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Homolytic C-NO_2 Bond Cleavage in Diaminodinitroethylene Isomers - A DFT Treatment

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Abstract

Diaminodinitroethylene (DADNE) has three isomers including the well known *geminal* isomer, FOX-7. In the present study, the homolytic cleavage of one of the C-NO_2 bonds of these isomers has been considered within the constraints of density functional theory at the level of UB3LYP/6-311++G(d,p). Transition states for that type of bond rupture are obtained. Various quantum chemical properties of the parent compounds and the decomposed systems are obtained, compared and discussed. Also the activation energies are calculated. The transition state originating from *cis* DADNE and the one from the *geminal* DADNE are found to be the most and least stable ones, respectively among the all.

1. Introduction

Diaminodinitroethylene possesses three structural isomers. One of them, the *geminal* one, is well known FOX-7 [1]. The others are *cis*- and *trans*-isomers. FOX-7, 1,1-diamino-2,2-dinitroethylene, is also known as DADNE or DADE. The FOI (Swedish Defense Research Agency) members synthesized it in 1998 [2, 3] and its explosive potential was thoroughly investigated [4-18]. Its synthesis was also achieved by the nitration of 4,6-dihydroxy-2-methylpyrimidine and followed by hydrolysis [19].

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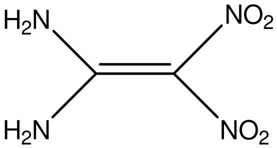
Keywords and phrases: DADNE, FOX-7, explosive, bond cleavage, activation energy, density functional.



FOX-7

FOX-7 is a novel high-energy insensitive material having good thermal stability and low sensitivity. 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 [20]). It exhibits excellent application performance in the field of insensitive ammunitions (IM) and solid propellants.

FOX-7 shows abundant and surprising chemical reactivity although its molecular composition and structure is simple [21, 22]. It is due to the amino and nitro groups (push-pull groups) it has.

FOX-7 has many polymorphic forms. Of those, the α-form reversibly turns into β-form by heat treatment [23, 24]. However, at higher temperatures, β-polymorph undergoes an irreversible conversion to γ-phase which undergoes decomposition at 504 K [23]. Its decomposition pathway has been extensively investigated [25]. Also the effect of high pressure on the crystal structure of FOX-7 has been searched [26].

FOX-7 is an attractive ingredient. It also possesses the ability of increasing the burning rate in propellants, thus it is of interest for high performance propellants [1]. In order to obtain a reduced or minimum smoke producing composite propellant with inherent IM-properties many FOX-7 based propellant formulations have been studied [27].

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, [28].

On the other hand, the effects of nitration and epoxidation on ballistic properties of FOX-7 were also investigated within the restrictions of density functional theory (DFT) [29]. Also, some ground state properties of FOX-7 were calculated based on B3LYP/aug-cc-pVDZ predictions [30]. The other isomers of DADNE are not as famous as FOX-7.

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, homolytic C-NO_2 bond cleavage in DADNE isomers have been investigated within the constraints of density functional theory (DFT).

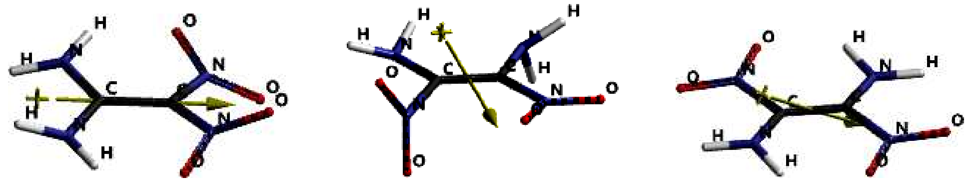
2. Method of Calculation

Structure optimizations leading to energy minima were initially achieved by using MM2 method which was followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [34, 35] at the restricted level [36, 37]. 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 UB3LYP functional [38, 39] at the level of 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]. The present vibrational analyses have been 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. To minimize the basis set superposition error a rather high level basis set has been employed. 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. Whereas in each case the IR spectrum shows a single imaginary frequency for the transition state structure. All these calculations were done by using the Spartan 06 package program [43].

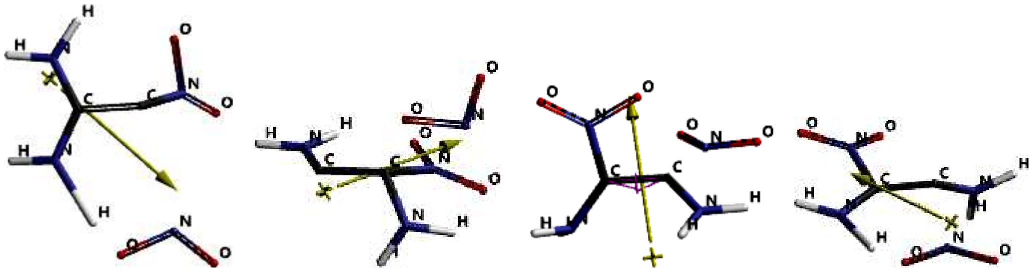
3. Results and Discussion

Fox-7 is a push-pull type structure. The amino groups present in its structure are capable of donating electrons whereas the nitro groups act as acceptors. In the *cis* and *trans* DADNE isomers this effect might be in varying extents. Note that the presently considered DADNE isomers are all isoconjugate with some even alternant hydrocarbon anions [44-46]. This phenomenon is discussed in the literature that non-Kekulé alternant hydrocarbon isoconjugates may engender explosive materials when are subjected to suitable carbon-heteroatom perturbations [47]. Fox-7, the geminal DADNE isomer, is a non-Kekulé system having $n^*=7$ and $\overset{o}{n}=3$ positions whereas the *cis* and *trans* isomers have $n^*= \overset{o}{n}=5$, thus they are isoconjugate with Kekulé systems (anions) (see refs. 44 and 45 for details of Kekulé and non-Kekulé systems). So, they are not expected, as a first approximation, to be explosive systems. However, they are worth investigating at the molecular level for mare scientific interest.

On the other hand, the initial step in thermal decomposition of nitro compounds is often the rupture of C-NO_2 or N-NO_2 bond [48]. The C-NH_2 bond is known to have a very high bond dissociation energy [49]. Therefore, in the present study only the homolytic C-NO_2 bond cleavage of DADNE isomers are considered. Figure 1 shows the optimized structures of DADNE isomers (parents) as well as the composite systems (daughters) obtained from them after the homolytic bond dissociation has occurred. The



Geminal *Cis* *Trans*



Geminal *Cis* A *Cis* B *Trans*

Figure 1. Optimized structures of the parents and the related transition states (daughters) considered.

figure also shows the directions of the dipole moment vectors. Figure contains two transition state structures for the *cis* form. Of those, *cis* A transition structure originally related to *cis* isomer (parent structure) but the program while obtaining the transition state modifies it (nevertheless called *cis* A) and the transition state eventually obtained does not preserve the *cis* configuration (see Figure 1 for the amino groups). When the double bond of parent structure is initially locked in the *cis* configuration the program yields *cis* B transition state structure. Table 1 includes the numerical magnitudes of the dipole moment vectors. The orders of dipole moments for the parents and the daughters are *geminal* > *cis* A = *cis* B > *trans* and *geminal* > *cis* B > *cis* A > *trans*, respectively.

Table 1. Dipole moments of the systems of present concern.

	Parents	**Daughters**
Geminal	8.53	7.62
***Cis* A**	6.66	2.84
***Cis* B**	6.66	6.77
Trans	0.00	2.53

In debye units.

Figure 2 shows the calculated bond lengths of the transition states considered. In all the cases carbon-carbon bond lengths fall into the domain of 1.40-1.48 Ǻ. Whereas an experimental value reported that it is in a substituted and conjugated nitroethylene, 1-bromo-1-nitro-2-piperidino-(cyclohexylamino)-2-phenylethene (the C=C bond length) is 1.399 Ǻ [50].

In Figure 2 in the *geminal* and *trans* cases, one of the N-H bonds is rather long than the other N-H bond on the same nitrogen atom and they have some tendency to form hydrogen bonding with oxygen atom of the departing NO_2 moiety. Then one of the N-O bonds of the departing NO_2 moiety elongates too.

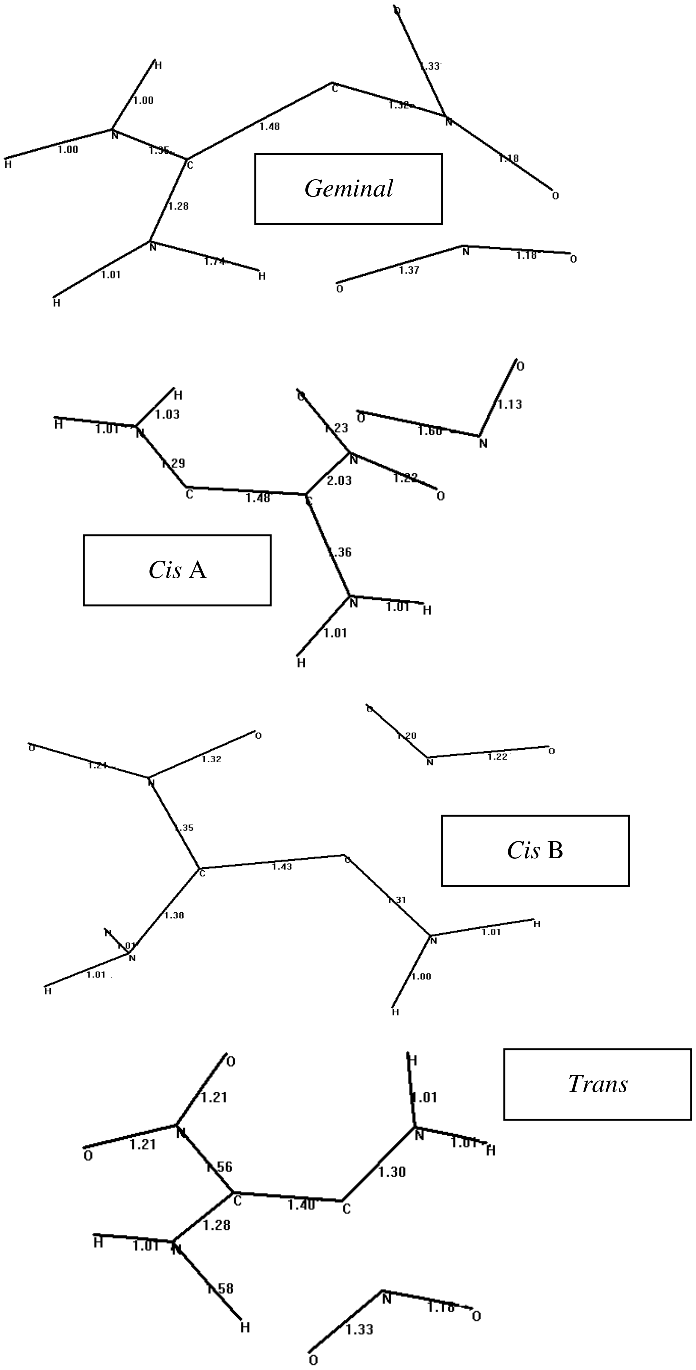


Figure 2. Calculated bond lengths (Å) of the transition states considered.

Figure 3 shows the IR spectra of the transition state structures considered. In the *geminal* case the weak peaks at 3701 and 3578 cm^{-1} stand for the asymmetric and symmetrical N-H stretchings belonging to the same NH_2 group. The peaks at 3501 cm^{-1} (weak) and 3116 cm^{-1} (very strong) are N-H stretchings of the other amino group. The one at 3116 cm^{-1} belongs to the hydrogen which bonds to NO_2 group departed. At 1783 cm^{-1} C-NO_2 stretching occurs. At 1670 cm^{-1} NH_2 bendings and C-NH_2 stretching of the other amino group happen.

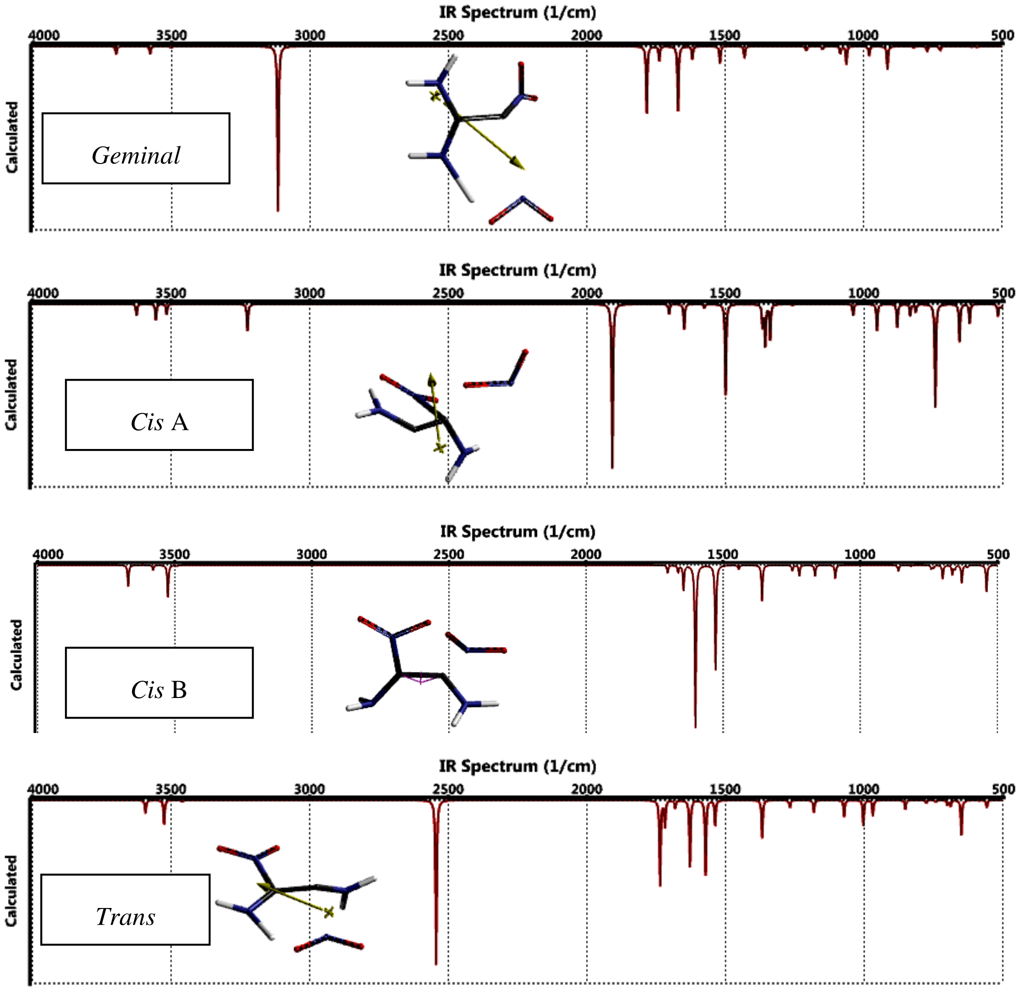
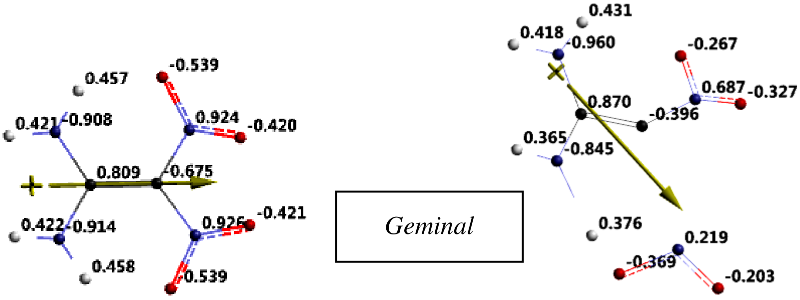


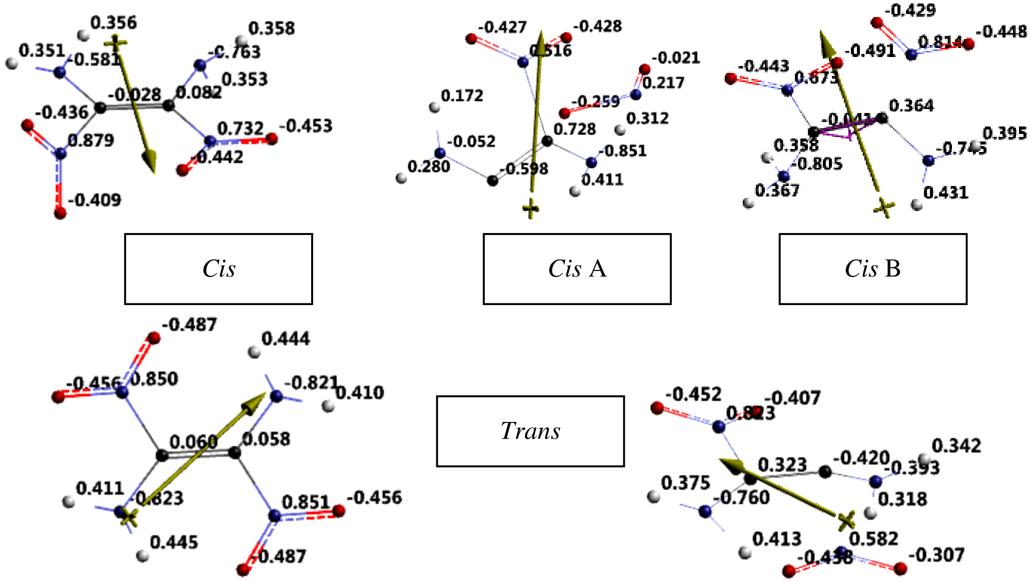
Figure 3. Calculated IR spectra of the transition states considered.

In the case of *cis* A transition state structure, various N-H stretchings occur in between 3625 and 3224 cm^{-1}. The N-O stretching of the departed NO_2 moiety occurs at 1908 cm^{-1}. The respective band for the other NO_2 group is at 1500 cm^{-1}. The spectrum of *cis* B is different from *cis* A. Note that although it is originally from *cis* parent and it is called *cis* A, it actually has *trans* form. The peaks for asymmetric and symmetrical N-H stretchings occur at 3670 cm^{-1} and 3525 cm^{-1}, respectively. The peak at 1601 cm^{-1} stands for N-O stretching overlapped with N-H scissoring. The C=C stretching coupled with various skeletal modes. As for the *trans* case, N-H stretchings occur 3592 cm^{-1} and 3525 cm^{-1} for different NH_2 groups. At 2544 cm^{-1} another N-H stretching (strong) happens. At about 1736 cm^{-1} various stretchings and bendings couple and overlap. The N-O stretchings are observed at 1628 and 1572 cm^{-1}.

Figure 4 shows the electrostatic potential (ESP) charges on the atoms of the transition state structures 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 [43].

The figure indicates that the NO_2 moiety in each case possesses some negative partial charge that is -0.353, -0.063, 0.063, -0.163 esu for the cases originated from *geminal*, *cis* A , *cis* B and *trans* isomers, respectively. The charge on the carbon atom from where NO_2 moiety is lost has the charge of -0.396, -0.598 and -0.420 esu, respectively for the isomers having the above mentioned sequence. Note that while a transition state progresses, some electron population can be conveyed from some other part of the molecule to the carbon atom at the terminus of the broken bond.




Cis

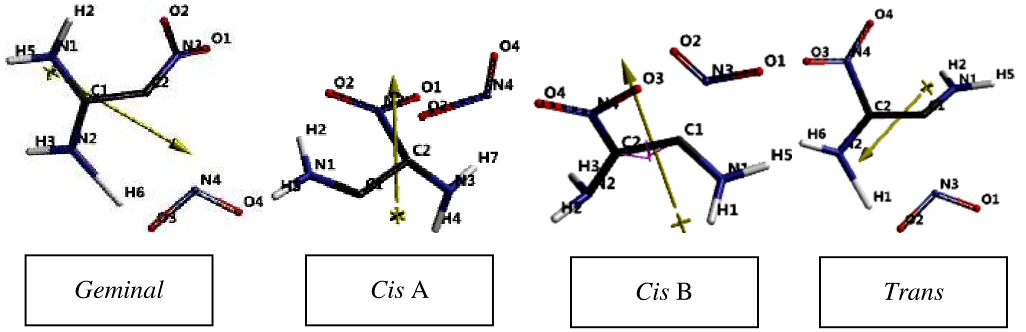
Cis A

Cis B

Trans

Figure 4. The ESP charges on atoms of the parent structures (left) and the transition states (right) considered.

Figure 5 shows the labeling of atoms of the transition state structures, a key to Table 2


Geminal

Cis A

Cis B

Trans

Figure 5. Labeling of atoms of the transition state structures.

which lists Mulliken bond orders and bond lengths. A careful inspection of Figures 1-5 indicates that in the case of transition state geometry, called *cis* A form, it is actually *trans* (in terms of amino groups) in spite of the fact that the parent structure was *cis*. In other words while the *cis* structure approaches the transition state as C-NO$_2$ bond homolytically cleaves (whatever the mechanism is) the structure turns about C1-C2 bond and owes the *trans* geometry. The Mulliken analysis shows that C1C2 bond is single in *cis* A structure but delocalized in the cases of *cis* B and *trans* forms.

Table 2 also indicates that *cis* A transition state structure has delocalized C1-N1 and elongated C2-N2 bonds (C-NO$_2$ is elongated to 2.03 Å).

Table 2. Mulliken bond orders and bond lengths of the transition state structures.

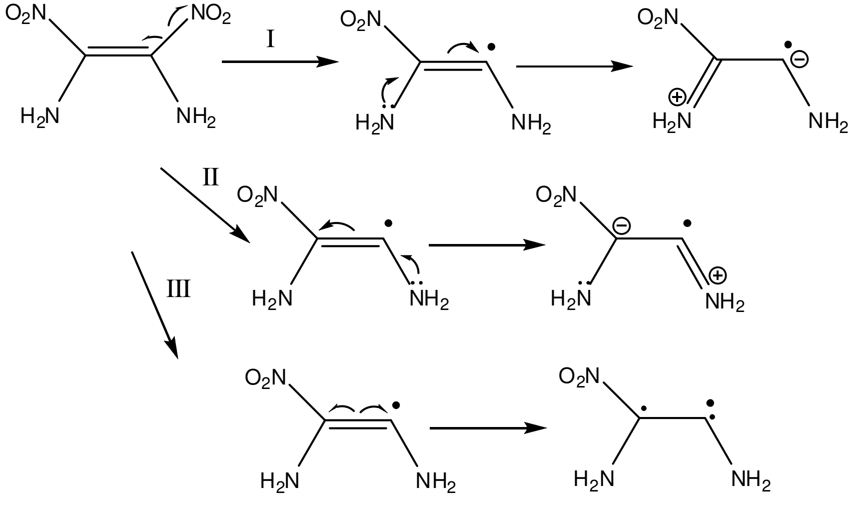
Bond	*Geminal*	
	Bond order	Bond length (Å)
C1 N1	1.205	1.3581 [single]
C1 N2	1.789	1.2841 [double]
C1 C2	1.426	1.4864 [deloc]
N1 H2	0.877	1.0087 [sing-H]
N1 H5	0.891	1.0072 [sing-H]
N2 H3	0.878	1.0183 [sing-H]
H6 O3	0.771	1.0018 [sing-H]
N3 O1	1.914	1.1878 [double]
N3 O2	1.165	1.3312 [single]
N3 C2	1.092	1.3252 [single]
O2 C2	0.838	1.7708 [single]
N4 O3	1.119	1.3738 [single]
N4 O4	2.019	1.1810 [double]

Cis A			*Cis* B		
Bond	Bond order	Bond length (Å)	Bond	Bond order	Bond length (Å)
C1 C2	0.966	1.4803 [single]	N4 O3	1.314	1.3297 [deloc]
C1 N1	1.524	1.2949 [deloc]	N4 O4	1.818	1.2186 [double]
C1 H2	0.063	2.0571 [Hbond]	N4 C2	1.066	1.3525 [single]
C1 H4	0.058	2.5098 [Hbond]	C2 N2	1.267	1.3850 [deloc]
C2 N3	1.198	1.3691 [single]	C2 C1	1.357	1.4333 [deloc]
C2 N2	0.588	2.0398 [single]	N2 H2	0.915	1.0129 [sing-H]
C2 O3	1.555	1.3480 [deloc]	N2 H3	0.908	1.0154 [sing-H]
N1 H2	0.767	1.0327 [sing-H]	C1N1	1.411	1.3149 [deloc]
N1 H5	0.873	1.0134 [sing-H]	C1 N3	0.651	1.5551 [single]
H2 O2	0.128	1.8866 [Hbond]	N1 H1	0.867	1.0088 [sing-H]
N3 H4	0.884	1.0117 [sing-H]	N1 H5	0.863	1.0141 [sing-H]
N3 H7	0.887	1.0150 [sing-H]	H5 O1	0.059	2.1601 [Hbond]
N2 O1	1.822	1.2218 [double]	N3 O1	1.772	1.2219 [double]
N2 O2	1.738	1.2373 [double]	N3 O2	1.925	1.2088 [double]
N4 O3	0.614	1.6059 [single]	N4 O3	1.314	1.3297 [deloc]
N4 O4	2.309	1.1362 [triple]			

Trans

Bond	Bond order	Bond length (Å)
C1 C2	1.494	1.4086 [deloc]
C1 N1	1.556	1.3018 [deloc]
C2 N2	1.651	1.2809 [deloc]
C2 N4	0.561	1.5691 [single]
N1 H2	0.851	1.0166 [sing-H]
N1 H5	0.871	1.0112 [sing-H]
N2 H1	0.109	1.5903 [Hbond]
N2 H6	0.845	1.0170 [sing-H]
H1 O2	0.719	1.0347 [sing-H]
H6 O3	0.067	2.2143 [Hbond]
N3 O1	2.1	1.1846 [double]
N3 O2	1.277	1.3367 [deloc]
N4 O3	1.852	1.2159 [double]
N4 O4	1.86	1.2166 [double]

Possible mechanistic routes to formation of the *cis* A transition state might be rationalized within the valence bond treatment as shown below where in path III electrons from the broken bond are shown in smaller size.



In each route, first vinylic type radical forms. In route I donation of electrons by the amino group, should form a radical anion but the electron pair of the anion and electron of the radical occupy different orbitals of the terminal carbon atom. Whereas in route II the electron pair and radical are on different carbons. Note that the anion formed in II is much better stabilized than the anion of route I because it is delocalized over a much larger space including the nitro group. Route III is less likely because it possesses three unpaired electrons. Note that electrons on the carbon atom of the reaction terminus occupy orthogonal orbitals, thus the initial vinylic radical does not gain extra stabilization by undergoing homolytic bond cleavage of the carbon-carbon double bond. Thus routes I and more likely route II result carbon-carbon single bond which allows rotation of the groups about it to access the *trans* orientation.

Table 3 shows the total electronic energy (E), zero point vibrational energy (ZPE) and the corrected total electronic energy (E_c) of the present parent structures. The order of E_C values is *geminal* < *trans* < *cis*. Note that the stability order is the reverse. These orders have to be dictated by the push-pull effects of the amino and nitro groups at different locations and different extents.

Table 3. Some energies of the parent structures.

Structure	E	ZPE	E_c
Geminal	-1571382.63	240.699871	-1571141.93
Cis	-1571317.89	239.235684	-1571078.65
Trans	-1571363.24	238.058343	-1571125.18

Energies in kJ/mol.

Whereas Table 4 displays some similar data for the transition state structures. This time the stability order based on E_c values is *cis* B > *cis* A > *trans* > *geminal*. It is note worthy that stability order of the composite systems (daughters) is parallel to the respective order of the parent structures.

Table 4. Some energies of the transition states considered.

Structure	E	ZPE	E_c
Geminal	-1571082.07	221.71	-1570860.36
Cis A	-1571189.37	226.70	-1570962.67
Cis B	-1571220.08	236.49	-1570983.59
Trans	-1571173.87	227.79	-1570946.08

Energies in kJ/mol.

Figure 6 displays distribution of some of the molecular orbital energies of the transition states considered. Whereas Table 5 shows the HOMO, LUMO energies and the interfrontier molecular orbital energy gaps (Δε) of the parent and daughter systems.

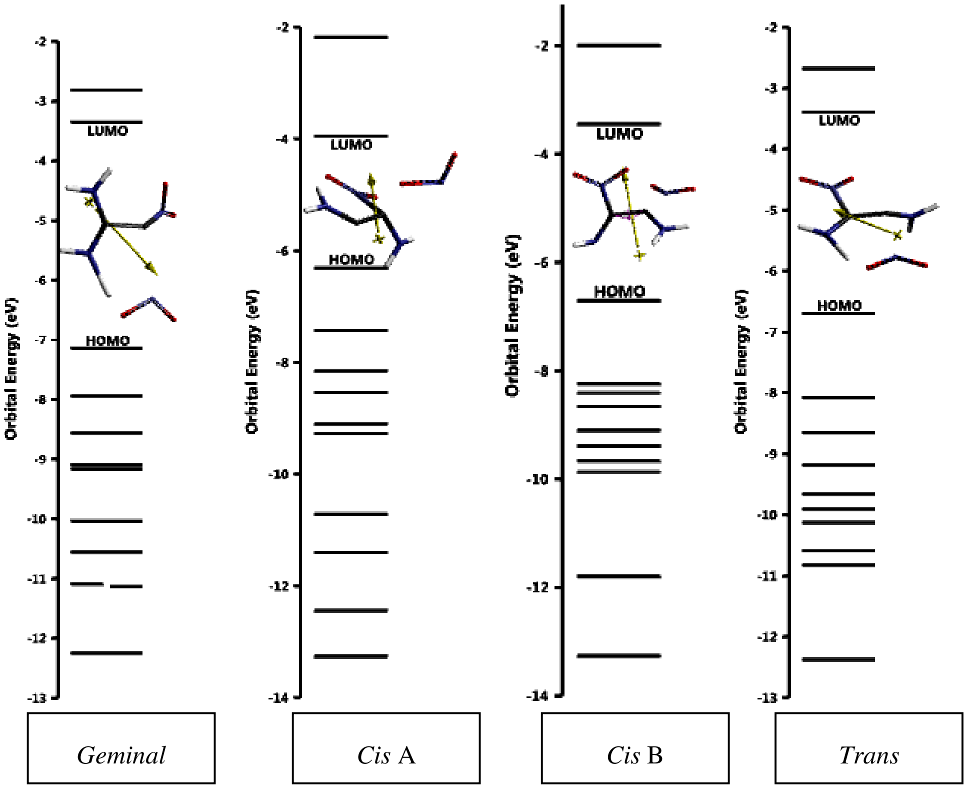


Figure 6. Some of the molecular orbital energies of the transition states considered.

The order of HOMO energies is *geminal* < *cis* < *trans* for the parents and *geminal* < *cis* B < *trans* < *cis* A for the daughter systems. As for the LUMO energies the order is *trans* < *cis* < *geminal* for the parents and *cis* A < *cis* B < *trans* < *geminal* for the daughters. Note that in the table the parents of *cis* A and *cis* B is the same. One more thing to be mentioned is that although *cis* A and *trans* daughters have *trans* orientation in terms of the NH_2 groups they are different.

Table 5. The HOMO, LUMO energies and Δε values of the structures of present concern.

Structure	**HOMO**	**LUMO**	Δε
Geminal	-724.45	-276.64	447.81
	-689.64	-324.10	365.54
Cis A	-717.60	-311.55	406.05
	-608.38	-381.38	227
Cis B	-717.60	-311.55	406.05
	-646.84	-332.34	314.5
Trans	-632.59	-381.93	250.66
	-646.81	-326.65	320.16

Energies in kJ/mol. In each row the first and second entries stand for the parent and daughter, respectively.

Figure 7 shows the HOMO and LUMO patterns of the transition states considered. As seen in the figure, in the case of *geminal* and *trans* transition structures the NH_2 groups either contribute little or nil into the HOMO because the overall electron pull effect should have been decreased due to the absence of departing NO_2 moiety. It is known that in general electron donors raise up the frontier molecular orbital energies and electron acceptors lower them. The overall electron pull-push effect is mainly dictated by the orientation of the groups and the conjugative possibilities. All these effects dictate the molecular orbital energies as well as shape the HOMO and LUMO patters.

Figure 8 shows the electrostatic potential maps of the transition states considered. In the figure the blue/bluish and red/reddish regions show the positive and negative potential regions, respectively.

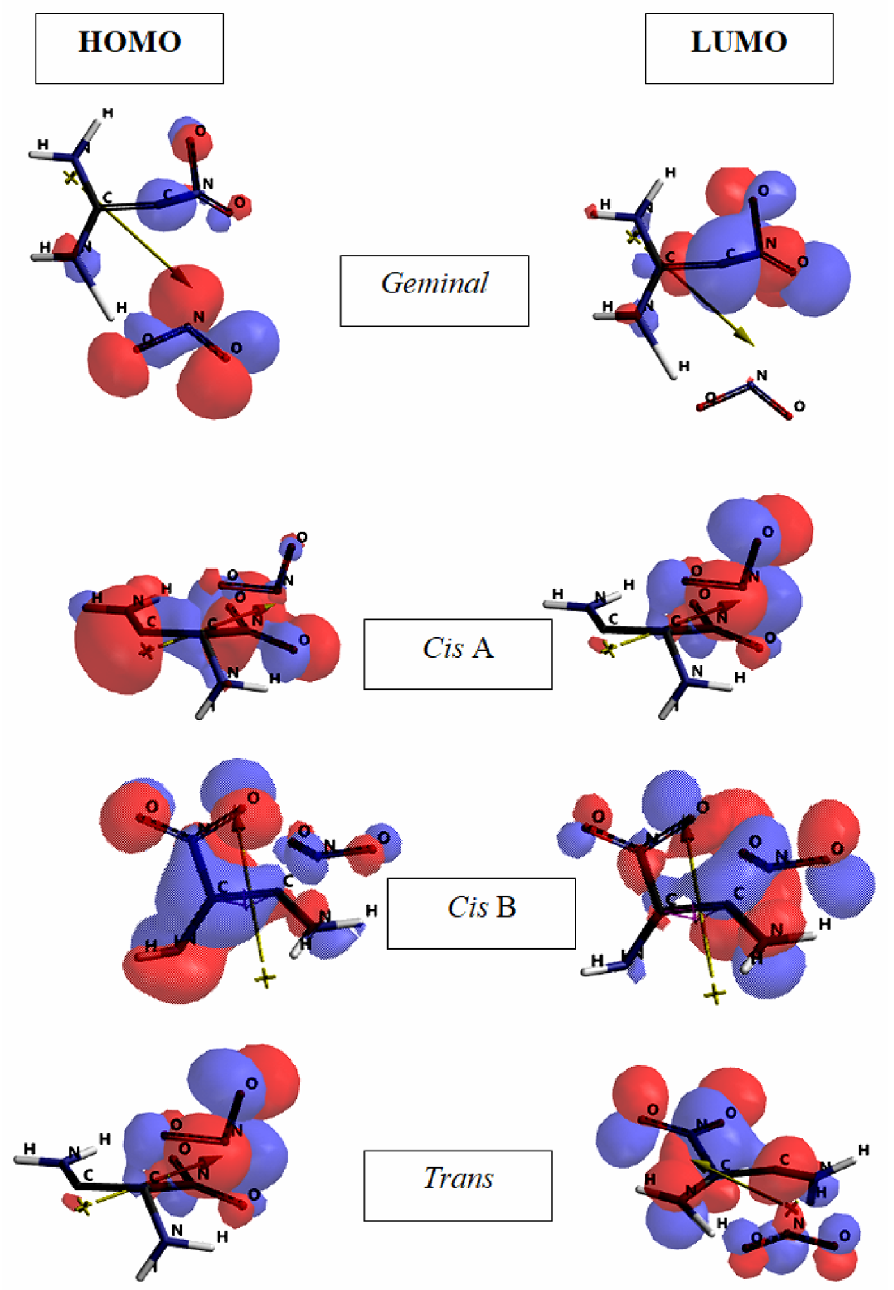


Figure 7. The HOMO and LUMO patterns of the transition states considered.

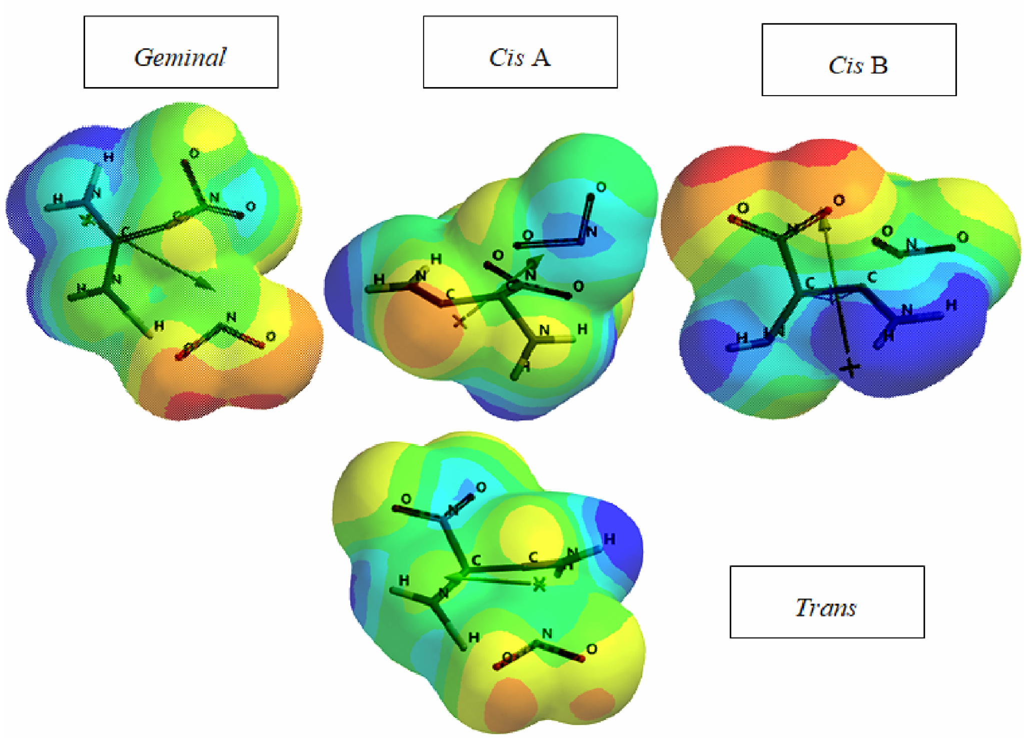


Figure 8. The electrostatic potential maps of the transition states considered.

Table 6 shows the activation energies of the homolytic dissociations considered. Whereas in Table 7 the $\Delta\overset{o}{G}^{\neq}$ values of the considered transition states are displayed.

Table 6. Activation energies of the homolytic dissociations considered ($R\text{-}NO_2 \longrightarrow R\bullet + \bullet NO_2$).

Geminal	*Cis* A	*Cis* B	*Trans*
281.5701	115.9843	95.06	179.1017

Energies in kJ/mol. Based on electronic energies. See Tables 2 and 3 for E_c values of the parent and the corresponding transition states, respectively.

Table 7. The $\Delta\overset{o}{G}^{\neq}$ values of the transition states considered.

Structure	**Parents ($\overset{o}{G}$)**	**Daughters ($\overset{o}{G}$)**	$\Delta G^{\neq}$
Geminal	-1571243.438	-1570968.288	275.1499
Cis A	-1571181.711	-1571068.992	112.7191
Cis B	-1571181.711	-1571086.011	95.7
Trans	-1571226.695	-1571050.501	176.1938

Energies in kJ/mol.

According to the data present in Table 7, $\Delta\overset{o}{G}^{\neq}$ values have the order of *geminal* > *trans* > *cis* A > *cis* B. Namely, *cis* B transition state is less activation energy demanding transition state. Consequently, *cis* B > *cis* A > *trans* > *geminal* order reflects the favorability of the homolytic dissociation of C-NO_2 bonds in the isomers considered. Namely, the homolytic cleavage of C-NO_2 bonds of the parents follow the order of *cis* > *trans* > *geminal*. Obviously, this order should be dictated by various configurational, conformational factors and charge and bond dipole effects in these isomeric structures.

4. Conclusion

Within the restrictions of density functional theory at the level of UB3LYP/6-311++G(d,p), the present investigation of the homolytic C-NO_2 bond cleavage of DADNE isomers has revealed that *cis* DADNE is the most, whereas the *geminal* one is the least susceptible parent structures. The transition state search for *cis* DADNE yields an unexpected configuration in which the amino groups occupy *trans* orientation. A plausible mechanisms has been suggested to explain the rotation about the carbon-carbon bond to generate *trans* configuration of the transition state structure. When the *cis* geometry of the parent compound is fixed, a transition state structure having the *cis* configuration is obtained which is electronically the most stable transition state whereas the *geminal* one (from FOX-7) has the least stable transition state (the most energetic). It requires the greatest activation energy among the isomers to undergo the homolytic C-NO_2 bond rupture.

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