

Atrans-Dinitrodiazenufuroxan Isomers-A DFT Treatise

Lemi Türker

Middle East Technical University, Department of Chemistry, Üniversiteler, Eskişehir Yolu No:1, 06800
Çankaya/Ankara

lturker@metu.edu.tr, lturker@gmail.com

Abstract:

1,2,5-oxadiazols (furoxanes) and their N-oxides are high-energy compounds. 4,4'-Dinitro-3,3'-diazenufuroxan is a powerful high-density high-explosives with performance comparable to that of other high-density high-explosives. Presently, isomers of trans-dinitrodiazenufuroxan are considered at the levels of B3LYP/6-31G (d, p) and B3LYP/cc-PVTZ. Various geometrical and quantum chemical characteristics obtained are discussed. For the density calculations and mono ionic forms of these isomers UB3LYP/6-31G(d,p) and UB3LYP/6-31+G(d) type calculations have been performed, respectively. These ionic species are also found to be stable. Calculated IR, UV-VIS, and ^{13}C spectra are discussed.

Keywords: Diazenufuroxan, Furoxans, Nitrofuroxan, High Explosives, Density Functional Theory, Spectra.

Introduction

Among high-energy (HE) compounds, of special interest 1,2,5-oxadiazols (furoxanes) and their N-oxides [1-3]. Furoxans are convenient building blocks (synthones) of molecules of powerful explosives. The addition of explosophoric groups to furoxans results in a number of highly effective compounds. This is due to the fact that the furoxan ring has a flat structure, which provides high density and is characterized by a positive enthalpy of formation. The element composition of the furoxan cycle in latent form is similar to that of the nitrozo groups with weak nitrogen–oxygen bonds, in contrast to the strong nitrogen–oxygen bonds in the nitro groups of nitro compounds. The high positive enthalpy of formation of furoxan compounds is due to the presence of active oxygen atoms in the furoxan cycle and the low energy of binding of oxygen atoms to nitrogen. Thermo chemical studies [4-9] have made it possible to reveal the high endothermic enthalpy of formation of compounds of the furoxan series and, based on experiment, to evaluate the dissociation energy of the nitrogen–oxygen bond to be equal to 240–255 kJ/mole [4-9]. Xia et al., computationally investigated the properties of double furazan-based and furoxan-based energetic materials [10].

The study of the detonation parameters has shown that explosives of the furoxan series have a wide range of power and detonation characteristics and a breakthrough detonation velocity of 10 km/sec, (for single crystal density of 2.00 g/cm³) which even surpasses the detonation velocity of HMX [11]. Powerful explosives of the furoxan series have a common drawback of high sensitivity [12]. However, relatively safe explosives in this series can be designed by reducing the power, stabilizing the molecules, and introducing amino groups capable of forming hydrogen bonds.

Dinitrodifuroxanyl (C₄N₆O₈) belongs to the class of hydrogen-free explosives of furoxan series [12]. It substantially exceeds HMX in both the density and detonation velocity. 4,4'-Dinitro-3,3'-diazenufuroxan obtained by Ovchinnikov et al., [13] is an analogue of dinitrodifuroxanyl, but its molecule contains one extra explosophoric group, azo group. This compound is considered to be the most powerful among the existing explosives. Experimental data on explosion excitation and detonatability [14] are indicative of its high sensitivity and explosiveness.

Dinitrodiazenufuroxan is an example of how a high energy content due to weak chemical bonds, which manifests itself in an extremely high enthalpy of formation, on the one hand, provides record detonation characteristics and, on the other, makes the HE unsuitable for practical use [15]. 4,4'-Dinitro-3,3'-diazenufuroxan (DDF) is a powerful experimental high explosive with performance comparable to that of other

high-density high-explosives such as octanitrocubane. It is synthesised by oxidative coupling of 4-amino-3-(azidocarbonyl)furoxan followed by Curtius rearrangement and further oxidation.

Coburn studied synthesis and unusual NMR spectra of 4,4'-dinitro-3,3'-bifurazanyl-4,4'- ^{13}C [16].

In the present study, *trans*-dinitrodiazenofroxane constitutional isomers have been investigated quantum chemically in the realm of density functional theory (DFT).

Method of calculation

In the present treatise, the geometry optimizations of the structures under consideration leading to energy minima were achieved by performing MM2 molecular mechanics calculations followed by PM3, HF (using hierarchical order of basis sets) and then closed shell density functional theory (DFT) [17] calculations using B3LYP hybrid exchange-correlation potential [18] employing 6-31G(d,p) and cc-PVTZ basis sets [19,20]. 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 [21]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [22] and Lee, Yang, Parr (LYP) correlation correction functional [23]. The BLYP method gives a better improvement over the SCF-HF results. The optimizations in the present study have been obtained by the use of SPARTAN 06 program [24]. For the density calculations UB3LYP/6-31G(d, p) treatment was employed. ^{13}C shift values were calculated at the level of B3LYP/6-31G(d, p). For the charged forms of the isomers UB3LYP/6-31+G(d) level of calculation was adopted.

Results and discussion

Structures

Three constitutional isomers of *trans*-dinitrodiazenofroxane are differentiated. They have 4,4'-, 3,4'- and 3,3'-azenefuroxan backbone having mononitro isomers (see Figure 1). The first and third ones are symmetrical structures whereas the second one asymmetrical structure based on the furoxanyl rings. Actually, arising from the positions of the nitro group and the point of linkage to azo bridge. Figure 1 indicates that in each optimized structure, the furoxanyl groups are not coplanar but oblique with respect to each other.

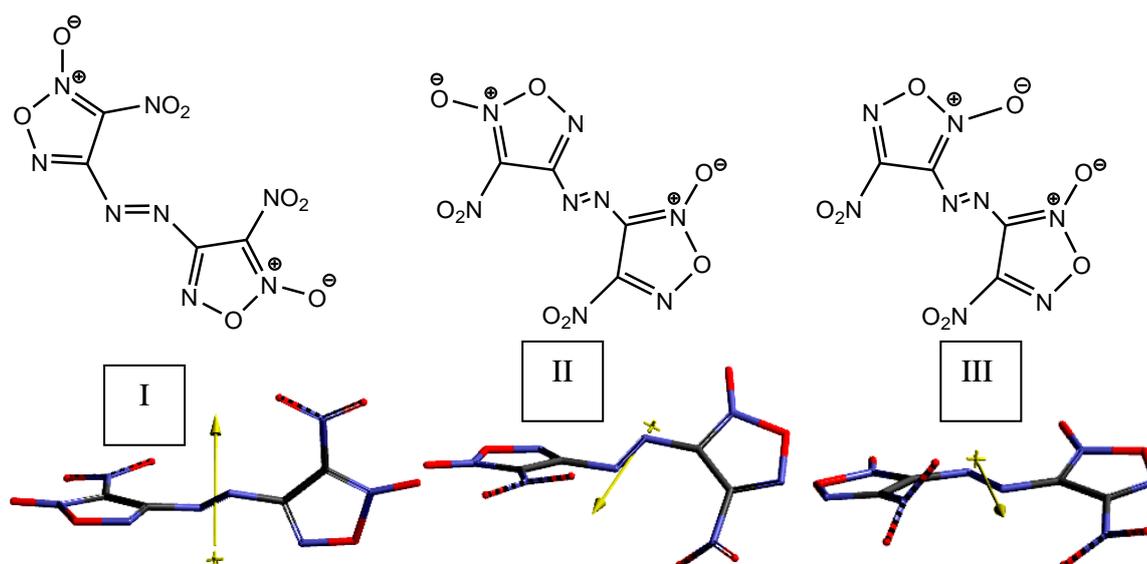


Figure 1. The isomers and their optimized structures of the present concern (B3LYP/6-31G(d, p)). All belong to C1 point group).

trans-Dinitro diazenofrozan and its constitutional isomers are analogous to benzofurozan (BFO). Some chemistry of such compounds has been reported in the literature [25]. Some computational studies on BFO also exist in the literature [26-28]. Zhu et al., using B3LYP/6-311+G (d, p) level of density functional theory calculated some quantum chemical properties of CL-14 and some others which possess furozan ring system [29].

Furozan ring undergoes ring opening and reclosure in certain substituted benzofurozans to give isomeric compounds [30-32]. In that sense, structure I and II are possibly interconvertible to each other. Structures II and III should be also interconvertible via ring opening and reclosure processes. Therefore, via structure II structures I and III might be interconvertible.

Figure 2 displays the bond lengths of the structures considered. The data reveal that the bond lengths are highly structure dependent but varies little for each bond considered.

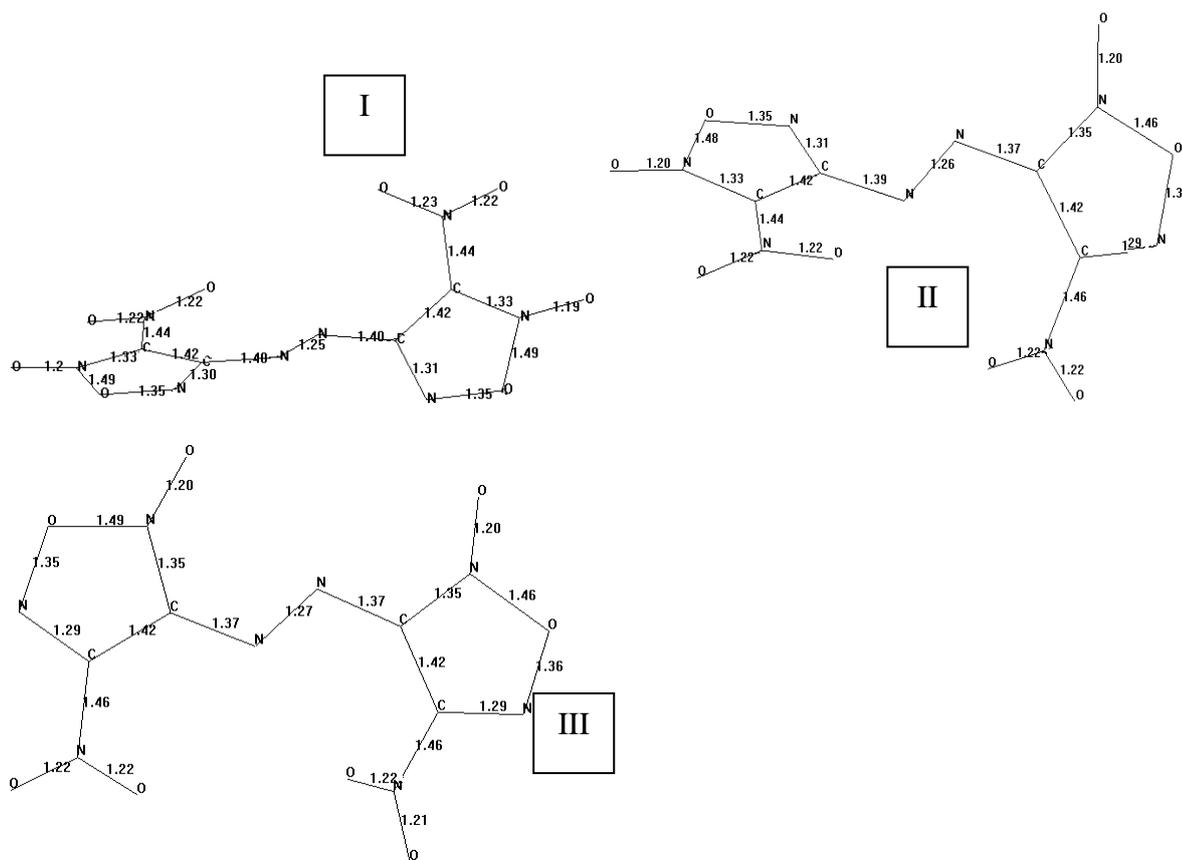


Figure 2. Bond lengths (Å) of the structures (B3LYP/6-31G(d,p)).

Electrostatic charge distribution some other properties.

Figure 3 shows the electrostatic (ESP) charge distribution. 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 [24].

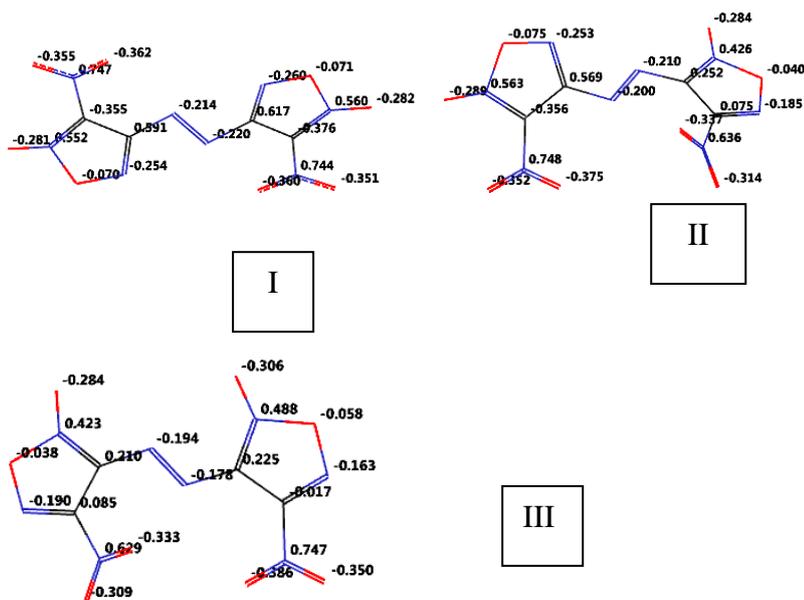


Figure 3. Electrostatic charges (ESP) on the atoms of isomers concerned (B3LYP/6-31G(d,p)).

The figure indicates that azo nitrogens in each isomer are negatively charged but in unequal magnitudes. The charges on the other atoms of furoxanyl rings of each isomer are also differ even in the structures having the same type furoxanyl ring system. This fact is due to imperfect conjugation of the rings with the azo linkage arising from deviation from the coplanarity. This fact also influences the ^{13}C chemical shift values (see Figure 4).

Table 1 shows some properties of the isomers considered. The order of dipole moments follows the sequence of $\text{II} > \text{III} > \text{I}$. Note that II is asymmetrical isomer. The direction of the dipole moment vector differs from one isomer to the other (see Figure 1). Heat of formation data reveals that they are all endothermic structures. Both of PM3// B3LYP/6-31G (d, p) and PM3// B3LYP/cc-PVTZ treatments yield ΔH_f° values in the order of $\text{III} > \text{II} > \text{I}$.

The volumes predicted are not very different from each other and have the order of $\text{III} > \text{I} > \text{II}$ for these isomeric compounds. So, the densities should be close to each other but the reverse order, namely $\text{II} > \text{I} > \text{III}$.

Table 1 . Some Properties of the isomeric structures considered.

No	Dipole moment (Debye)	Area (\AA^2)	Volume (\AA^3)	Polarizability	log P	C_v J/mol	Heat of formation kJ/mol
I	1.69	234.38	191.25	55.96	5.68	173.43	812.192
		233.76	190.55	55.88	5.68	173.24	812.203
II	2.32	234.38	191.21	56.02	5.68	173.00	826.060
		234.34	190.54	55.95	5.68	172.86	824.560
III	2.20	234.76	1.91.30	56.10	5.68	173.06	849.088
		234.70	190.61	56.04	5.68	172.89	847.528
							833.030

In each row, the first and second entry data are based on B3LYP/6-31G(d,p) and B3LYP/cc-PVTZ optimized structures, respectively. The heat of formation data are sequentially, PM3// B3LYP/6-31G(d,p), PM3// B3LYP/cc-PVTZ and T1 calculations for the heat of formation values.

Energies and stabilities

Table 2 tabulates some energies of the isomers where E, ZPE, and E_c stand for the total electronic energy, zero-point vibrational energy, and ZPE-corrected total electronic energy, respectively. Note that one obtains the same stability order of the isomers as III>II>I by using either 6-31G(d,p) or cc-PVTZ basis sets. It is to be mentioned that these isomers differ from each other due to different linkage positions of the furoxanyl rings to the azo group and different positions of nitro groups with respect to N-oxide moieties. Combined effects of these two structural variations electronically dictate the calculated stability order obtained. Table 3 includes some energies as well as the densities calculated. Although Table 3 is constructed mainly for the density calculations based on eq.1 [33] which required UB3LYP/6-31G(d,p) level of calculations, E_c values (in au) obtained also yield the same stability order as the level of calculations mentioned in Table 2.

Table 2. Some energies of the isomeric structures considered.

No	B3LYP/6-31G(d,p)			B3LYP/ cc-PVTZ		
	E	ZPE	E_c	E	ZPE	E_c
I	-3128549.79	242.96	-3128306.82	-3129703.53	241.83	-3129461.69
II	-3128562.96	243.71	-3128319.24	-3129718.41	242.44	-3129475.97
III	-3128575.95	243.19	-3128332.76	-3129731.47	241.99	-3129489.48

Energies in kJ/mol.

Although, the densities of these isomers are very comparable up to four digits the sequence III>II>I.

Table 3. Some energies of the isomeric structures considered (UB3LYP/6-31G(d,p)).

No	E	ZPE	E_c	d (g/cm ³)
I	-1191.6931	0.092561	-1191.6006	1.877835
II	-1191.6981	0.092814	-1191.6053	1.877846
III	-1191.7031	0.092613	-1191.6105	1.877857

Energies in au.

$$d = -0.6538(E/M) - 0.8264 \quad (1)$$

Figure 4 shows the calculated ((B3LYP/6-31G(d,p)) ¹³C chemical shift values of the isomers of present interest. In structure I, the chemical shift values are the same for each furoxanyl rings, whereas this is not the case in isomers II and III. Note that in structure III carbons linked to N=N group are much less deshielded than the carbons of the other isomers. It is related to charge distribution (see Figure 3).

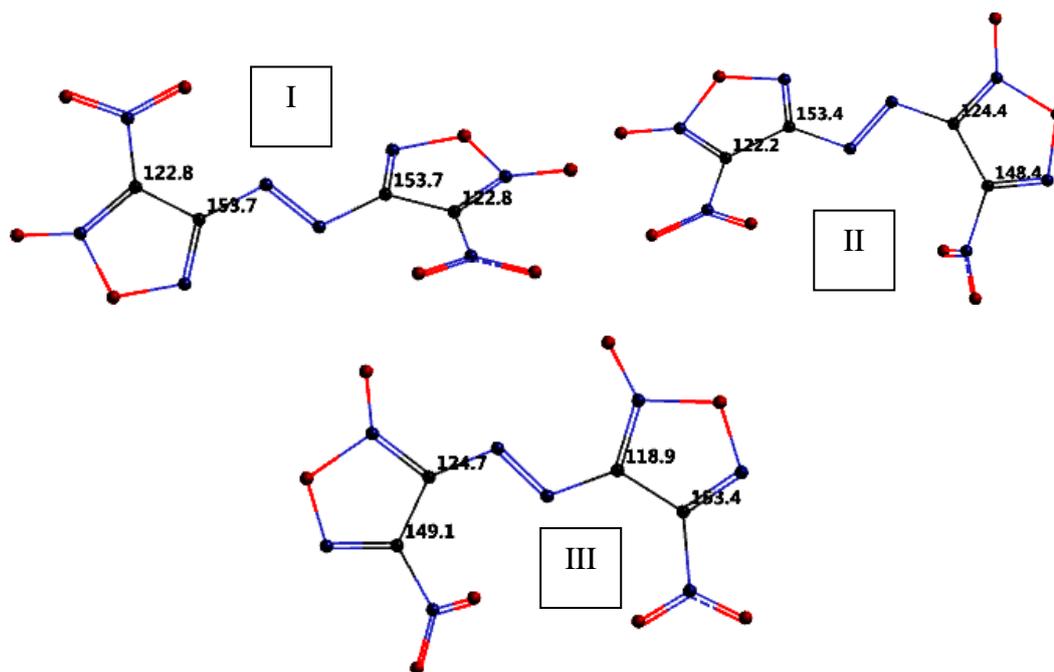


Figure 4. ^{13}C chemical shift values of the isomers of present interest ((B3LYP/6-31G(d,p)).

Molecular orbital energies

Table 4 includes some molecular orbital energies as well as the interfrontier molecular orbital energy gaps ($\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$) of the isomers considered. The HOMO energy level of the isomers follows the order of $\text{III} > \text{II} > \text{I}$ for each kind of basis set used. Whereas, a reverse order exists for the LUMO energy order that is $\text{I} > \text{II} > \text{III}$ by either of the basis sets. Then, the interfrontier molecular orbital energy gaps constitute the order of $\text{I} > \text{II} > \text{III}$. Note that this is the same with LUMO energy order.

Table 4. Some molecular orbital energies and the interfrontier molecular orbital energy gaps of the structures considered.

No	B3LYP/6-31G(d,p)			B3LYP/ cc-PVTZ		
	HOMO	LUMO	$\Delta\epsilon$	HOMO	LUMO	$\Delta\epsilon$
I	-795.05	-415.01	380.04	-809.11	-421.11	388.00
II	-777.09	-423.70	353.39	-793.42	-434.95	358.46
III	-751.17	-428.54	322.62	-766.84	-442.112	324.72

Energies in kJ/mol.

Figure 5 displays the distribution of some of the molecular orbital energies at two different level of calculations.

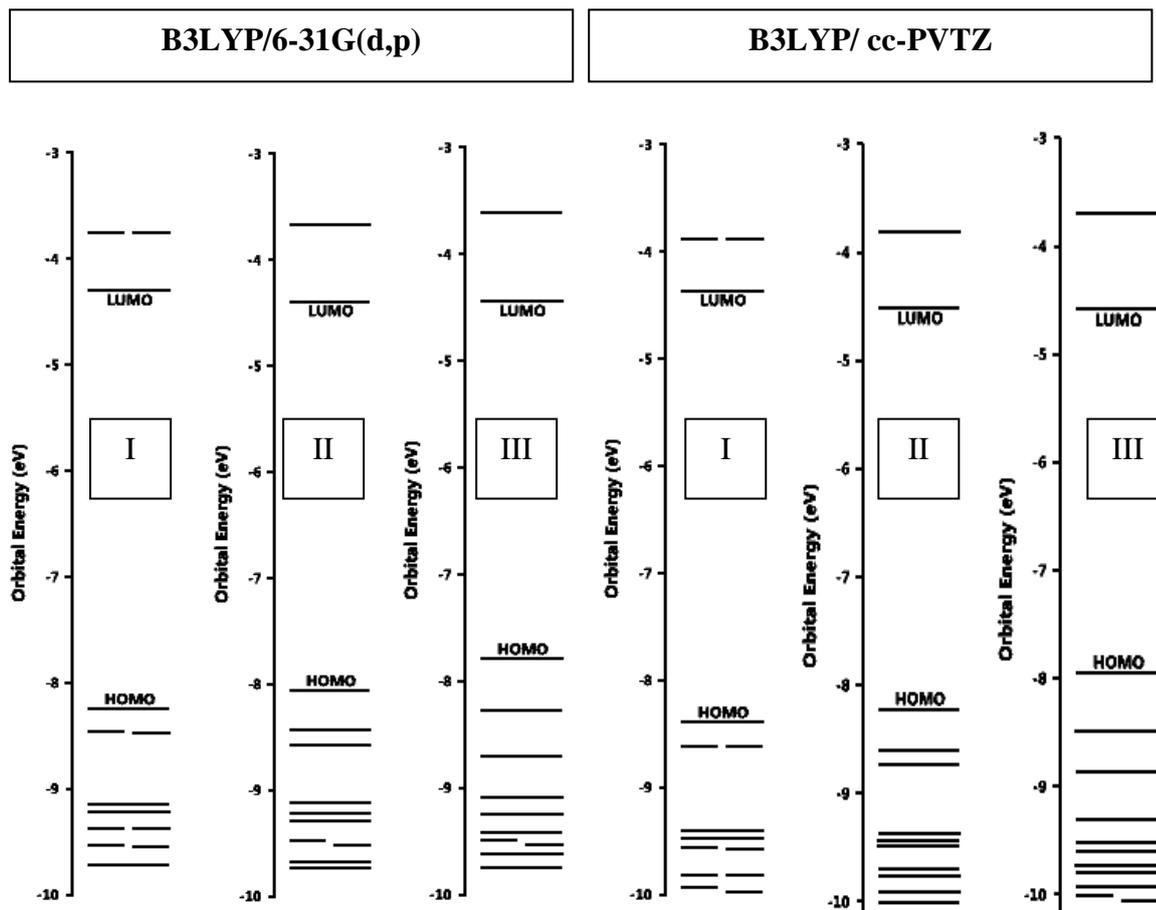
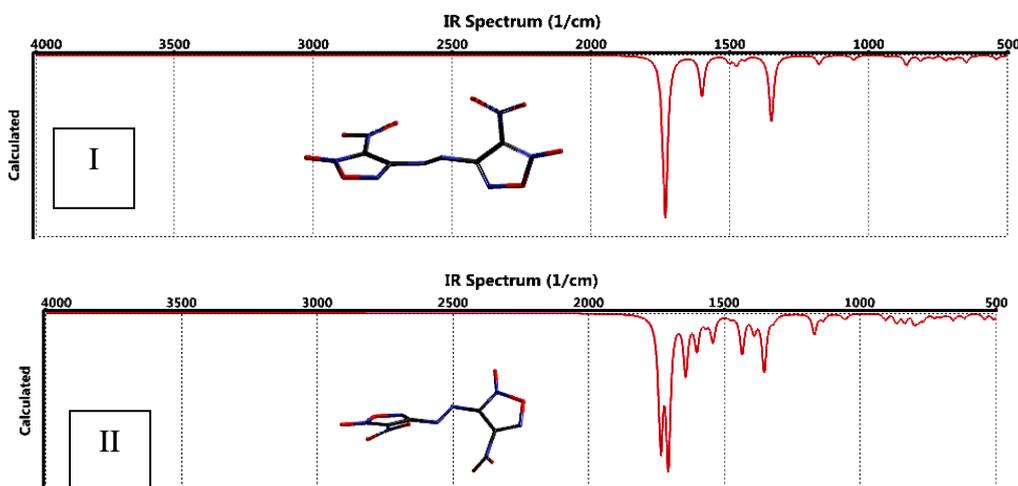


Figure 5. Some of the molecular orbital energy levels of the structures considered.

IR and UV-VIS spectra

Figure 6 stands for the IR spectra of the isomers calculated at the level of B3LYP/cc-PVTZ. However, the IR spectra obtained by B3LYP/6-31G(d,p) treatment are also very similar to spectra displayed in Figure 6. Therefore, only the spectra belonging to one kind of them are shown.

Figure 7 shows the UV (time-dependent DFT) spectra of the isomers obtained at the level of B3LYP/cc-PVTZ. Both of the basis sets used produce the same pattern for any of the isomers investigated. The absorptions spread over UV and VIS regions.



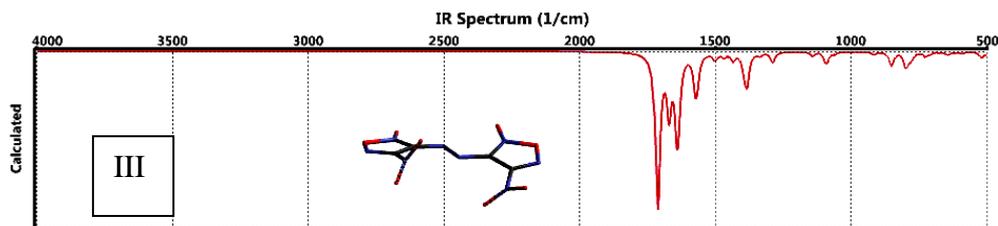


Figure 6. IR spectra of the isomers concerned (B3LYP/cc-PVTZ).

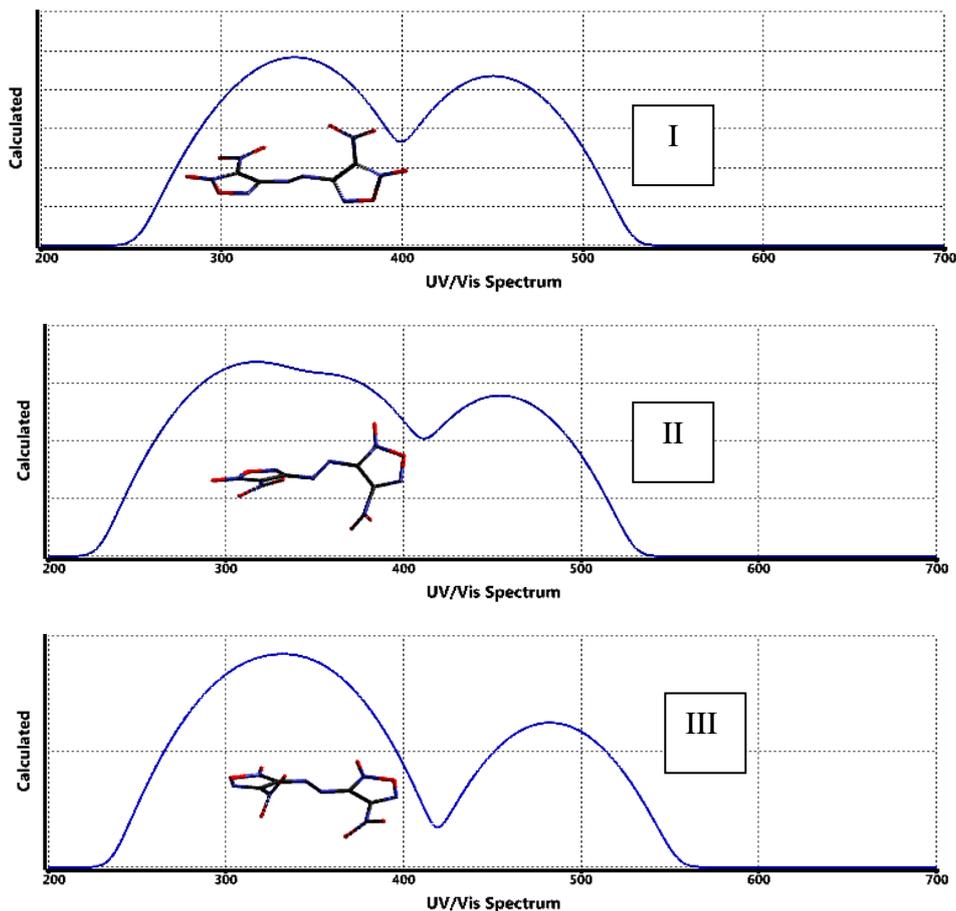


Figure 7. UV-VIS spectra of the isomers concerned (B3LYP/cc-PVTZ).

Charged forms

Safety has prime importance in the case of explosive materials. Explosives, like every object, have an inherent electrical field as a result of the electrons in the material. Static electricity may accumulate on materials by various means and may cause polarization/ionization of some molecules in the bulk, which may act as hot points to initiate some decomposition reactions [34-36]. In the present study, mono ionic forms of *trans*-dinitro diazenofru xane constitutional isomers have been considered as well (UB3LYP/6-31+G(d) type calculations). Figures 8 stands for the optimized structures of the mono anions and cations of the presently considered structures. As seen in the figure both the anions and cations considered have intact bonds (no cleavage occurs) and all the monoionic species have reasonable bond lengths. Due to obvious reasons direction of the dipole moments are different for the anion and cation of the same compound. The N=N bond in anions is 1.33 Å whereas in the case of cations it varies between 1.24-1.26 Å. Note that in the neutral state of these structures the N=N bond varies in between 1.25-1.27 Å (at the same level of calculations, UB3LYP/6-31+G(d)). To explain the elongation of that bond, ESP charges have been calculated and shown in Figure 9. In the case of anions the N=N nitrogens have negative charges whereas in the cationic forms with

the exception of structure –I have opposite charges. Note that in the neutral forms of these structures the nitrogens of N=N bond are negatively charged (UB3LYP/6-31+G(d)) but their magnitudes are less than the respective structures in the anion form. Thus, more repulsive interaction makes that bond longer in the anions compared to neutral as well as cation forms in which opposite charges reside.

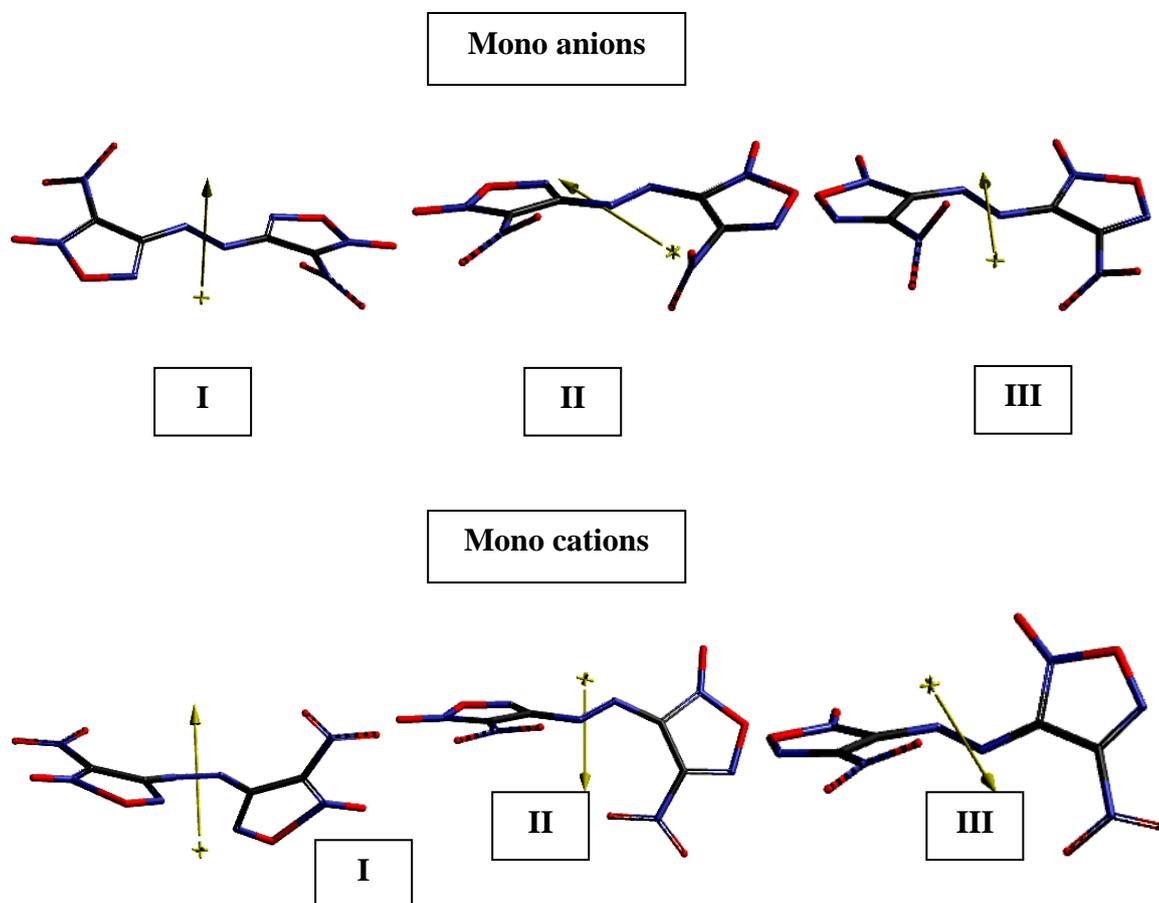
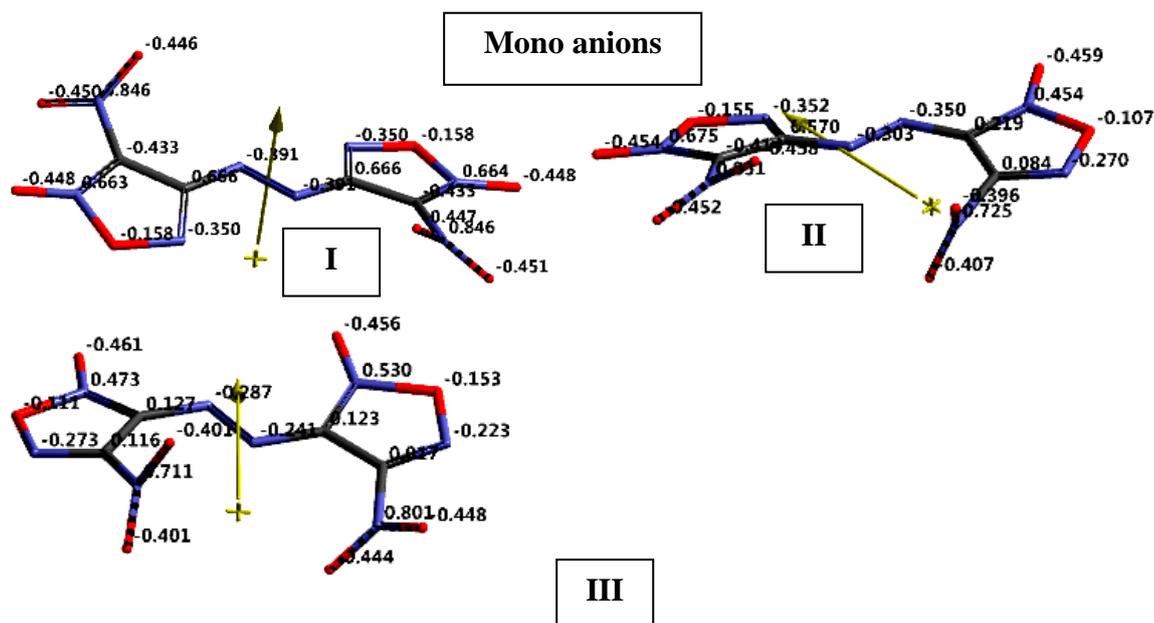


Figure 8. Optimized structures of the mono anions and cations (UB3LYP/6-31+G(d)) level of calculations



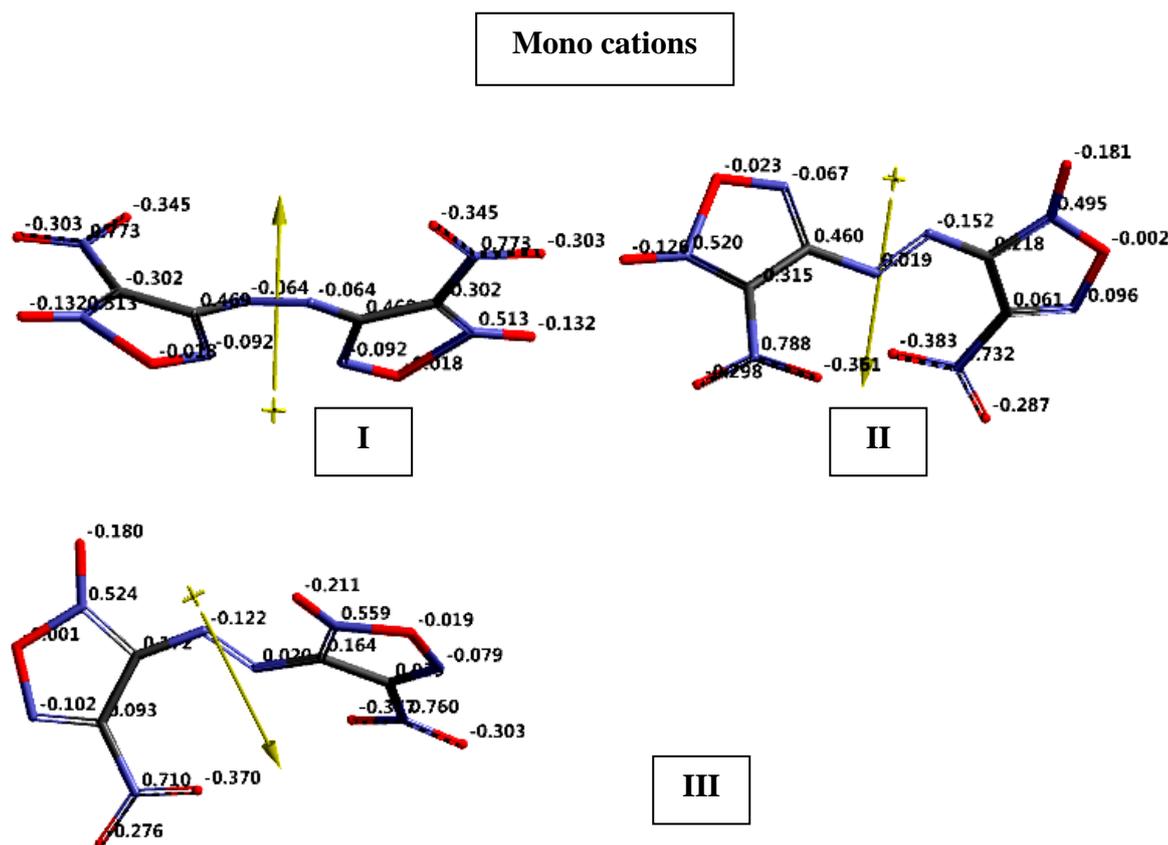


Figure 9. Electrostatic charges (ESP) on the atoms of charged isomers concerned

(UB3LYP/6-31+G(d)).

Various energies of the mono anions and cations of the structures considered are shown in Table 5. The data reveals that stability orders of the cations and anions are the same as $\text{III} > \text{II} > \text{I}$, which is the stability order of their neutral parent forms. The stability exhibited by these ionic forms implies as a first approximation that the isomers should be insensitive to electrostatic discharge up to a certain potential.

Table 5. Various energies of the mono anions and cations of the structures considered.

Structure	Cation			Anion		
	E	ZPE	E_c	E	ZPE	E_c
I	-3127749.59	235.70	-3127513.89	-3129018.47	236.87	-3128781.60
II	-3127772.46	237.91	-3127534.55	-3129027.68	236.06	-3128791.62
III	-3127790.85	239.23	-3127551.62	-3129032.10	233.17	-3128798.93

Energies in kJ/mol. UB3LYP/6-31+G(d)level of calculations.

Table 6 shows Some molecular orbital energies and the interfrontier molecular orbital energy gap ($\Delta\epsilon$) of the monoionic structures considered. For the anions the HOMO and LUMO energy orders are the same as $\text{I} < \text{II} < \text{III}$. As for the cations the HOMO and LUMO energy orders follow the same trend as $\text{III} < \text{II} < \text{I}$. The interfrontier molecular orbital energy gaps for the anions and cations are $\text{I} > \text{II} > \text{III}$ and $\text{I} > \text{III} > \text{II}$, respectively.

Table 6. Some molecular orbital energies and the interfrontier molecular orbital energy gap $\Delta\epsilon$ monoionic structures considered.

No	Anion			Cation		
	HOMO	LUMO	$\Delta\epsilon$	HOMO	LUMO	$\Delta\epsilon$
I	-226.13	-52.26	173.87	-1193.42	-921.39	272.03
II	-208.33	-43.14	165.19	-1198.20	-932.61	265.59
III	-191.40	-38.03	153.38	-1226.83	-957.92	268.90

Energies in kJ/mol. UB3LYP/6-31+G(d) level.

Conclusion

Isomers of *trans*-dinitrodiazenurofan are considered at various level of calculations within the constraints of density functional theory. The stability order of isomers in each case is found to be III>II>I. Various geometrical and quantum chemical characteristics obtained are discussed. The order of dipole moments follows the sequence of II>III>I. Calculated IR and UV-VIS spectra are discussed. For the mono ionic forms of these isomers UB3LYP/6-31+G(d) type calculations have been performed. These ionic species are also found to be stable, and the stability orders of the cations and anions are the same as III>II>I, which is the stability order of their neutral parent forms.

References

1. Klapötke TM, Schmid PC, Stierstorfer J. Crystal structures of furazanes Crystals 2015; 5: 418-432;
2. Francois EG, Chavez DE, Sandstrom MM. The development of a new synthesis process for 3,3'-diamino-4,4'-azoxyfurazan (DAAF). Propellants Explos. Pyrotech. 2010; 35: 529-534.
3. Klapötke TM, Leroux M, Schmid PC, Schnell S, Stierstorfer J. Energetic materials based on 5,5'-diamino-4,4'-dinitramino-3,3'-bi(1,2,4-triazole). Chem. Asian J. 2015; doi: 10.1002/asia.201500701.
4. Matyushin YP, Pepekin VI, Golova SP, Golovikova TI. Enthalpy of formation of dimethylfurofan and dimethylfurazane. Izv. Akad. Nauk SSSR, Ser. Khim. 1971; 1: 181-183.
5. Pepekin VI, Matyushin YN, Feshchenko AG, Smirnov SP, Apin AY. Dissociation energy of the N→O bond in benzofurofan. Dokl. Akad. Nauk SSSR 1972; 202 (1): 91-92.
6. Pepekin VI, Matyushin YN, Nikolaeva AD, Kirsanov AP, Platonova LV, Lebedev YA. Dissociation energy of the N→O-bond in dinitratodimethylolufurofan. Izv. Akad. Nauk SSSR, Ser. Khim. 1975; 8: 1870-1872.
7. Matyushin YN, Lebedev VP, Chironov VV, Pepekin VI. Energy of the N→O bond in benzofurofanes. Khim. Fiz. 2002; 21: 58-61.
8. Guo T, Liu M, Huang XC, Ge ZX, Meng ZH. Efficient preparation and comprehensive properties of thermal decomposition and detonation for 4,4'-dinitro-3,3'-azofurofan. Journal of Analytical and Applied Pyrolysis 2017; 128: 451-458.
9. He JX, Lu YH, Lei Q, Cao YL. Synthesis and properties of high energetic compound 3,3'-dinitro-4,4'-azofurofan. Huozhayao Xuebao/Chinese Journal of Explosives and Propellants 2011; 34(5):9-12.
10. Xia M, Chu Y, Wang T, Lei W, Wang F. Computational investigation of the properties of double furazan-based and furofan-based energetic materials. Journal of molecular modeling 2016; 22(11): 268.
11. Agrawal JP. High energy materials. Cornwall: Wiley-VCH ; 2010.

12. Pepekin VI, Korsunskii BL, Matyushin YN. Explosive properties of furoxans. *Combustion, Explosion, and Shock Waves* 2008; 44(1):110–114.
13. Ovchinnikov IV, Makhova NN, Khmel'nitskii LI, Kuz'min VS, Akimova LN, V.I. Pepekin. Dinitrodiazonofuroxan - New super-power explosive. *Dokl. Akad. Nauk* 1998; 359: 499-502.
14. Akimova LN, Afanas'ev GT, Shchetinin VG, Pepekin VI. Explosive properties of 4,4'-dinitro-3,3'-diazonofuroxan. *Combustion Explosion and Shock Waves* 2002; 44(1):110-114.
15. Pepekin VI. Tendencies in the development of studies of high explosives. *Russian Journal of Physical Chemistry B* 2010; 4(6): 954–962.
16. Coburn MD. Synthesis and unusual NMR spectra of 4,4'-dinitro-3,3'-bifurazanyl-4,4'-¹³C. *Journal of Labelled Compounds and Radiopharmaceuticals* 1985; 22(2):183-187.
17. Kohn W, Sham L. Self-consistent equations including exchange and correlation effects. *J. Phys. Rev. A* 1965; 140: 1133-1138.
18. Parr RG, Yang W. *Density functional theory of atoms and molecules*. London: Oxford University Press; 1989. [19] Young, DC. *Computational chemistry*. NY: Wiley; 2001.
19. Levine IN. *Quantum chemistry*. NJ: Prentice Hall; 2000.
20. Becke AD, Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* 1988; 38: 3098-3100.
21. Vosko SH, Vilk L, Nusair M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Can. J. Phys.* 1980; 58: 1200-1211.
22. Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* 1988; 37 :785-789.
23. Spartan 06 Program. Wavefunction Inc., Irvine, CA 92612 USA, 2006.
24. Veronina VA, Kurbatov SV, Olekhovich LP. New dipolar spiro- σ -complexes derived from 4,6-dinitrobenzofuroxan. *Russ. J.Org. Chem.* 2004; 40: 1384-1385.
25. Rauhut G.. Combined *Ab Initio* and density functional study of ring chain tautomerism in benzofuroxan-1-oxide. *J. Comput. Chem.* 1996; 17 : 1848-1856.
26. Rauhut G, Jarzechi AA, Pulay P. Density functional based vibrational study of conformational isomers: Molecular rearrangement of benzofuroxan. *J. Comput. Chem.* 1997; 18: 489-500.
27. Friedrichsen W. Benzofuroxan-O-dinitrosobenzene equilibrium. A computational Study. *J. Phys. Chem.* 1994; 98: 12933-12937.
28. Zhu JP, Liu SN, Li YX, Wang J-H, Cao DL, Ren J. Structures and detonation performance for several explosive molecules of azoles by density functional theory. *Zhongbei Daxue, Ziran Kexueban* 2011; 32(2) :200-206.
29. Katritzky AR, Gordeev MF. Heterocyclic rearrangements of benzofuroxans and related compounds. A review about the chemistry of benzofuroxans. *Heterocycles*. 993; 35 : 483- 518.
30. Türker L. Isomerization of 4,6-dinitrobenzofuroxan- A DFT study. *J. Energ. Mater.* 2011; 29 :127-149.

31. Türker L. A DFT study on benzotrifuroxan and its isomers. *Polycycl. Aromat. Comp.* 2010; 30: 44-60.
32. Türker L. The total energy and density of certain explosives: A curious relation. (in *Energetic science and technology in central Europe*, Eds: Armstrong RW, Short JM, Kavetsky RA, Davinder KA), 73-95, Calce, Maryland; 2012.
33. Boddu V, Redner P. *Energetic materials*. Boca Raton: CRC press Taylor and Francis; 2011.
34. Zeman S, Jungová M. Sensitivity and performance of energetic materials. *Propellants, Explosives, Pyrotechnics* 2016; 41: 426-451.
35. Zeman S, Majzlík J, Kočí J. Electric spark sensitivity of polynitro arenes. Part I. A comparison of two instruments. *Central European Journal of Energetic Materials* 2007; 4: 15-24.