Some DADNE Embedded Push-Pull Type Structures – A DFT Study

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Abstract

In the present study, some diaminodinitroethylene, (*geminal* (FOX-7) and *cis*-DADNE) embedded isomeric structures ($C_4H_2N_4O_6$) are considered. They are consisted of a five or a six-membered ring having DADNE moiety (linked across the amino groups of DADNE) and two exocyclic keto groups. The structures have been subjected to density functional treatment at the levels of B3LYP/6-31G(d,p) and ωB97X-D/6-31G(d,p). Some geometrical, quantum chemical, spectral and thermodynamic properties are obtained and discussed. Also bond dissociation energies for the scission of $C-NO_2$ bonds are calculated at the level of UB3LYP/6-311++G(d,p) and found that the DADNE embedded structures have less stable $C-NO_2$ bond as compared to FOX-7.

1. Introduction

In the presently considered structures one of the embedded subunits is FOX-7, (1,1-diamino-2,2-dinitroethylene, geminal DADNE), which is also known as DADNE or DADE [1]. FOX-7 was synthesized in 1998 by the Swedish Defense Research Agency (FOI) [2, 3]. A short time later, its explosive potential was thoroughly investigated [4-18]. Another approach to its synthesis involves the nitration of 4,6-dihydroxy-2-methylpyrimidine and then subsequent hydrolysis [19]. An isomer of FOX-7 is *vicinal* DADNE. Also *trans* DADNE is possible.

| FOX-7 *Geminal* DADNE | | *Vicinal (cis)* DADNE |
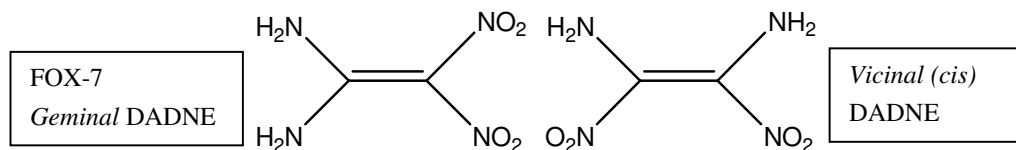
FOX-7 is a novel high-energy insensitive material having good thermal stability and low sensitivity. Although no structural resemblance exists among FOX-7, RDX and HMX they have the same C/H/N/O ratio. However, in terms of impact, friction, and electrostatic discharge sensitivities FOX-7 is much less sensitive than RDX [20].

Although structure of FOX-7 is simple, it surprisingly exhibits diverse and abundant chemical reactivity because of the amino and nitro groups it has (including coordination reactions, nucleophilic substitutions, electrophilic addition reactions, salification reaction, acetylate reactions, oxidizing and reduction reactions, etc., [21, 22]).

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

FOX-7 possesses many polymorphic forms. It is known that the α-form reversibly turns into β-form by heat treatment [23, 24]. Also, at higher temperature, β-polymorph exhibits an irreversible conversion to γ-phase which decomposes at 504 K [23]. Its decomposition has been extensively investigated [25]. Also the effect of high pressure on the crystal structure of FOX-7 has been searched [26].

So far many FOX-7 based propellant formulations have been studied in order to obtain a reduced or minimum smoke producing composite propellant with inherent insensitive munition properties [27].

On the other hand, thermo chemical calculations have been reported indicating that PBX's based on FOX-7 and energetic binders could serve as a replacement of Comp-B. Even at rather low solid loadings, such as a plastic bound explosive based on FOX-7 and an energetic binder have been prepared, [28].

Various ground state properties of FOX-7 were calculated based on B3LYP/aug-cc-pVDZ predictions [29]. The effects of nitration and epoxidation on ballistic properties of FOX-7 were also investigated within the realm of density functional theory (DFT) [30].

Laser ignitibility of FOX-7 was investigated in order to achieve the direct optical ignition of an insensitive explosive [31]. Also quite recently, some novel derivatives of FOX-7 (*geminal* DADNE) and their properties as energetic materials have been reported [32, 33].

In the present study, *geminal* or *cis*-DADNE embedded isomeric structures ($C_4H_2N_4O_6$) and some of their tautomeric forms are considered within the constraints of density functional theory (DFT).

2. Method of Calculation

Optimizations of all the structures leading to energy minima were initially achieved by using MM2 method and then 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 using various basis sets hierarchically. Then, the subsequent optimizations were managed within the framework of density functional theory [38, 39], finally at the level of RB3LYP /6-31G(d,p) [36] and ωB97X-D/ 6-31G(d,p) [40, 41]. The exchange term of B3LYP consists of hybrid Hartree-Fock (HF) and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [39, 42]. Note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [43] and Lee, Yang, Parr (LYP) correlation correction functional [44]. Also note that ωB97XD functional provides excellent geometries and energies. It has high HF percentage (ωB97XD is a long-range corrected functional), which helps mitigate the self-interaction error and the difficult excitation energies required for charge transfer reactions [40, 41].

The bond dissociation energy calculations have been done at the level of UB3LYP/6-311++G(d,p) level. For all the systems considered, the vibrational analyses were also done. The total electronic energies are corrected for the zero point vibrational energy (ZPE). The stationary points to energy minima were proved in all the cases by calculation of the second derivatives of energy with respect to the atom coordinates. 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 [45]. In the present treatment the calculations (except the bond

dissociation energy calculations) have been performed at the levels of B3LYP/6-31G(d,p) and ωB97X-D/ 6-31G(d,p). Note that in these two groups of calculations the basis set is common but the functionals are different.

3. Results and Discussion

3.1. *Structures and some properties*

In isomeric structures I and II ($C_4H_2N_4O_6$, MW: 202 g), *geminal* (FOX-7) and *vicinal* (*cis*)-diaminodinitroethylene), are respectively present as subunits. These structures have the oxygen balance (OB) value of −23.76 compared to −21.62 of FOX-7. They are supposed to be obtainable from the parent DADNE compounds by means of oxalyl chloride treatment.
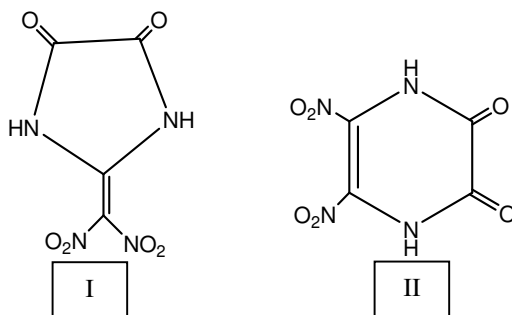

Figure 1 shows the optimized structures I and II as well as 1,3-tautomers of them. The figure also displays the directions of the dipole moment vectors. Structure II is different from the others because the direction of dipole moment vector is from the side of nitro groups to the six-membered ring. The same behavior is displayed in the case of ωB97X-D/ 6-31G(d,p) level of optimization (Figure 2). In *geminal* and *vicinal*(*cis*) DADNE the direction of dipole moment is from site of amino groups to the site of nitro groups. This is a normally expected push-pull behavior. Therefore, the situation in structure-II is odd. It seems that the amino groups in II are strongly under the effect of carbonyl groups and this effect might be assisted by the topology of the six-membered ring.

Figure 3 shows the bond lengths of the structures considered. The both level of calculations yield similar results for the bond lengths and the values are reasonable.
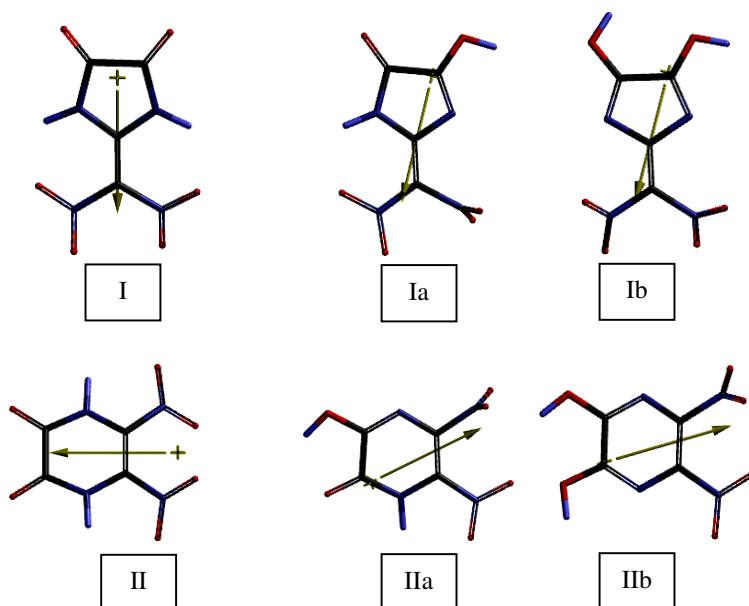
Figure 1. Optimized structures of the molecules considered (B3LYP/6-31G(d,p)).
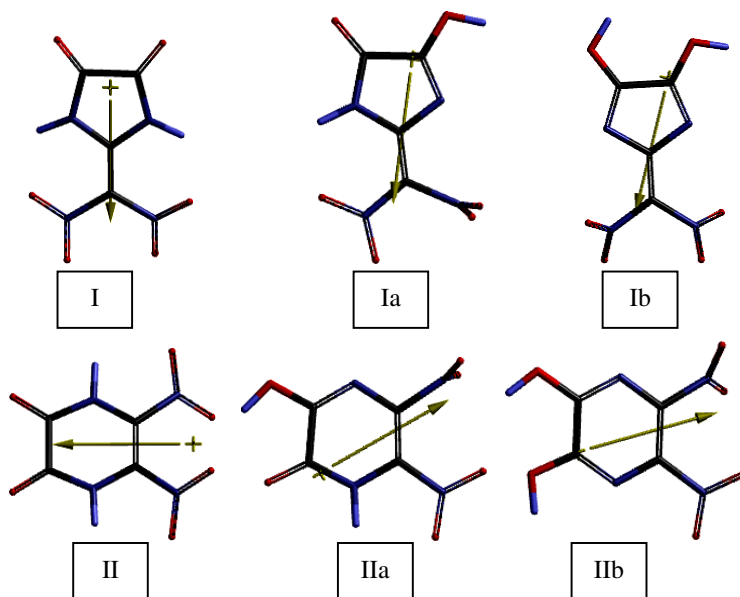
Figure 2. Optimized structures of the molecules considered (ωB97X-D/6-31G(d,p)).
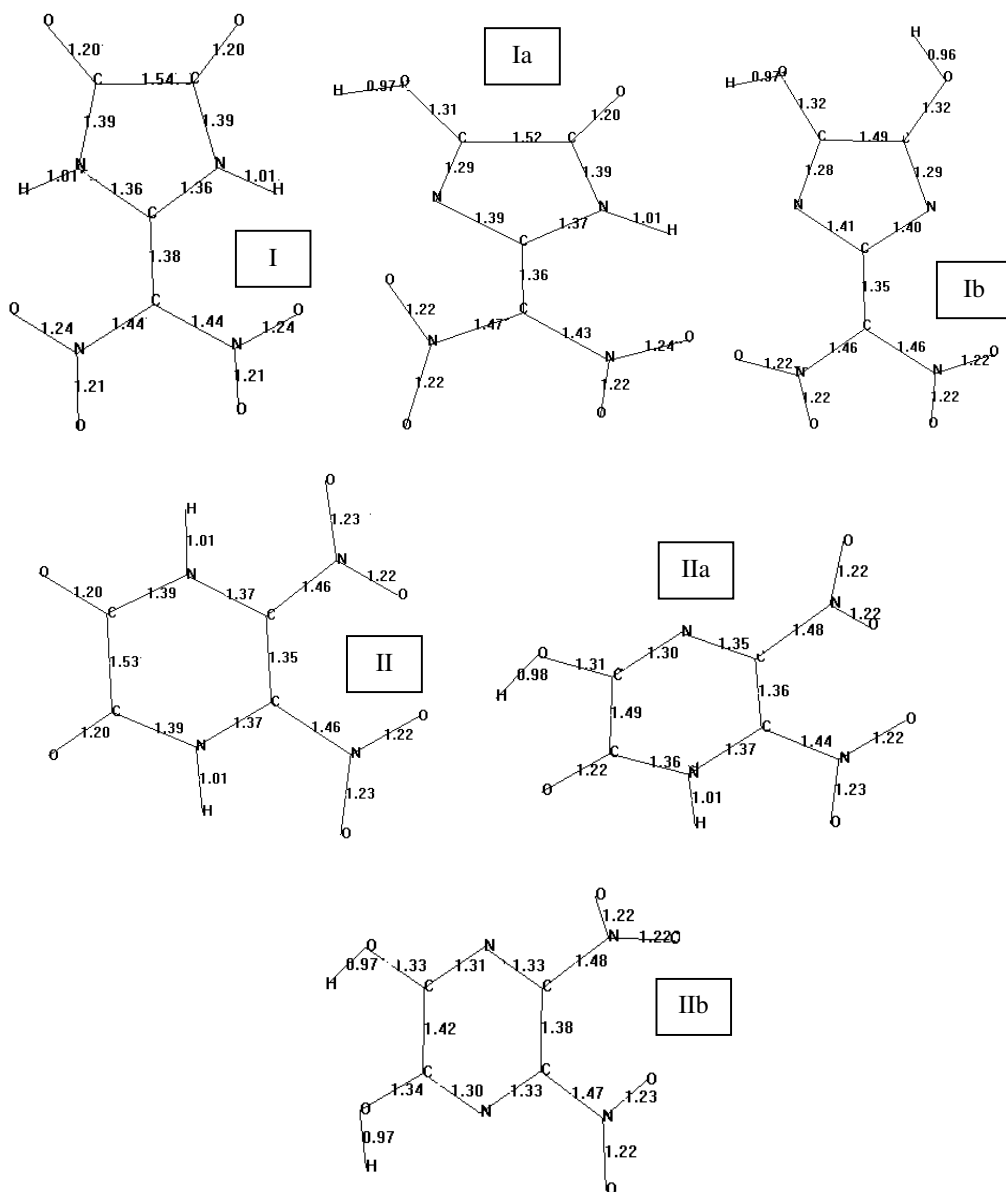
Figure 3. Bond lengths (Å) of the structures (B3LYP/6-31G(d,p)).

In Table 1 some properties of the structures are tabulated. Note that the tautomers of I (Ia, Ib) and II (IIa, IIb) have less heat of formation values as compared to the parent

structures. Also, structure-I is characterized with more negative ΔH_f° as compared to structure-II.

Table 1. Some properties of the structures considered.

			Structures			
Property	I	Ia	Ib	II	IIa	IIb
Area ($\mathring{A}^2$)	172.25	177.51	179.92	172.95	173.01	174.59
	(171.54)	(176.62)	(179.00)	(172.32)	(172.13)	(173.58)
Volume ($\mathring{A}^3$)	144.42	145.13	145.56	144.68	143.70	143.89
	(143.82)	(144.49)	(144.88)	(144.09)	(143.04)	(143.22)
Ovality	1.29	1.33	1.34	1.30	1.30	1.31
	(1.29)	(1.33)	(1.34)	(1.30)	(1.30)	(1.31)
Polarizability	52.07	52.25	52.27	52.32	52.14	51.98
	(51.10)	(51.29)	(51.29)	(51.34)	(51.17)	(50.99)
logP	-0.36	0.51	1.38	-0.36	0.51	1.38
	(-0.36)	(0.51)	(1.38)	(-0.36)	(0.51)	(1.38)
ΔH_f° (kJ/mol)	-244.842	-159.175	-49.124	-188.251	-169.079	-184.884

B3LYP/6-31G(d,p) level; ωB97X-D/6-31G(d,p) level of calculations are in parenthesis. ΔH_f° values from PM3//B3LYP/6-31G(d,p) level.

Figure 4 shows the electrostatic charges (ESP) for atoms of the structures. 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 [45]. The charge distribution in I or II is highly symmetrical. In the case of tautomers, the symmetry is lost which affects the charge distribution, e.g., the fulvene system in Ib has unsymmetrical charge distribution, even at NO_2 groups which are farthest away from the OH substituents.
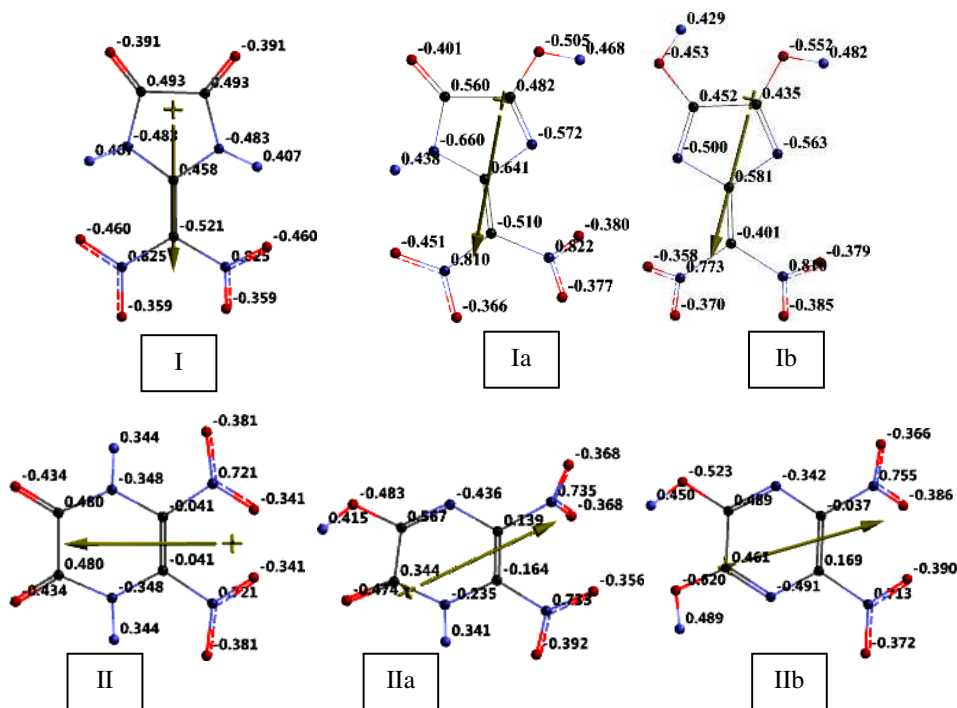
Figure 4. Electrostatic charges (ESP) on the atoms of the structures considered (ωB97X-D/6-31G(d,p) level).

3.2. *Energies and stabilities*

Table 2 shows the total electronic energy (E), zero point vibrational energy (ZPE) and the corrected total electronic energy (E_c) for the structures considered. Note that these structures are isomeric. Therefore, their E_c values can reflect their relative stabilities in someway. The stability order is I>IIa>II>IIb>Ia>Ib (B3LYP/6-31G(d,p) and I>IIa>IIb>II>Ia>Ib (ωB97X-D/6-31G(d,p)) (reverse order of E_c values). Structure-I appears to be more stable than structure-II, even though it has a five-membered ring which is expected to have more ring strain compared to a six-membered ring.

3.3. *IR spectra*

Figure 5 shows the IR spectra of the structures considered. Structures I and II possess the N-H stretching peaks at 3567 cm^{-1} and 3557 cm^{-1}, respectively. At 1886 cm^{-1}

Table 2. Various energies of the systems considered.

Structure	E	ZPE	E_c
I	-2162825.57	237.53	-2162588.04
	(-2162138.48)	(243.98)	(-2162626.44)
Ia	-2162760.48	237.02	-2162523.46
	(-2162070.77)	(243.33)	(-2162314.1)
Ib	-2162660.23	235.18	-2162425.05
	(-2161969.86)	(241.74)	(-2162211.6)
II	-2162782.97	237.61	-2162545.36
	(-2162093.22)	(243.98)	(-2162337.2)
IIa	-2162787.19	238.45	-2162548.74
	(-2162096.82)	(245.06)	(-2162586.94)
IIb	-2162766.14	236.72	-2162529.42
	(-2162078.34)	(243.35)	(-2162529.42)

Energies in kJ/mol. B3LYP/6-31G(d,p) level; ωB97X-D/6-31G(d,p) level of calculations are in parenthesis.

asymmetrical C=O stretching of I and at 1840 cm^{-1} symmetrical stretching of II occur. The C=C bond stretches at 1670 cm^{-1} and 1652 cm^{-1} in structures I and II, respectively. In the case of tautomers, O-H stretching occurs at 3736 cm^{-1} and 3588 cm^{-1} in structures Ia and IIa, respectively. The C=O bond vibrates at 1872 cm^{-1} in structure-I. The corresponding value is 1875 cm^{-1} for structure-II. The C=C vibration in I is coupled with the skeletal breathing of the ring at 1674 cm^{-1} whereas it occurs at 1687 cm^{-1} in II. In the case of structures –Ib and –IIb, the O-H stretchings occur in the region of 3792-3760 cm^{-1}.

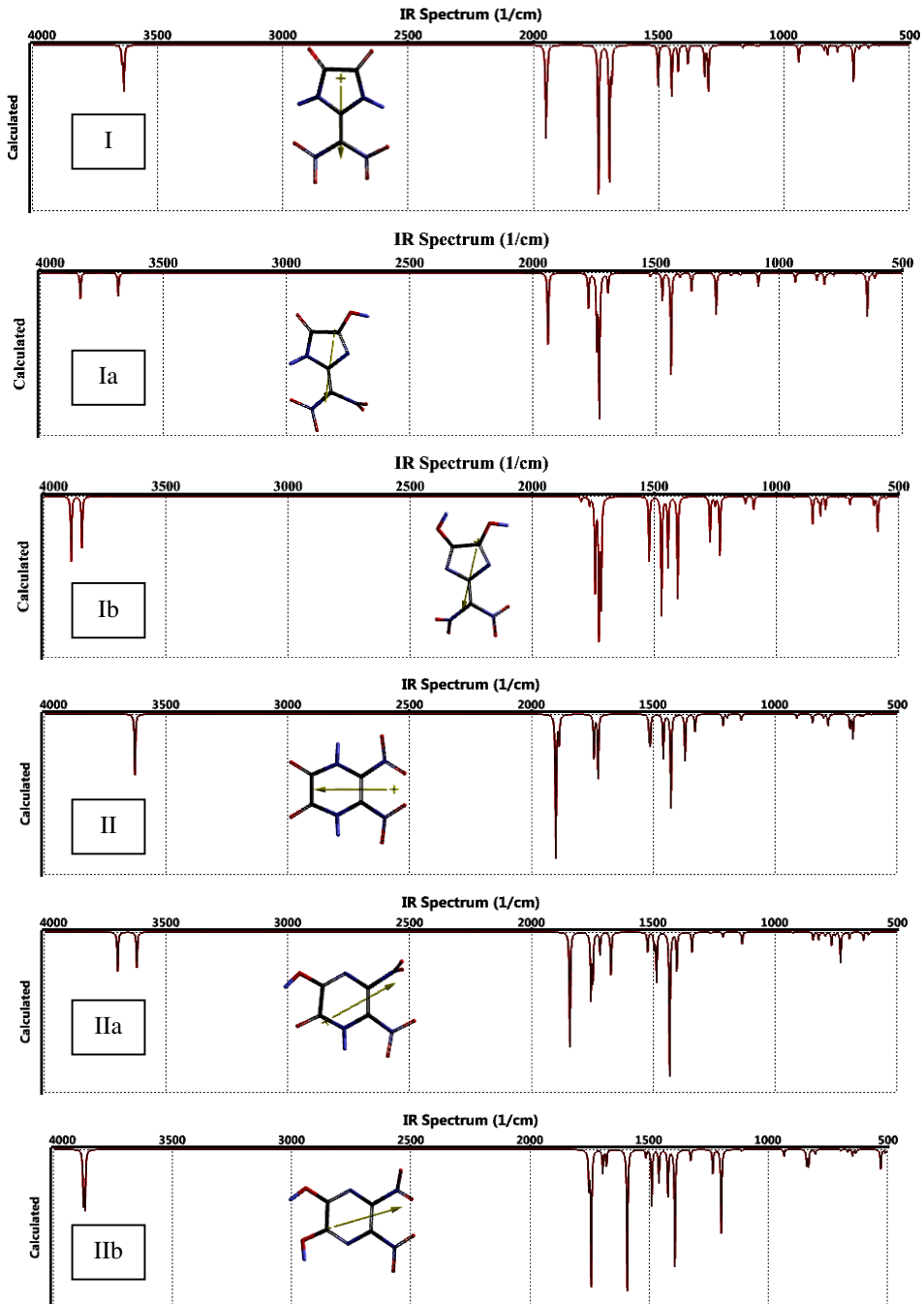**Figure 5.** IR spectra of the structures considered (ωB97X-D/6-31G(d,p) level).

3.4. *Thermodynamical properties*

Table 3 contains some thermodynamical properties of the structures according to the level of calculations have been performed. The $H°$ and $G°$ values follow the order of I<IIa<II<IIb<Ia<Ib. The variations of $H°$ among these structures arise from the variations in their internal energies (U) and molar volumes (V) by $H° = U+PV$ [46]. As for the variations in $G°$ values also the entropy factor contributes as $G° = H° + TS°$.

Table 3. Some thermochemical properties of the structures considered.

| Structures	Property			
	$H°$ (kJ/mol)	$S°$ (J/mol)	$G°$ (kJ/mol)	Cv (J/mol)
I	-2162579.68	405.73	-2162700.65	128.63
	(-2161886.46)	(404.04)	(-2162006.92)	(126.57)
Ia	-2162514.814	414.25	-2162638.324	129.72
	(-2161819.091)	(412.57)	(-2161942.103)	(127.90)
Ib	-2162415.808	417.05	-2162540.155	130.18
	(-2161719.224)	(414.96)	(-2161842.944)	(128.33)
II	-2162536.83	412.62	-2162659.85	129.56
	(-2161840.93)	(410.89)	(-2161963.44)	(127.92)
IIa	-2162540.47	410.95	-2162663.00	128.45
	(-2161843.82)	(408.83)	(-2161965.72)	(126.56)
IIb	-2162520.61	413.62	-2162643.94	130.10
	(-2161826.56)	(411.13)	(-2161949.14)	(128.00)

B3LYP/6-31G(d,p) level; ωB97X-D/6-31G(d,p) level of calculations are in parenthesis.

3.5. *Molecular orbital energies*

Figure 6 shows some of the molecular orbital energy levels of the structures considered. As seen in the figure an isomeric variation in the embedded DADNE moiety makes structures I and II to have highly different molecular orbital energy spectra. The

NEXTHOMO level of structure-I is more closely spaced to its HOMO as compared to the case of its tautomers Ia and Ib. A similar case is valid for the NEXTLUMO and LUMO levels. As for the case of structure-II and its tautomers the NEXTHOMO of II is closer to the HOMO as they are in the tautomers. On the other hand, structure-IIb has noticeable closely spaced LUMO and NEXTLUMO levels.
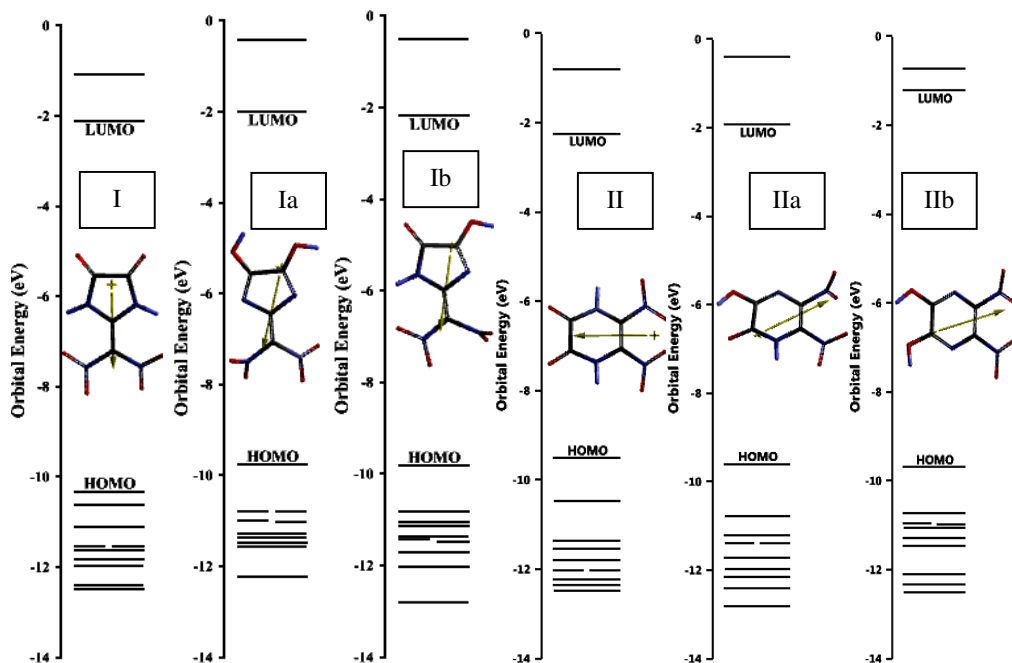
Figure 6. Some of the molecular orbital energy levels of the structures considered (ωB97X-D/6-31G(d,p)).

Table 4 includes the HOMO, LUMO energies and the interfrontier molecular orbital energy gaps ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$). The HOMO energy order is I<Ia<Ib~IIb<IIa<II. The LUMO energies follow the order of II<Ia<I<Ib<IIa<IIb. Consequently, the order of $\Delta\varepsilon$ values become IIb>I>Ib>Ia>IIa>II (B3LYP/6-31G(d,p). At the level of ωB97X-D/6-31G(d,p) the same order of $\Delta\varepsilon$ values holds except IIa>Ia. When the values for structurally main isomers, I and II, are compared, one observes that the six-membered ring having isomer (II) has higher HOMO but lower LUMO energy as compared to the five-membered ring owner isomer (Ia), so going from five to six-membered ring $\Delta\varepsilon$ decreases.

Table 4. The HOMO, LUMO energies and Δε values.

Structure	HOMO	LUMO	Δε
I	-799.15	-381.93	417.22
	-996.69	-203.48	793.21
Ia	-751.69	-384.64	367.05
	-947.86	-209.63	738.23
Ib	-741.75	-368.91	372.84
	-942.18	-191.88	750.3
II	-726.53	-403.55	322.98
	-917.75	-216.60	701.15
IIa	-732.77	-367.93	364.84
	-926.55	-186.77	739.78
IIb	-741.12	-308.31	432.81
	-935.80	-117.97	817.83

Energies in kJ/mol. The first and second entries in each row stand for B3LYP/6-31G(d,p) and ωB97X-D/6-31G(d,p) level of calculations, respectively.

It has been reported that as the HOMO-LUMO energy gap (Δε) decreases, the explosive becomes more sensitive to impact [47-51]. Therefore, structure-II is expected to be more sensitive to impact stimulus than structure-I.

3.6. *UV-VIS spectra*

Figure 7 shows the UV-VIS spectra of the structures considered. As seen in the figure, structure-II absorbs at relatively higher UV region as compared to structure-I which has an exocyclic carbon-carbon double bond. The nitrogen atoms embedded in the five-membered ring of structure-I seem to be less willingly to denote electrons to ethylenic or carbonyl chromophore(s) in order to extend the conjugation, thus to cause a bathochromic effect (shift) to longer wavelenghts. This might be due to the presence of more ring strain present in the five-membered ring as compared to the six-membered ring of structure-II. Structure-II is characteristic because it does not have any shoulder albeit the fact that the others have.
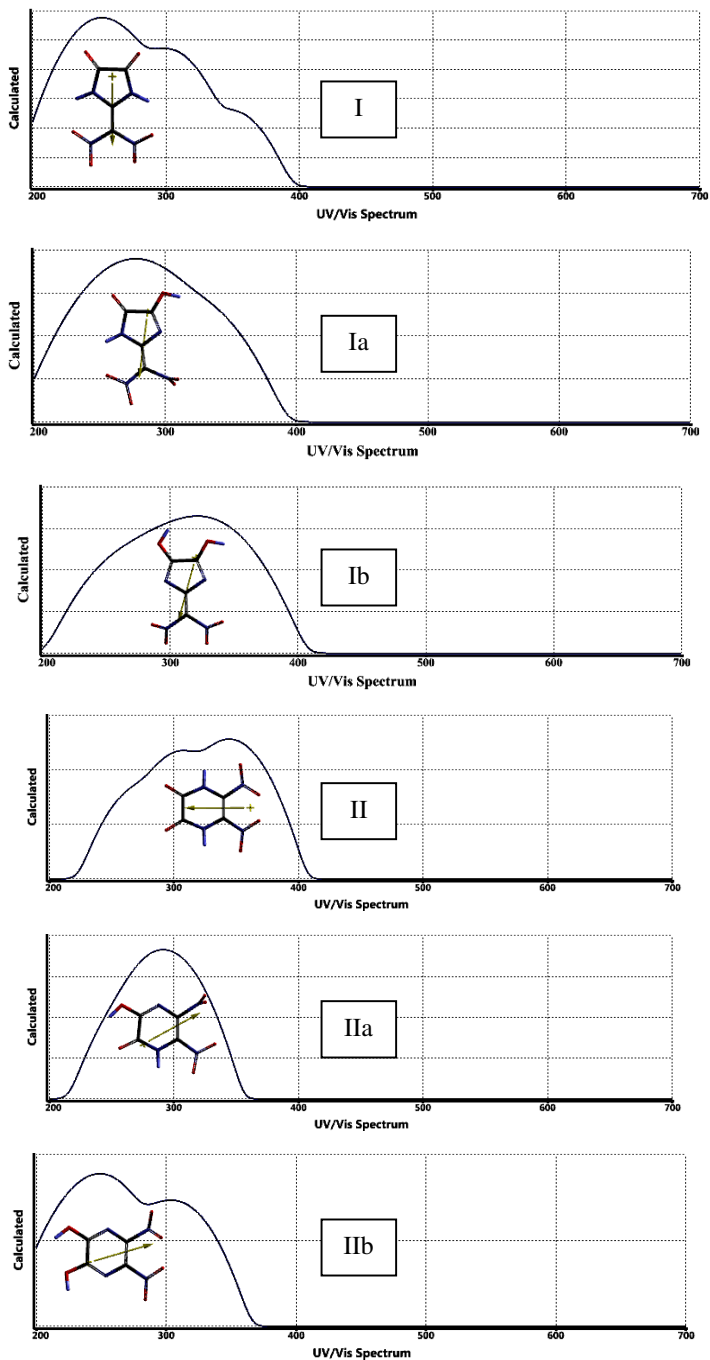
Figure 7. UV-VIS spectra of the structures considered (ωB97X-D/6-31G(d,p) level).

Figure 8 displays the electrostatic potential maps of the structures considered. In structures I and II, central part of them is characterized with some positive potential whereas various degree of negative potential reside on the keto-oxygens and nitro-oxygens. In the tautomers, the negative potential regions spread over greater part of the structures at the expense of positive potential regions.
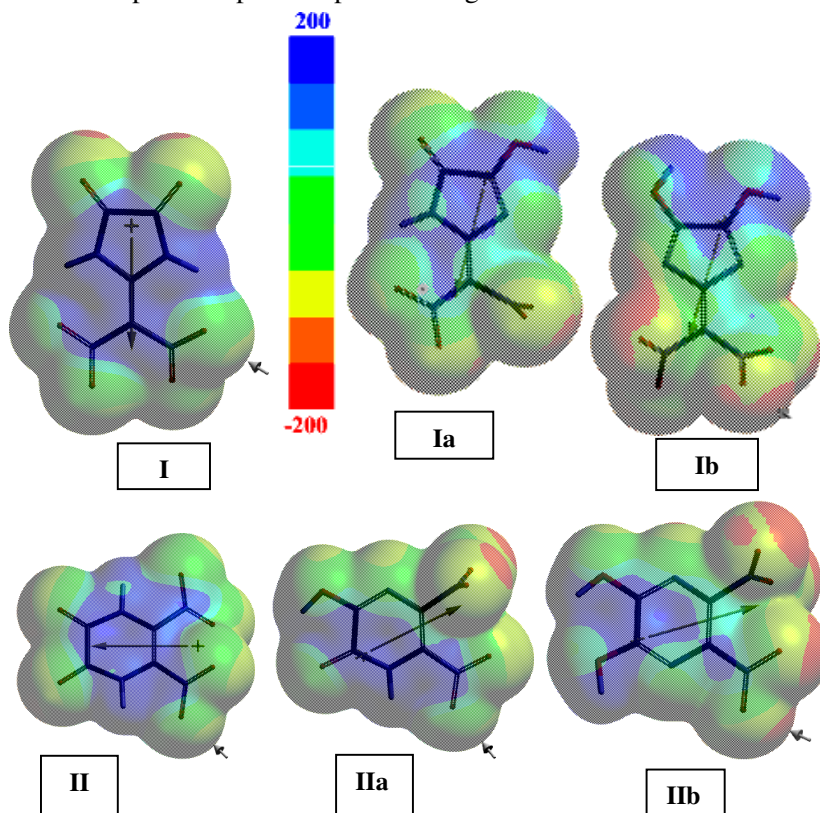
Figure 8. Electrostatic potential maps of the structures considered (B3LYP/6-31G(d,p)).

3.7. *Bond dissociation energies*

The sensitivity of an energetic material under different heat, impact, friction conditions may vary. Impact sensitivities of energetic compounds can be examined experimentally by physical tests, particularly drop height test. Additionally, there are theoretical methods for the computational determination of the impact sensitivity. Murray et al., [52] have indicated that there is an association between the bond dissociation energies (BDEs) of the nitro bonds and the electrostatic potentials on the molecular surfaces of some energetic molecules. In the literature there are several

appreciated studies [53-56] on the homolytic BDE of the nitro compounds such as nitroaromatic and nitramine molecules. They have indicated that there is a parallel correlation between the BDE for the weakest nitro bond scission in the molecule and its impact sensitivity. The typical tendency is that the larger the homolytic BDE value for scission of nitro bond, the lower the sensitivity is.

Numerous experimental studies show that nitramine (N-NO$_2$) bond homolysis is the initial step in the thermal decomposition of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and other nitramines [57-61]. In the present study, in order to compare the C-NO$_2$ bond strengths of the compounds, homolytic bond dissociation energy (BDE) calculations considering the removal of nitrogen dioxide moiety from the parent structures were performed at UB3LYP/6-311++G(d,p) level of theory. 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 [62]. The expressions for the homolysis of R–NO$_2$ bond and for calculating its homolytic BDE are shown as follows,

$$R-NO_2(g) \rightarrow R^{\cdot}(g) + NO_2^{\cdot}(g) \tag{1}$$

$$BDE(R-NO_2) = [E_R^{\cdot} + E_{NO_2}^{\cdot}] - E_{(R-NO_2)} \tag{2}$$

where R–NO$_2$ denotes the neutral molecule and R$^{\cdot}$ and NO$_2^{\cdot}$ stand for the corresponding product radicals after the bond dissociation. The BDE(R–NO$_2$) is the bond dissociation energy of the bond R–NO$_2$ whereas E(R–NO$_2$), E(R$^{\cdot}$) and E(NO$_2^{\cdot}$) are the zero-point energy corrected total energies of the parent compound and the corresponding radicals, respectively [63-65].

Table 5 shows various energies of the systems considered in bond dissociation energy calculations. At UB3LYP/6-311++G(d,p) level of calculations structure-I appears to be more stable than structure-II (same as the results of previous level of calculations). The radicals from structures-I and II possess stability order of I(R)>II(R). Figure 9 shows the optimized structures of these radicals.

The bond dissociation energies of FOX-7 and structures I and II are shown in Table 6. As seen there, the bond dissociation energies follow the order of II < I < FOX-7,
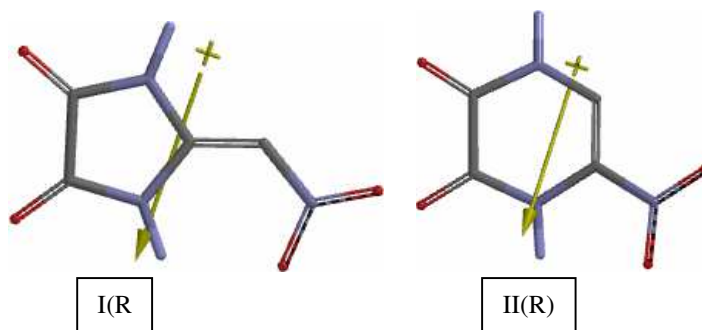
Figure 9. Optimized structures of radicals I(R) and II(R).

Table 5. Various energies of the systems considered in bond dissociation energy calculations.

Structure	E	ZPE	E_c
FOX-7	-1571382.65	240.80	-1571141.85
FOX-7 (R)	-1032511.29	199.89	-1032311.4
I	-2163466.62	235.99	-2163230.63
I(R)	-1624613.13	195.87	-1624417.26
II	-2163424.44	235.50	-2163188.94
II(R)	-1624600.64	196.26	-1624404.38
$NO_2(R)$	-538597.24	23.03	-538574.21

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

namely FOX-7 structure is less likely to undergo $C-NO_2$ bond cleavage by certain stimulus. As pointed out in section 3.2, structure-I is over all more stable than structure-II and its $C-NO_2$ bond is more stable than the respective bond of structure-II.

Table 6. The $C-NO_2$ bond dissociation energies of some of the structures considered.

Structure	BDE
FOX-7	256.24
I	239.16
II	210.35

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

4. Conclusion

In the present study, some diaminodinitroethylene, (*geminal* and *cis*-DADNE) moiety embedded isomeric structures and some of their tautomers are considered. Their oxygen balance values are slightly less than the respective value of FOX-7. Structure-I having a five membered ring system is more stable than structure-II which has a six-membered ring. Structure-I has lower HOMO energy than II but the reverse is true for the LUMO energies. Consequently, the interfrontier molecular orbital gap is narrower for II compared to I. Then, the later one is expected to be more sensitive to impact stimulus. On the other hand, tautomer IIa is more stable than structure-II: So it is expected to accompany structure-II in various concentrations depending on the conditions.

On the other hand, BDE calculations have revealed that C-NO$_2$ bond in FOX-7 is more stable than the others (and C-NO$_2$ bond in structure-I is more stable than it is in structure-II). So, five or six-membered ring building across the NH$_2$ groups of FOX-7 results completely different isomeric structures in terms of stability and energy, thus very different behavioral aspects emerge.

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