311++G(d,p))

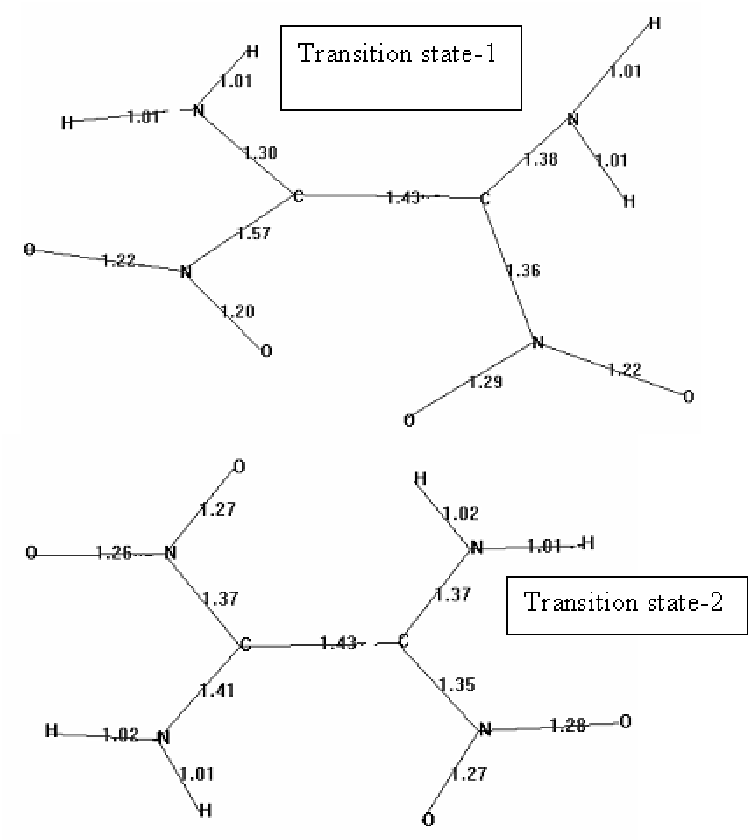


Figure 13. Bond lengths (Å) in transition states-1 and 2 (B3LYP/6-311++G(d,p))

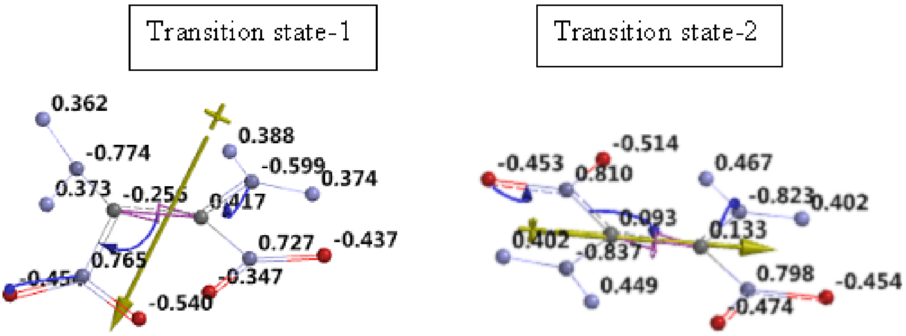


Figure 14. Electrostatic charges (ESP) of transition states -1 and 2 (esu) (B3LYP/6-311++G(d,p))

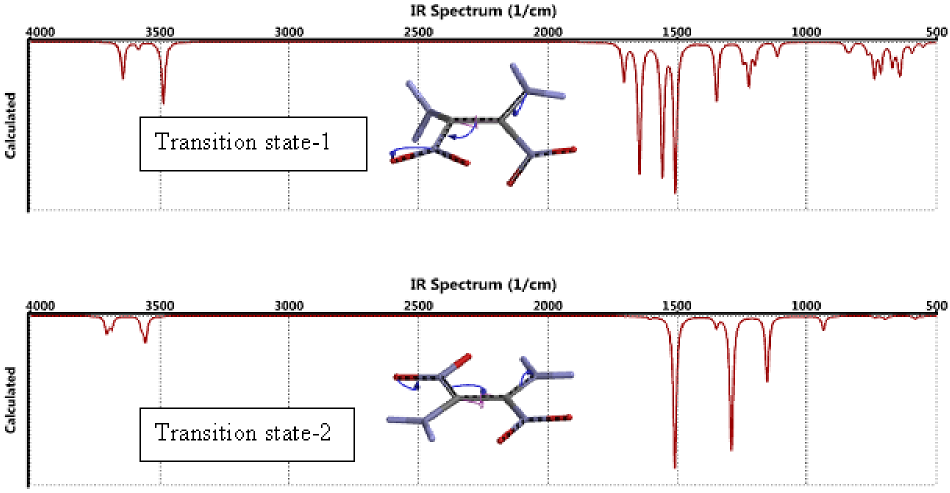


Figure 15. IR spectra of transition states 1 and 2 (B3LYP/6-311++G(d,p))

Charged forms

Spark sensitivity is an important property of energetic materials because of safety considerations while handling and storage purposes. Organic molecules in solid state are classified as insulators, more physically speaking as dielectric materials. However, as the applied potential increases, molecules of dielectric materials become polarized and eventually ionize. Then the phenomenon known as "dielectric break down" happens which means the material becomes certain sorts of conductor (Hinchliffe & Munn, 1985; Tareev, 1975). Therefore, ionic forms of energetic materials are worth investigating. Hence, in the present study, the mono anion of and cation forms of DADNE isomers have been investigated.

According to the results of UB3LYP/6-311++G(d,p) level calculations (Table 6) the stability order of anions is *trans* > *cis* > *geminal*, whereas the cations follow the order of *trans* > *cis* >= *geminal*.

Table 6. Some energies of the charged forms presently considered

	Anion			**Cation**		
	E	**ZPE**	**E_c**	**E**	**ZPE**	**E_c**
geminal- DADNE	-1571499.52	232.01	-1571267.51	-1570501.13	238.86	-1570262.27
cis- DADNE	-1571529.05	235.45	-1571293.6	-1570501.06	238.73	-1570262.33
trans- DADNE	-1571595.52	235.34	-1571360.18	-1570562.05	239.67	-1570322.38

Energies in kJ/mol. UB3LYP/6-311++G(d,p) level.

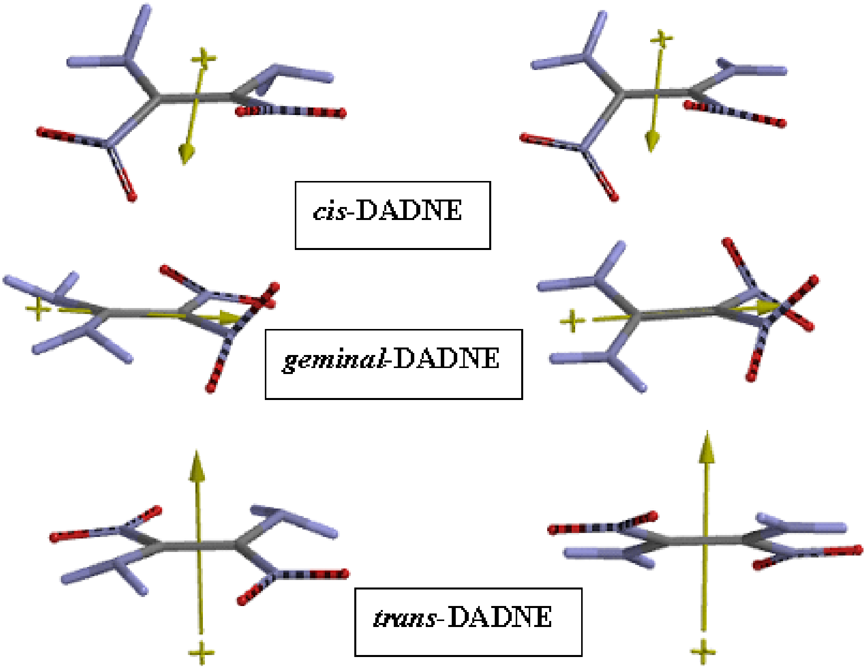


Figure 16. Optimized structures of DADNE ions (UB3LYP/6-311++G(d,p))

On the other hand, the HOMO energy order is **1**<**2**<**3**, namely *geminal*< *cis* < *trans*. Whereas the LUMO energy order is **3**<**2**<**1** (*trans*<*cis*<*geminal*). Hence, to remove an electron from the HOMO and add an electron to the LUMO of the *trans*-isomer is more favorable than the others. Fig. 16 shows the optimized structures of the DADNE mono ions. These charged structures keep their integrity, although some conformational changes occur as compared to their neutral forms.

Conclusion

Within the constraints of density functional theory**,** all the isomers of diaminodinitroethylene (DADNE) and their mono anions and cations have been found to be stable. The *geminal* one (FOX-7) is the most stable isomer among all. Based on interfrontier molecular orbital energy gap consideration, the *geminal*-isomer is expected to be the least sensitive and the *trans*-isomer the most sensitive to impact. The estimated values of densities and detonation velocities are obtained comparative to each other for these isomeric compounds.

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