



Epoxides of DADNE Isomers – A DFT Study

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Abstract

Diaminodinitroethylene (DADNE) has three constitutional isomers; *cis*, *trans* and *geminal*. In the present study, epoxides of these isomers are considered within the restrictions of density functional theory at the level of UB3LYP/6-31G(d,p). Certain geometrical and quantum chemical properties of them are computed. The homolytic dissociation energy for C-NO₂ bond in each case has been calculated at the level of UB3LYP/6-311++G(d,p). Based on the calculations performed, certain predictions are made for the impact sensitivities and specific impulse values of these epoxide derivatives of DADNE isomers.

1. Introduction

Of the three isomers of diaminodinitroethylene, the *geminal* one possesses reputation as FOX-7 [1] which is 1,1-diamino-2,2-dinitroethylene. It is also known as DADNE or DADE. The others are *cis*- and *trans*-isomers. FOX-7 was synthesized in 1998 by researchers of the Swedish Defense Research Agency (FOI) [2, 3]. Since then, its explosive potential has been thoroughly investigated [4-18]. Another method of its synthesis involves the nitration of 4,6-dihydroxy-2-methylpyrimidine and then hydrolysis [19].

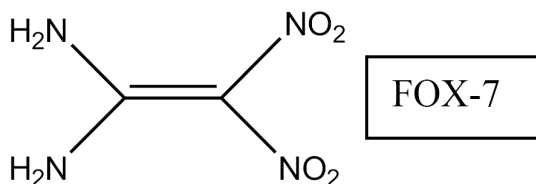
FOX-7 is a novel high-energy insensitive material which possesses good thermal stability and low sensitivity. It exhibits excellent application performance among the

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known insensitive ammunitions and solid propellants. No structural resemblance exists among FOX-7, RDX and HMX however 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 [20]).



FOX-7, although its structure and molecular composition is simple, exhibits abundant and surprising chemical reactivity (including coordination reactions, nucleophilic substitutions, electrophilic addition reactions, acetylate reactions, oxidizing and reduction reactions, etc., [21, 22]). It is due to the presence of amino and nitro groups in its structure.

FOX-7 have many polymorphic forms of which the α -form reversibly turns into β -form by heat treatment [23, 24]. Evers et al., reported that at higher temperature, β -polymorph undergoes an irreversible conversion to γ -phase which decomposes at 504 K [23]. Its decomposition has been extensively investigated [25]. The effect of high pressure on the crystal structure of FOX-7 also has been searched [26].

FOX-7 possesses the ability of increasing the burning rate in propellants, thus it is of interest for high performance propellants [1]. For application in high performance insensitive munition (IM) compliant explosive recipes, FOX-7 is an attractive ingredient.

Many FOX-7 based propellant formulations, have been studied through the years in order to obtain a reduced or minimum smoke producing composite propellant with inherent IM-properties [27]. A plastic bound explosive based on FOX-7 and an energetic binder have been prepared [28].

Within the realm of density functional theory (DFT), the effects of nitration and epoxidation on ballistic properties of FOX-7 have been also investigated [29]. Also, various ground state properties of FOX-7, based on B3LYP/aug-cc-pVDZ predictions, were calculated by Dorsett [30].

In order to achieve the direct optical ignition of an insensitive explosive, laser ignitibility of FOX-7 was investigated [31].

Recently, some novel derivatives of FOX-7 (*geminal* DADNE) and their properties as energetic materials have been reported [32, 33]. In the present study, epoxides of the isomers of DADNE have been investigated within the constraints of density functional theory (DFT).

2. Method of Calculations

Initially MM2 method was employed for the structure optimizations leading to energy minima. Then, semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [34, 35] at the restricted level [36, 37] was used. 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 [38, 39] at the level of UB3LYP/6-31G(d,p). The bond dissociation energies for C-NO₂ bonds are calculated at the level of UB3LYP/6-311++G(d,p). 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 [39, 40]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [41] and Lee, Yang, Parr (LYP) correlation correction functional [42]. Also, the vibrational analyses were done at the same level of calculations employed 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 [43].

3. Results and Discussion

DADNE isomers have mesomerically electron attracting nitro groups and electron donating amino groups. Therefore, they have some pull-push type properties depending on the positions of those groups around the ethylenic π -system. In the case of their epoxides, π -conjugation in between these groups is blocked. Hence, the interaction between the donor and acceptor groups could be via σ -structure through inductive effects or/and via field effect. Figure 1 shows optimized structures of the isomeric DADNE epoxides considered. As seen in Figure 1, in terms of the direction of the dipole moment

vectors, these effects are highly dependent on the position of the donor acceptor groups. The epoxide of *geminal*-DADNE has the dipole moment vector having the same direction as it is in FOX-7, *geminal*-DADNE.

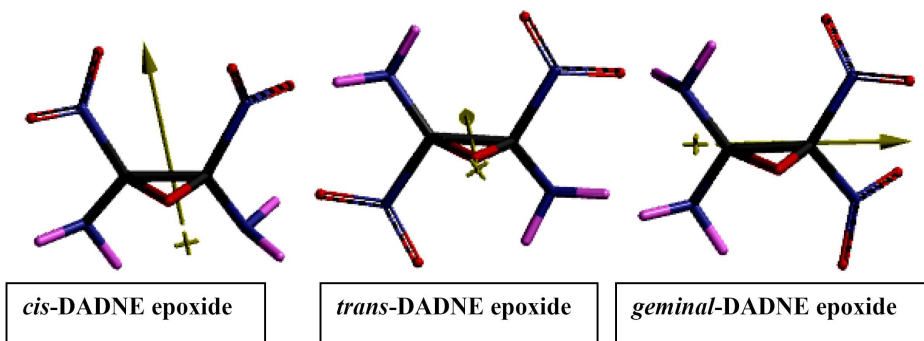


Figure 1. Optimized structures of the isomeric DADNE epoxides considered.

Figure 2 shows the calculated bond lengths in optimized structures of the isomeric

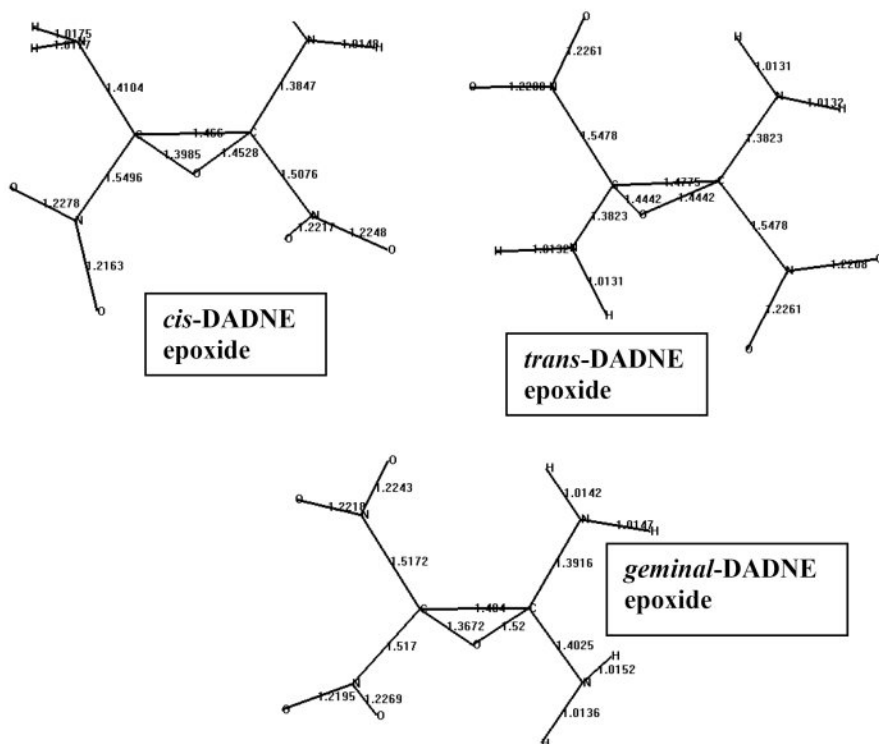


Figure 2. Calculated bond lengths of the epoxides considered.

DADNE epoxides considered. As seen there, C-O bonds of the epoxide rings within the same structure, differ in length in the *cis*- and *geminal* isomers but the *trans* isomer has equivalent C-O bond lengths. On the other hand, the C-C bond in each epoxide differs from the others.

Figure 3 shows the ESP charges on the atoms of the isomeric epoxides considered. 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 [43]. The charges on the carbon atoms are positive except in the case of *geminal*-DADNE epoxide.

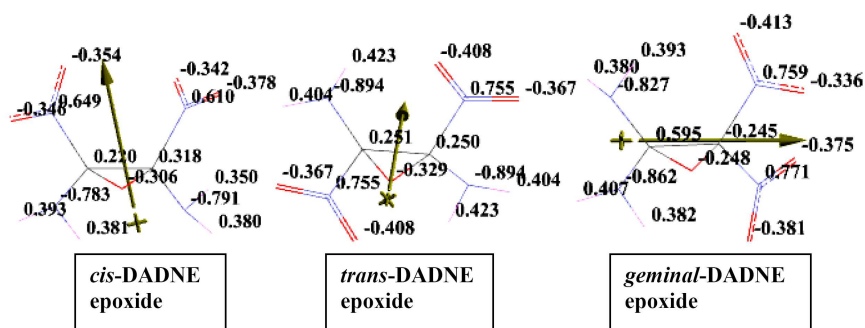


Figure 3. ESP charges on the atoms of the isomeric epoxides considered.

Table 1 displays some calculated properties of the epoxides considered. As seen there *trans*-DADNE epoxide generally has smaller property values than the others. The isomer has equal or very comparable LogP values and polarizabilities.

Table 1. Some calculated properties of the epoxides considered.

Property	<i>cis</i> -DADNE epoxide	<i>trans</i> -DADNE epoxide	<i>geminal</i> -DADNE epoxide
Area (\AA^2)	153.22	146.61	151.60
Volume (\AA^3)	118.24	116.92	117.96
Dipole moment (Debye)	5.64	0.53	4.43
Ovality	1.32	1.27	1.30
LogP	0.44	0.44	0.44
Polarizability	49.68	49.72	49.77
E_{aq} (kJ/mol)	-1768320.11	-1768316.81	-1768303.22

Some thermo chemical properties of the epoxides considered are shown in Table 2. The heat of formation values indicate that all these epoxides are endothermic and the order of endothermicity is *trans* > *geminal* > *cis*.

Table 2. Some thermo chemical properties of the epoxides considered.

Property	<i>cis</i> -DADNE epoxide	<i>trans</i> -DADNE epoxide	<i>geminal</i> -DADNE epoxide
Heat of formation*	14.05	27.54	17.26
H°	-1768004.63	-1768019.96	-1767997.27
S° (J/mol°)	390.54	381.62	393.48
G°	-1768121.07	-1768133.74	-1768114.59
Cv (J/mol°)	116.24	119.56	116.79

*PM3//UB3LYP/6-31G(d,p) level. Otherwise indicated energies are in kJ/mol.

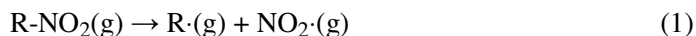
Table 3 tabulates some energies of the isomeric epoxides considered where, E, ZPE and E_c stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. The order of E_c values at the level of UB3LYP/6-31G(d,p) is *trans* < *cis* < *geminal*, whereas at UB3LYP/6-311++G(d,p) level it is *geminal* < *trans* < *cis*. Therefore, the *trans*-isomer, as expected, is more stable than the *cis*-isomer but the calculations on the *geminal*-isomer yield controversial results. The *geminal*-isomer is the least stable in the first case but the most stable in the case of UB3LYP/6-311++G(d,p) level.

Table 3. Some energies of the isomeric epoxides considered.

Structure of epoxide	E	ZPE	E _c
<i>cis</i> -DADNE	-1768267.29	252.30	-1768014.99
epoxide	-1768812.59	249.95	-1768562.64
<i>trans</i> -DADNE	-1768281.71	251.65	-1768030.058
epoxide	-1768822.57	249.33	-1768573.24
<i>geminal</i> -DADNE	-1768259.69	251.81	-1768007.88
epoxide	-1768919.45	246.51	-1768672.94

Energies in kJ/mol. The 1st and 2nd entries in each row are energies at the levels of UB3LYP/6-31G(d,p) and UB3LYP/6-311++G(d,p), respectively.

In nitroaliphatics, nitramines and nitrate esters, the attachment of nitro groups is relatively weak, and therefore scission of that bond is an important step in decomposition of these energetic materials. The expressions used for the homolysis of R-NO₂ bond and for computing its homolytic BDE are shown as follows:



$$\text{BDE}(\text{R-NO}_2) = [\text{E}_{\text{R}\cdot} + \text{E}_{\text{NO}_2\cdot}] - \text{E}_{(\text{R-NO}_2)} \quad (2)$$

where R-NO₂ signifies the neutral molecule and R· and NO₂· signify the corresponding product radicals after the bond dissociation. BDE(R-NO₂) is the bond dissociation energy of the bond R-NO₂; E_(R-NO₂), E_{R·}, and E_{NO₂·} are the zero-point energy corrected total energies of the parent compound and the corresponding radicals, respectively [44].

There are various valuable studies in the literature [44, 45-48] on the homolytic BDE of the nitro compounds, which have shown that there is a parallel correlation between the BDE for the weakest R-NO₂ bond in the molecule and its sensitivity. The ordinary trend is that the greater the homolytic BDE value for scission of R-NO₂ or C-NO₂ bonds are, the lower the sensitivity is.

Figure 4 shows the optimized structures of the DADNE epoxides and radicals obtained from them and used in BDE calculations. In the figure *cis*-NO₂, *trans*-NO₂ and *geminal*-NO₂ stand for NO₂-radical-missing epoxides of *cis*-, *trans*- and *geminal*-DADNE structures, respectively. Note that in the case of *cis*-epoxide the radical shown in Figure 4 is obtained after the cleavage of the longest C-NO₂ bond (assumably the weakest one). In the *trans*-epoxide C-NO₂ bond lengths are equal, so the cleavage of any of them yields the radical shown in Figure 4. As for the *geminal*-epoxide, UB3LYP/6-311++G(d,p) calculations predict C-O bonds of the ring as 2.36 and 1.21 Å. So the epoxide is predicted to be not stable. Typical C-O bonds in ethers are in the range 1.40-1.43 Å [49]. It is 1.45 Å in ethylene epoxide [50]. The corresponding NO₂-radical-missing epoxide has C-O bonds of 2.34 and 1.23 Å. Another point to be emphasized is that carbon radicals obtained from *cis*- and *trans*-DADNE epoxides, shown in Figure 4 are not planar contrary to the general case for carbon radicals. The radical from *geminal* isomer is planar as expected.

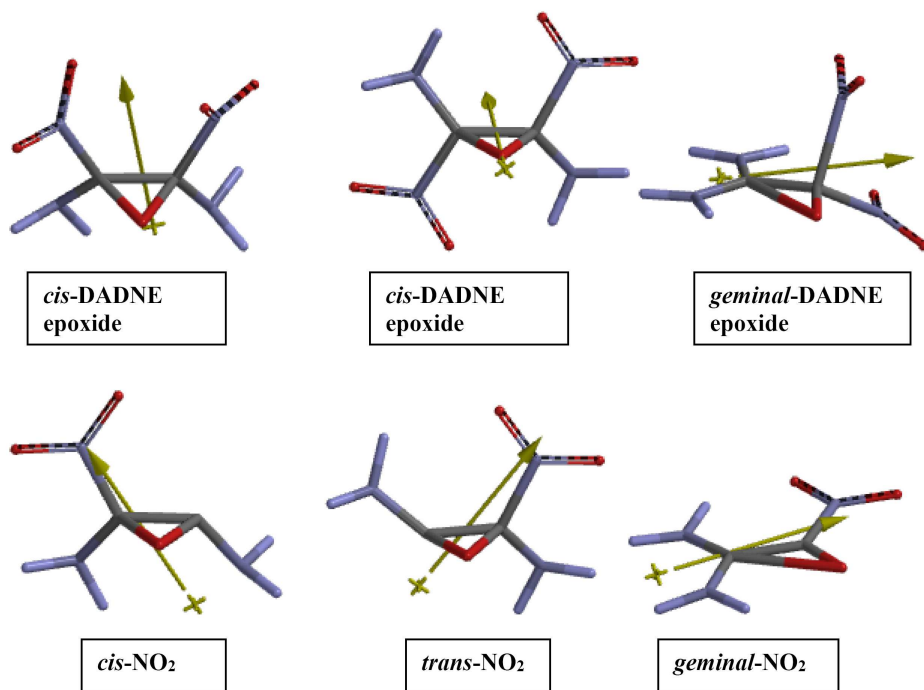


Figure 4. Optimized structures of the DADNE epoxides and radicals used in BDE calculations (B3LYP/6-311++G(d,p)).

Table 4 shows some energies of the species used in BDE calculations of the epoxides. A rather high basis set has been employed to minimize the basis set superposition error (BSSE) because it would vanish in the limit using a complete set for each system involved in BDE calculations [51].

Table 4 shows some energies of the species used in BDE calculations of the epoxides considered.

Note that in the BDE calculations, the longest C-NO₂ bond of the *cis*-isomer is considered. In the case of *trans*-isomer C-NO₂ bonds have the same bond lengths. The order of BDE values for C-NO₂ is *trans* > *cis* > *geminal*. So, the *geminal*-DADNE epoxide is the least and *trans* the most stable to certain stimulus. According to BDE calculations, the *cis*-epoxide is more vulnerable to cleavage of C-NO₂ bond as compared to the *trans*-epoxide. The value for the *geminal*-epoxide is not directly comparable with the others because it seems the C-O bond of it is highly elongated (ring opened!) and the result is the homolytic BDE of the C-NO₂ bond of the ring opened structure.

Table 4. Some energies of the species used in BDE calculations of the epoxides.

Structure	E	ZPE	E _c	BDE
<i>cis</i>-DADNE epoxide	-1768812.59	249.95	-1768562.64	181.18
<i>trans</i>-DADNE epoxide	-1768822.57	249.33	-1768573.24	193.96
<i>geminal</i>-DADNE epoxide	-1768919.45	246.51	-1768672.94	42.66
(FOX-7 epoxide)				
*<i>cis</i>-NO₂	-1230018.34	211.09	-1229807.24	
*<i>trans</i>-NO₂	-1230015.16	210.09	-1229805.07	
*<i>geminal</i>-NO₂	-1230267.53	211.46	-1230056.07	
NO₂	-538597.241	23.03	-538574.21	

B3LYP/6-311++G(d,p) level of calculations. Energies in kJ/mol. *See the text for notation.

Figure 5 shows the IR spectra of the epoxides considered. In the spectrum of the *cis*-isomer the peaks at 3629 cm⁻¹ and 3590 cm⁻¹ are asymmetric N-H stretchings. The symmetrical ones occur at 3524 cm⁻¹ and 3497 cm⁻¹. The strong peak at 1695 cm⁻¹ stands for asymmetrical N-O stretchings. The bendings of N-H bonds occur at 1629 cm⁻¹.

In the *trans*-isomer asymmetric N-H stretchings occur around 3661 cm⁻¹ followed by symmetrical ones at 3549 cm⁻¹. Asymmetrical N-O stretchings and the bendings of N-H bonds happen at 1703 cm⁻¹. At 1589 cm⁻¹ scissoring of N-H bonds occurs.

In the case of *geminal*-isomer, asymmetric and symmetric N-H stretchings occur at 3644 cm⁻¹ and 3547 cm⁻¹. The bending and scissoring of N-H bonds and stretchings of N-O bonds occur in the region of 1696-1656 cm⁻¹.

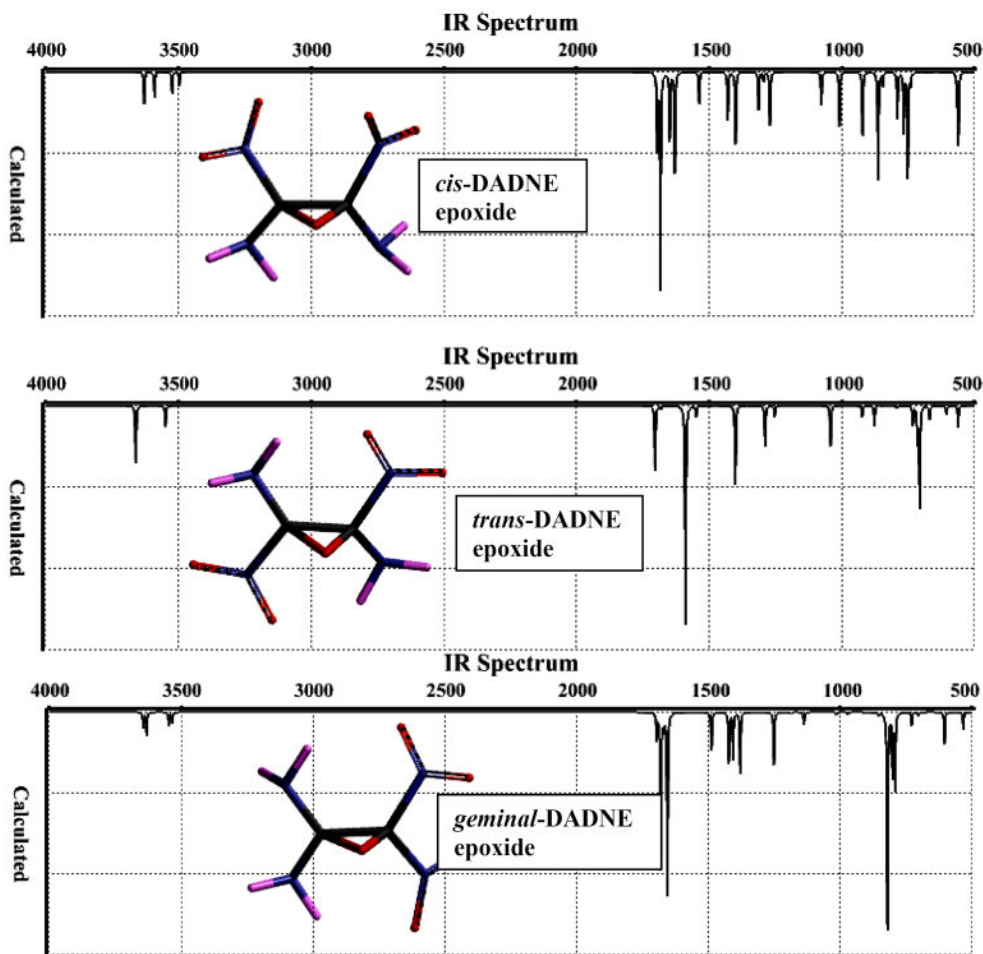


Figure 5. IR spectra of the isomers epoxides considered.

Figure 6 shows some of the molecular orbital energy levels of the isomeric epoxides considered. The HOMO, LUMO energies and the interfrontier molecular orbital energy gaps ($\Delta\epsilon$) of the epoxides considered are shown in Table 5.

The order of $\Delta\epsilon$ values for the epoxides is *cis*- > *geminal*- > *trans*- (UB3LYP/6-31G(d,p)) and *cis*- > *trans*- > *geminal*- (UB3LYP/6-311++G(d,p)).

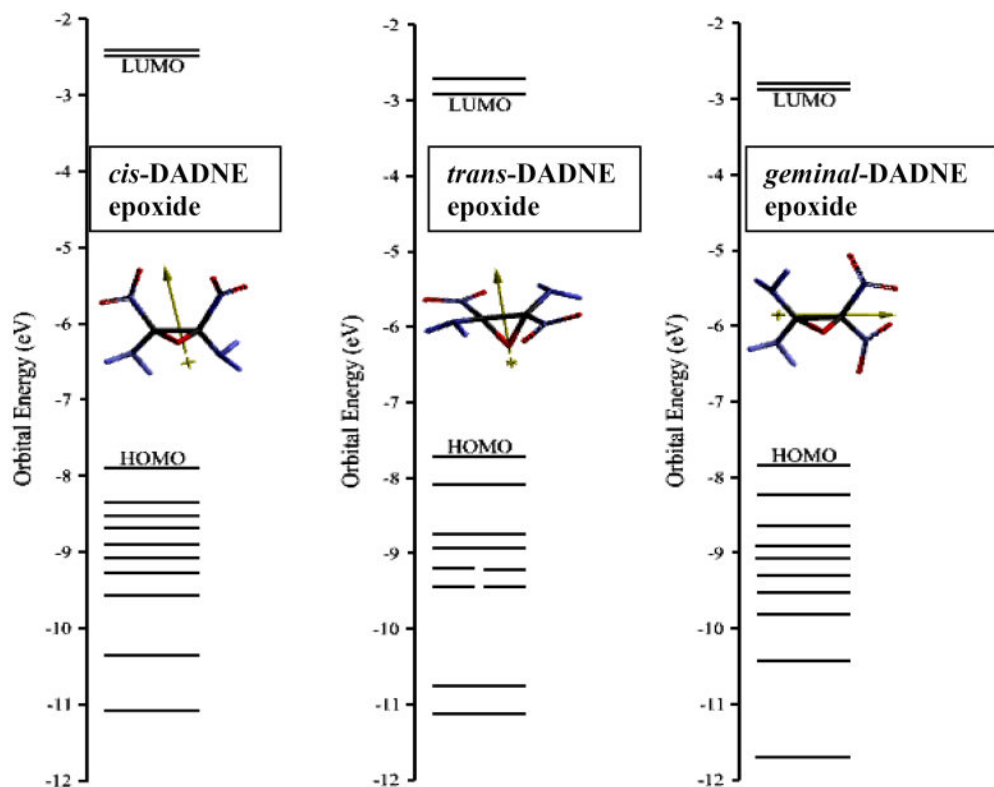


Figure 6. Some of the molecular orbital energy levels of the isomers considered.

Table 5. The HOMO, LUMO energies and the interfrontier molecular orbital energy gaps ($\Delta\varepsilon$) of the epoxides considered.

Structure of epoxide	HOMO	LUMO	$\Delta\varepsilon$
<i>cis</i> -DADNE epoxide	-762.25 -804.42	-239.02 -286.69	523.23 517.72
<i>trans</i> -DADNE epoxide	-744.54 -785.66	-281.59 -327.11	462.95 458.56
<i>geminal</i> -DADNE epoxide	-756.70 -683.84	-277.35 -266.51	479.35 417.33

Energies in kJ/mol. The 1st and 2nd entries in each row are energies at the levels of UB3LYP/6-31G(d,p) and UB3LYP/6-311++G(d,p), respectively.

It is known that as the HOMO-LUMO energy separation decreases, the sensitivity to impact increases [52-56]. Thus, at each level of calculations the *trans*-isomer is more sensitive than the *cis* one. Since, UB3LYP/6-311++G(d,p) level of calculations yield elongated C-O bond in the *geminal*-epoxide, clear conclusions between the $\Delta\epsilon$ value and sensitivity could not be obtained.

Figure 7 shows the HOMO and LUMO patterns of the isomeric epoxides considered.

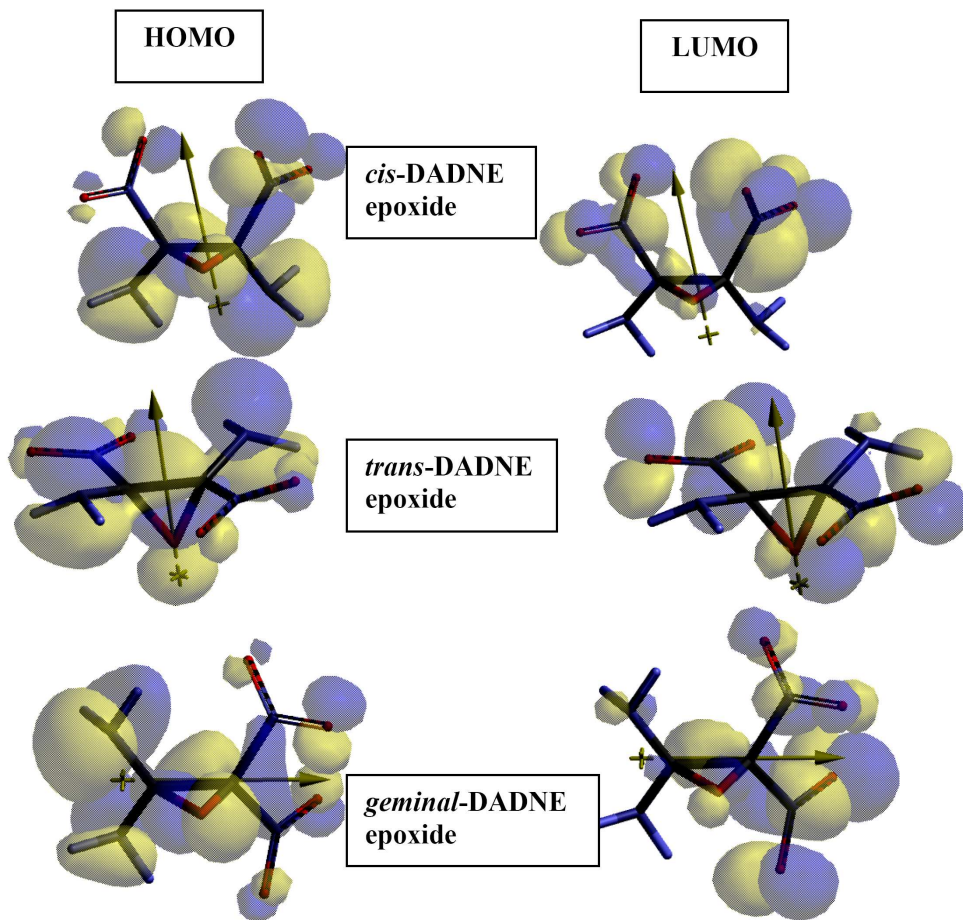


Figure 7. The HOMO and LUMO patterns of the isomeric epoxides considered.

Figure 8 shows the electrostatic potential maps of the isomeric epoxides considered. As seen in the figure, in the *cis*-isomer the amino groups and the nitro groups have highly positive and negative potential regions, respectively. In the others, such a strong effect is less apparent.

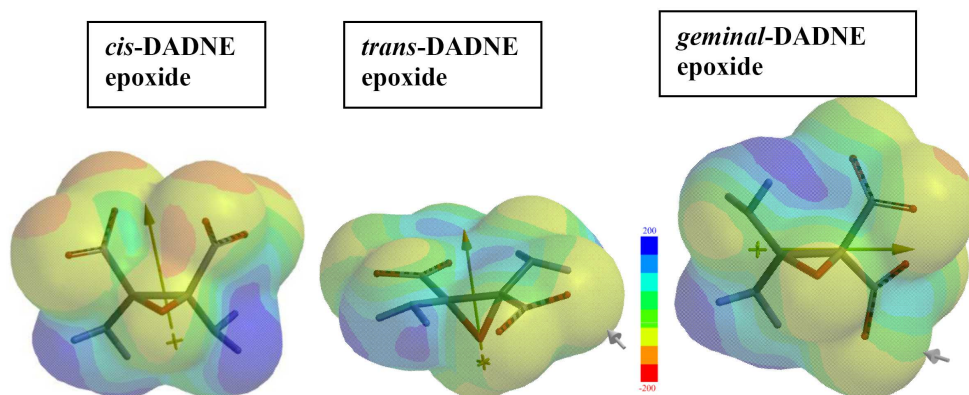


Figure 8. Electrostatic potential maps of the isomeric epoxides considered.

On the other hand, for propellants, the material's potential is best measured by its specific impulse, I_{sp} , presently that property has been estimated for the epoxide structures considered. The specific impulse in units of seconds can be approximated with the following equation [57].

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

Table 6 shows the heat of formation values and specific impulses of the epoxides considered.

Table 6. The heat of formation values and specific impulses of the epoxides considered.

Structure of epoxide	Heat of formation*	Heat of formation**	I_{sp} (sec)
<i>cis</i> -DADNE	14.05	3.36	37.92
<i>trans</i> -DADNE	27.54	6.59	53.10
<i>geminal</i> -DADNE	17.26	4.13	42.04

*PM3//UB3LYP/6-31G(d,p) level, kJ/mol. **kcal/mol.

On the other hand, it has been demonstrated that E/M ratio dictates density (d) [58] and detonation velocity (D) of (at least certain explosives) materials [59] where E and M are the total electronic energy (in au unit) and molecular weight (g/mol), respectively. As that ratio gets more negative values, d and D increase. The epoxides considered have E/M ratios at UB3LYP/6-31G(d,p) level in the order of $trans < cis < gem$. Hence, the

trans-isomer having more negative E/M ratio should be expected as possessing higher density and detonation velocity than the others. Indeed the volume of the *trans*-isomer (see Table 1), obtained by other means, is the smallest of all. Hence, its density has to be the greatest of all.

4. Conclusion

The isomeric DADNE epoxides are structurally found to be stable at the UB3LYP/6-31G(d,p) level, but UB3LYP/6-311++G(d,p) level of calculations suggest ring opening in the *geminal*-isomer. Even in the former level of calculations predict one of the C-O bonds of the *geminal*-isomer to be elongated compared to the ethylene oxide. Except the case of *trans*-isomer, C-O bonds of the same ring have different lengths. The C-C bonds are polarized but the carbons are positively charged in the *cis*- and *trans*-isomers. The *geminal*-isomer has opposite but highly different charges on the carbons. All the isomers considered are endothermic. In terms of homolytic cleavage of C-NO₂ bonds, the *trans*-isomer is the most stable one. Based on the interfrontier molecular orbital energy gaps, the *cis*-isomer is found to be less sensitive to impact and friction but the *trans*-isomer is expected to be characterized with greater specific impulse value as well as higher density and detonation velocity.

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