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Some Diazodinitrophenol Isomers - A DFT Treatment

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Abstract

The present study considers a series of diazodinitrophenol isomers within the constraints of density functional theory at the level of B3LYP/311++G(d,p). One of the isomers in the series is known as DDNP which is a primary explosive material. Presently various dinitro substituted benzoxadiazol (bicyclic) and 2-diazo-1-oxide (azide) isomers analogous to DDNP have been focus of investigation. In all the cases the azide isomers have been found to be more stable electronically than the bicyclic counterparts. Various properties of them including quantum chemical ones are harvested, compared and discussed. Also NICS(0) values are obtained for the ring(s) and the local aromaticity values are discussed.

1. Introduction

Diazodinitrophenol (DDNP) (for a long time it was assumed to be 4,6-dinitrobenzene-2-diazo-1-oxide) was first prepared by Griess in 1858 [1,2]. It is obtained by the diazotization of picramic asit (2-amino-4,6-dinitrophenol) by means of $NaNO_2/HCl$ or oxidation of picramic acid with chromic acid [3]. It is also prepared by diazotization of magnesium picramate [4]. It occurs as yellow needles which decompose without melting on heating to 188°C. Its explosive nature however reported later in 1892 by Lenze [5]. It is less sensitive to impact than mercury fulminate, lead azide, or lead styphnate [6], more stable and brisant than mercury fulminate. It is used in blasting caps, loading fuse detonators and priming compositions for military use. The initiating power

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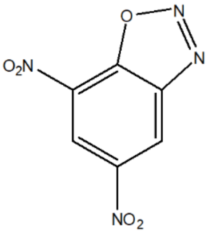
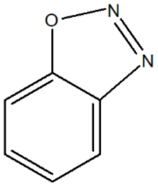
of DDNP is slightly less than that of lead azide. It was first found application as in initiating as non-toxic types of primer [7].

Although DDNP has been known more than a century, its structure is still beyond any general consensus [8]. For a long period of time structure I was adopted as structure of DDNP. However, structure II was prepared and shown to be unstable even in solid argon matrix [9,10]. Structure I which could be thought as cyclization product of III seems improbable based on the property-related assumptions [8]. Computational studies based on AM1 level of calculations support this conclusion [10]. Later on researchers inclined to the adoptation of structure IV based on X-ray crystallography, C13 NMR and molecular orbital studies [9-11].



I



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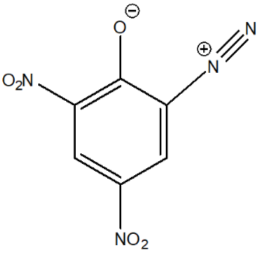

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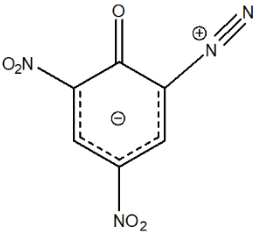
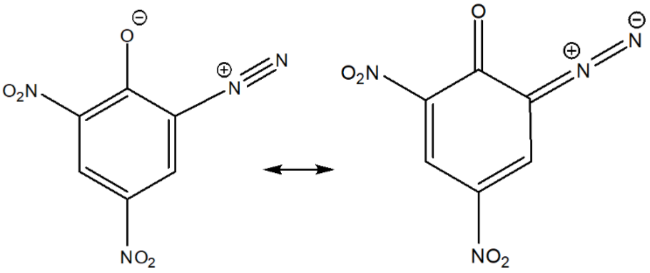


IV

Structure of IV has been questioned whether IVa or IVb better represents structure of DDNP [10].



IVa IVb

The present treatise considers various isomers of DDNP which contains the nitro groups on different locations of the aromatic ring of two models presently adopted within the constraints of density functional theory.

2. Method of Calculations

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [12,13] at the restricted level [14,15]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, geometry optimizations were managed within the framework of density functional theory [16,17] at the level of 6-311++G(d,p) [14,18]. 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 [17,19]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [20] and Lee, Yang, Parr (LYP) correlation correction functional [21]. The vibrational analyses were also done. The total electronic energies are corrected for the zero point vibrational energy (ZPE). 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 [22]. For the NICS calculations Gaussian 03 program was employed [23].

3. Results and Discussion

As mentioned above, structure of DDNP is still obscure although recently structure-IV has been getting more popular. However, a question arises whether positional isomerism of the nitro groups in other cases results in structures in favor of analogs of I or IV. In Model-I, the system comprises dinitrobenzoxadiazol moiety (like structure I) whereas in Model-II an azido group is linked to 2-position of the dinitrophenolate ring (like structure IV).

Figure 1 shows the optimized structures of bicyclic (dinitrobenzoxadiazol) isomers (A-F) and the direction of the dipole moment vectors. In all the cases, except structure-E, the vector originates from somewhere around the hexagonal ring.

Figure 2 displays two of the resonance structures of phenolate azide. In classical terms they are charge-separated canonical structures and should be more energetic than the isopolar bicyclic counterpart isomers. However, as will be presented below, molecular orbital treatment predicts some contradictory results. Some other level of molecular orbital calculations carried on DDNP (structures F and Fa) also revealed that the azide isomer is more preferable energetically [10].

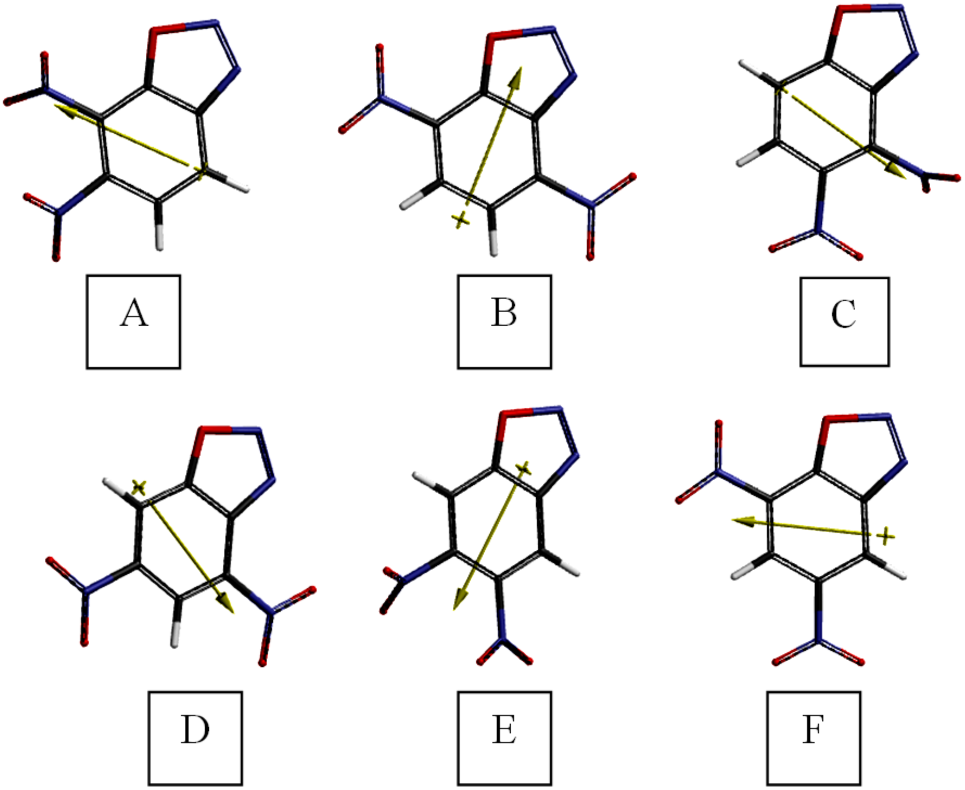


Figure 1. Optimized structures of the bicyclic isomers (Model-I).

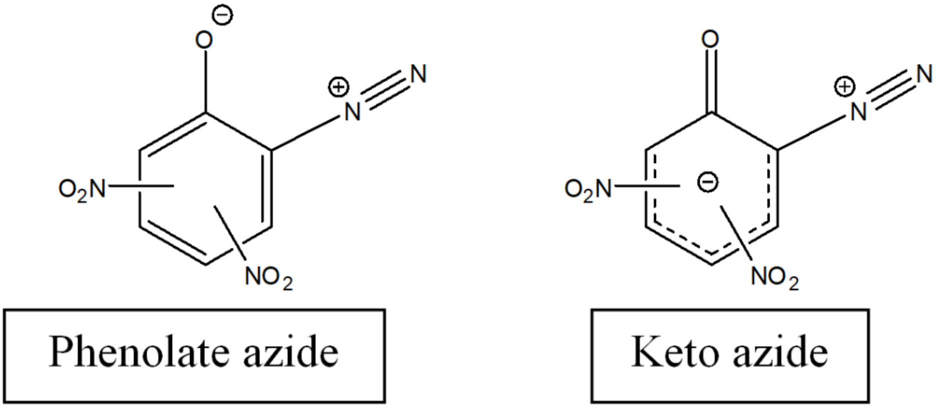


Figure 2. General resonance structures of the azides considered.

Figure 3 shows the optimized structures of the dinitrophenolate azide isomers (Aa through Fa) presently considered. As seen in the figure the azido moiety in all the cases somewhat tilted towards the oxygen atom of the phenolate ring.

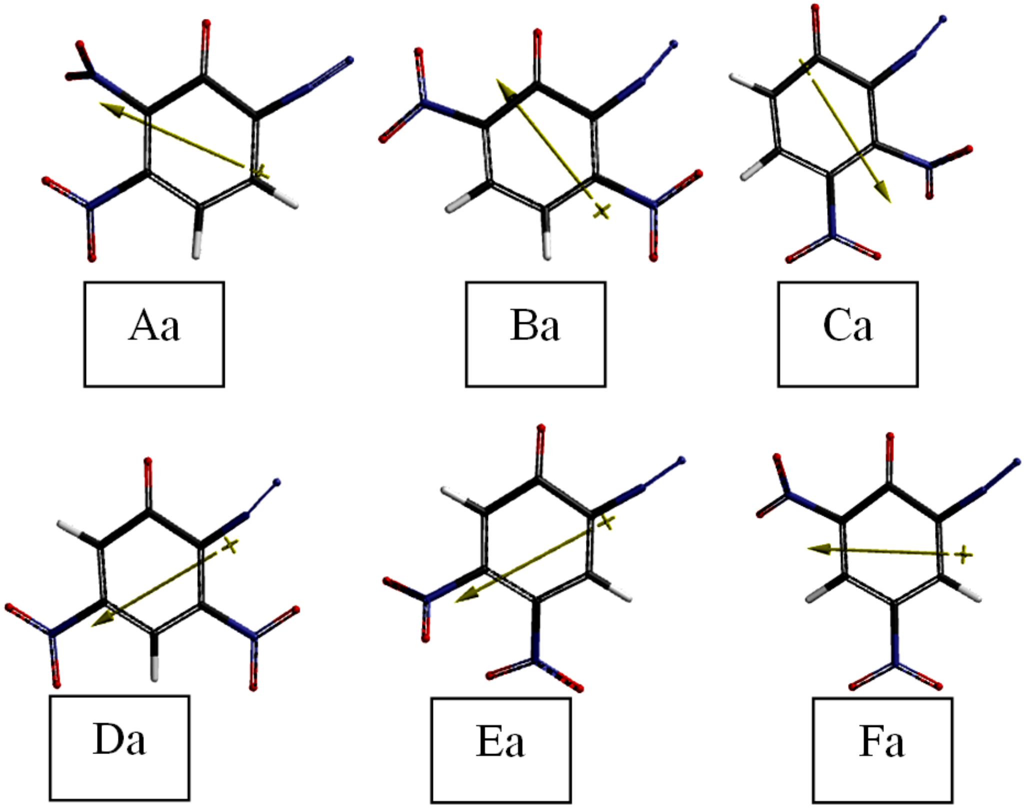


Figure 3. Optimized structures of the azide isomers (Model-II).

Figures 4 and 5 display the electrostatic potential (ESP) maps of the bicyclic and azide isomers, respectively. Note that the ESP charges are obtained by the program based on a numerical method that generate charges that reproduce the electrostatic potential field from the entire wavefunction [22]. In general, in such a map the red and blue regions stand for the optimum negative end positive potential fields, respectively.

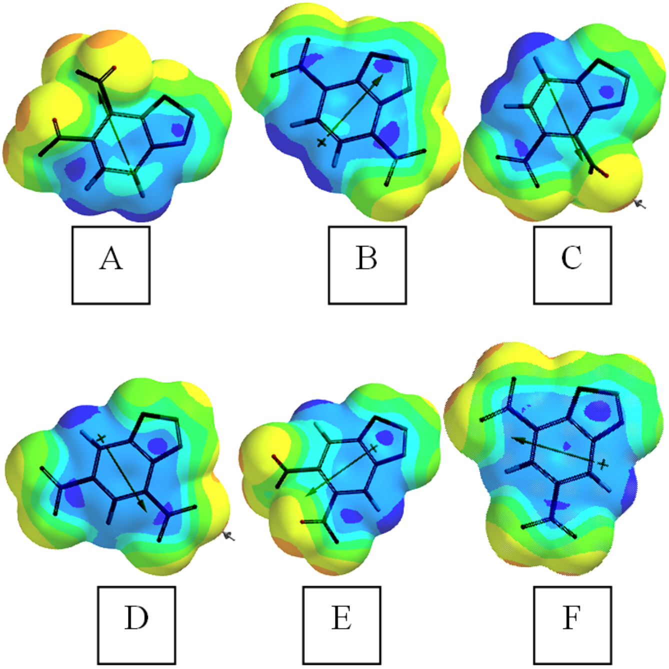


Figure 4. The ESP maps of the bicyclic isomers (Model-I) considered.

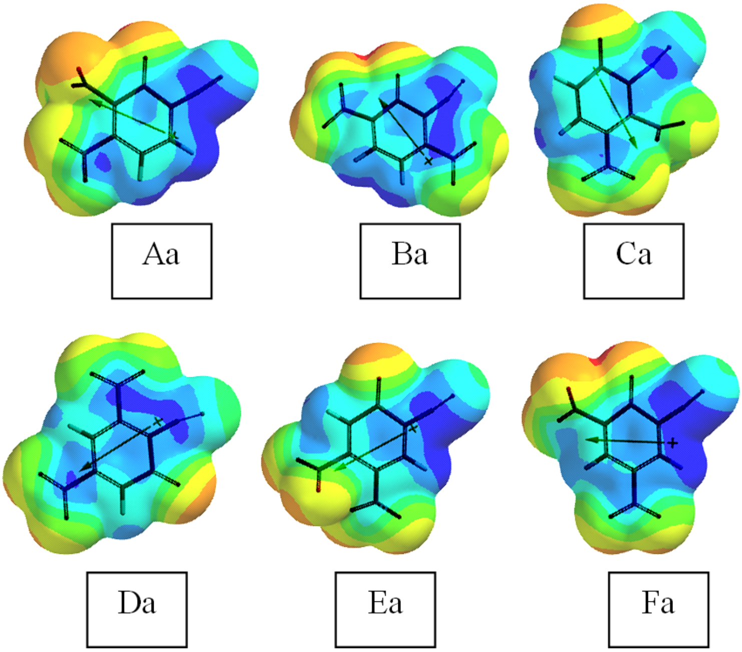


Figure 5. The ESP maps of the azide isomers (Model-II).

Table 1 tabulates the total electronic energy (E), zero point vibrational energy (ZPE) and the corrected total electronic energy (E_C) values of the isomers considered. The data reveal that they are all electronically stable and all the azides are more stable than their respective bicyclic counterparts. The stability order is Fa>Da>Ea>Ba>Ca>Aa among the azides. In classical terms the stable azide isomers over the respective bicyclic isomers could be due to a longer conjugated path existing in the azide form and destabilization of the bicyclic structure having some resonance structures possessing positively charged oxygen atom.

Table 1. Some energies of the isomers considered.

Structure	**E**	**ZPE**	**E_c**
A	-2165800.01	251.17	-2165548.84
Aa	-2165815.13	247.24	-2165567.89
B	-2165814.26	250.26	-2165564.00
Ba	-2165831.14	246.82	-2165584.32
C	-2165804.13	251.03	-2165553.10
Ca	-2165818.15	247.16	-2165570.99
D	-2165829.15	250.76	-2165578.39
Da	-2165851.79	246.99	-2165604.80
E	-2165815.33	250.87	-2165564.46
Ea	-2165833.86	247.58	-2165586.28
F (DDNP)	-2165840.67	250.22	-2165590.45
Fa	-2165853.59	247.60	-2165605.99

Energies in kJ/mol.

Table 2 lists some properties of the isomers considered. As seen in the table dipole moment of an azide isomer is greater than the bicyclic one for Aa, Ba, Ea and Fa. The polarizability values of the azides are greater than the corresponding bicyclic isomers in all the cases. Hardness and electronegativity of the azides are less than the corresponding bicyclic isomers.

Table 2 . Some properties of the isomers considered.

Structure	**Dipole moment** (Debye)	**Polarizability**	**Log P**	**Hardness** (kJ/mol.)	**Electronegativity** (kJ/mol.)
A	5.72	53.15	2.70	213.93	611.05
Aa	8.61	53.69	1.72	155.82	566.57
B	2.78	53.16	2.70	206.62	643.79
Ba	3.83	53.71	1.72	145.82	596.51
C	5.47	53.05	2.70	230.93	602.51
Ca	2.91	53.63	1.72	166.29	575.62
D	2.25	53.11	2.70	215.03	638.66
Da	1.49	53.68	1.72	148.59	587.51
E	3.51	53.05	2.70	232.92	599.94
Ea	5.83	53.59	1.72	174.06	573.08
F (DDNP)	2.63	53.04	2.70	230.12	624.17
Fa	5.83	53.59	1.72	170.55	582.68

Electronegativity and hardness are in kJ/mol.

Electronegativity and hardness are defined as

$$\text{Electronegativity} = -(\varepsilon_{\text{HOMO}}+\varepsilon_{\text{LUMO}})/2$$

$$\text{Hardness} = -(\varepsilon_{\text{HOMO}}-\varepsilon_{\text{LUMO}})/2$$

Figure 6 displays some of the molecular orbital energy levels of the isomers considered. As seen in the figure, in all the structures, the bicyclic ones have lower HOMO energy levels than their azide analogs. The reverse case holds for the LUMO energies (also for the NEXT LUMO energies). The HOMO energy order for the bicyclic isomers is F<D<B<C<E<A. Whereas for the azides it is F<Ea<Ba<Ca<Da<Aa. As for the LUMO energies, the orders for the bicyclic and the azide isomers are B<D<A<F<C<E and Ba<Da<Fa<Aa<Ca<Ea, respectively. Consequently the Δε values for the bicyclic structures follow the order of E > C > F > D > A > B. Whereas the azides

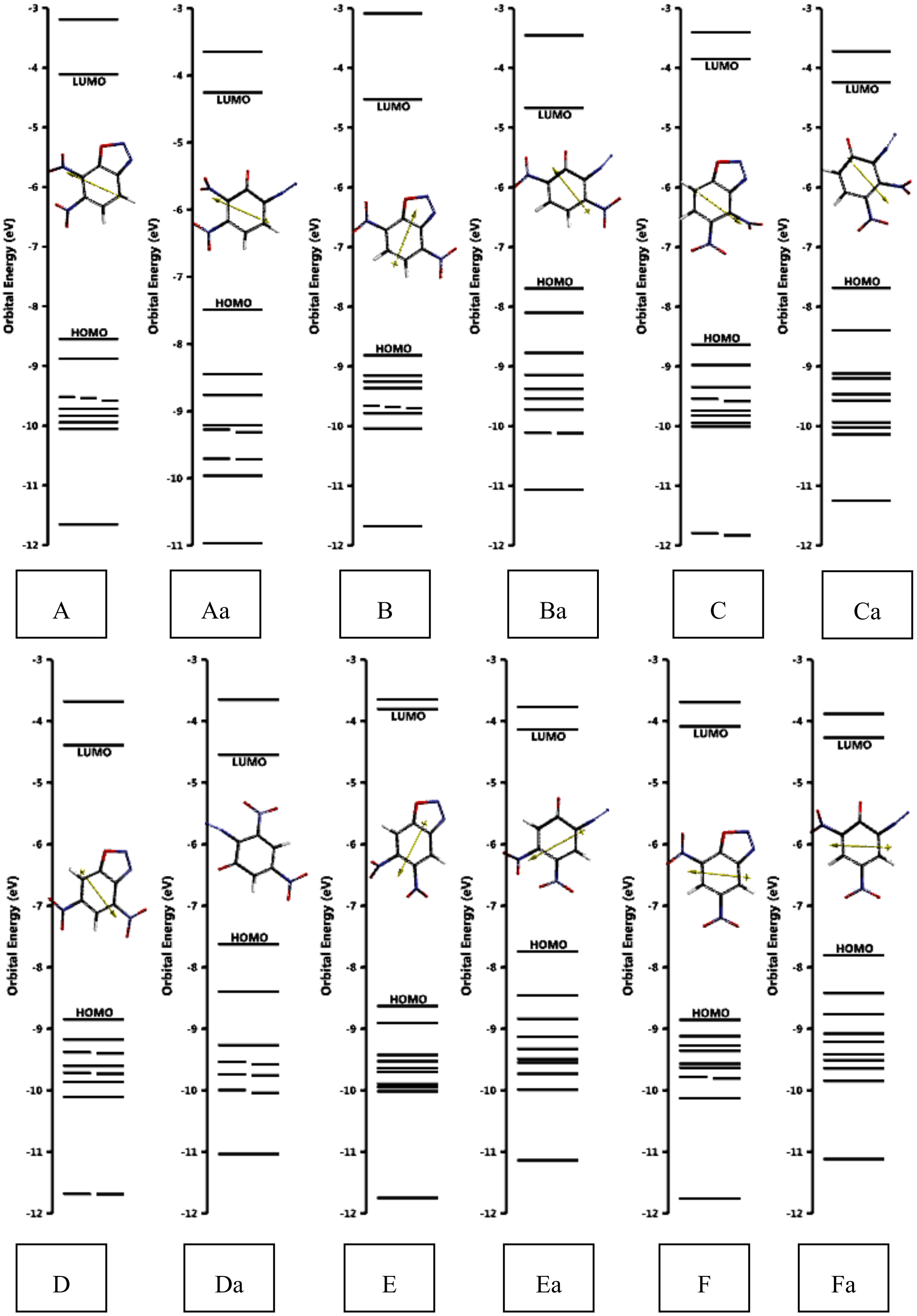


Figure 6. Some of the molecular orbital energy levels of the isomers considered.

produce the order of Ea>Fa>Ca>Aa>Da>Ba. In the bicyclic isomers NEXT HOMO energy level is much closer to the HOMO level compared to the case in azide isomer.

Table 3 lists the HOMO and LUMO energies and the interfrontier molecular orbital energy gap values ($\Delta\varepsilon = \varepsilon_{LUMO}-\varepsilon_{HOMO}$) of the isomers of present interest. According to Δε data of the table, isomers B and Ba are the most sensitive ones to impact stimulus because Δε values are related to impact sensitivity in explosives [24,25]. Namely, as the FMO energy gap (Δε) becomes less and less the impact sensitivity increases more and more. Whereas E and Ea seem to be less sensitive than F and Fa, respectively (namely less sensitive than DDNP).

Table 3. The HOMO and LUMO energies and Δε values of the structures considered.

Structure	HOMO	LUMO	Δε
A	-824.98	-397.12	427.86
Aa	-722.39	-410.75	311.64
B	-850.41	-437.18	413.23
Ba	-742.32	-450.69	291.63
C	-833.43	-371.58	461.85
Ca	-741.91	-409.32	332.59
D	-853.69	-423.63	430.06
Da	-736.10	-438.91	297.19
E	-832.85	-367.02	465.83
Ea	-747.13	-399.02	348.11
F (DDNP)	-854.29	-394.05	460.24
Fa	-753.23	-412.13	341.10

Energies in kJ/mol.

Figures 7 and 8 display the local ionization maps of the bicyclic and azide isomers, respectively. In a local ionization potential map conventionally red regions on the density surface indicate areas from which electron removal is relatively easy, meaning that they

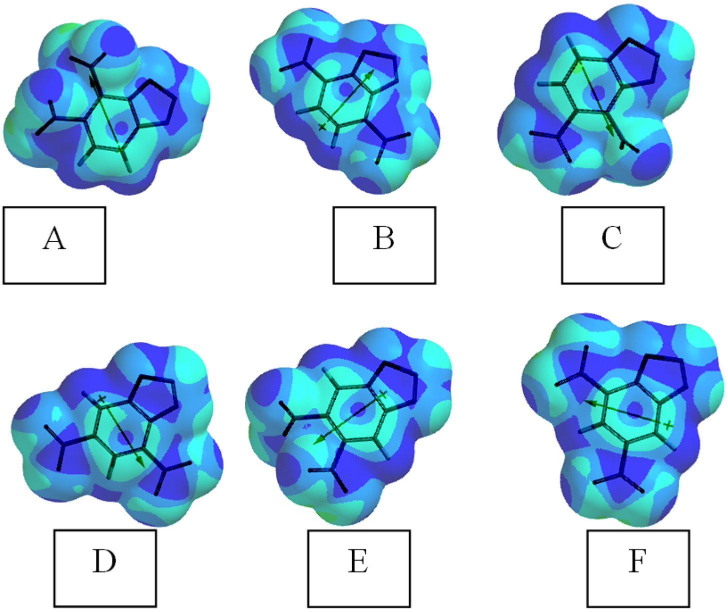


Figure 7. Local ionization maps of the bicyclic isomers considered.

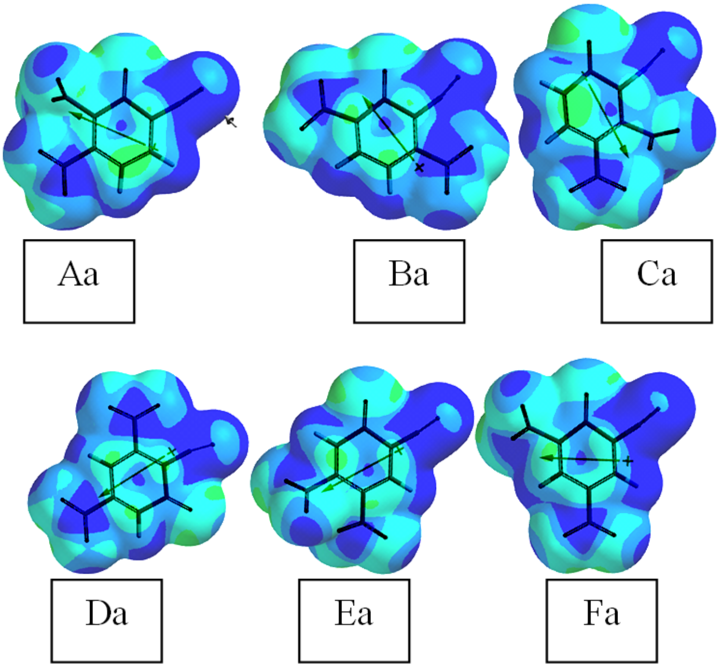


Figure 8. Local ionization maps of the azides considered.

are subject to electrophilic attack. On the other hand, regions having blue color represent areas where ionization is relatively difficult. In the case of bicyclic isomers the blue regions are distributed all over the structure whereas in the azide isomers they spread mainly regions around the azido moiety.

Figures 9 and 10 display the LUMO maps of the bicyclic and azide isomers, respectively. A LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color stands for the maximum value of the LUMO and the color red, the minimum value. Hence, a nucleophile attacks on the atom having the blue color. Hence, yellowish/green regions in the present case are relatively more susceptible to nucleophilic attack. Note that the terminal nitrogen atom of the azido moiety in most of the structures is relatively susceptible site for nucleophiles (especially in Ea and Fa) which gives some clue about the bonding of the azido moiety.

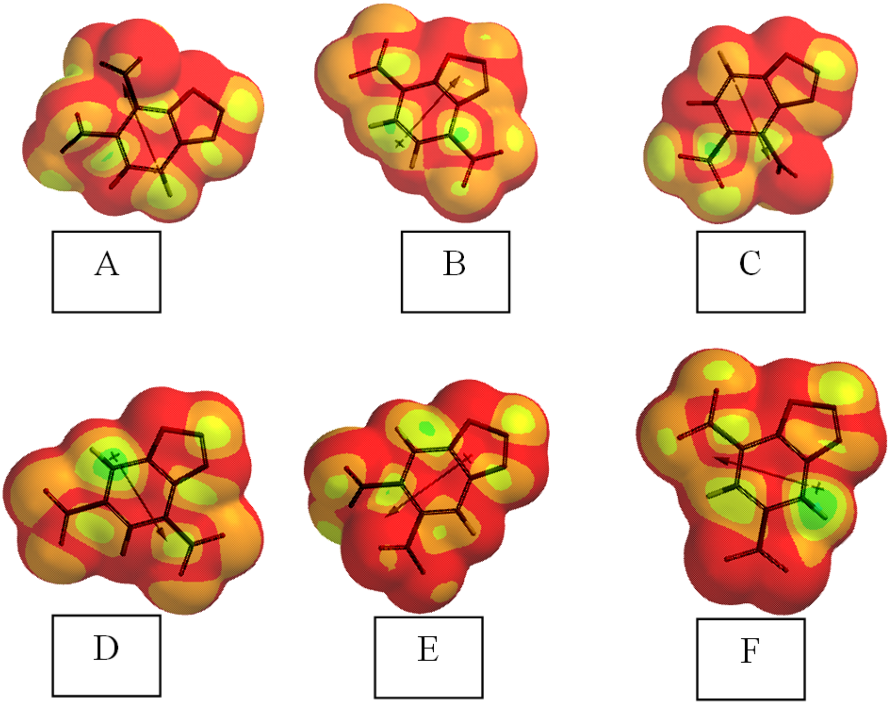


Figure 9. The LUMO maps of the bicyclic isomers considered.

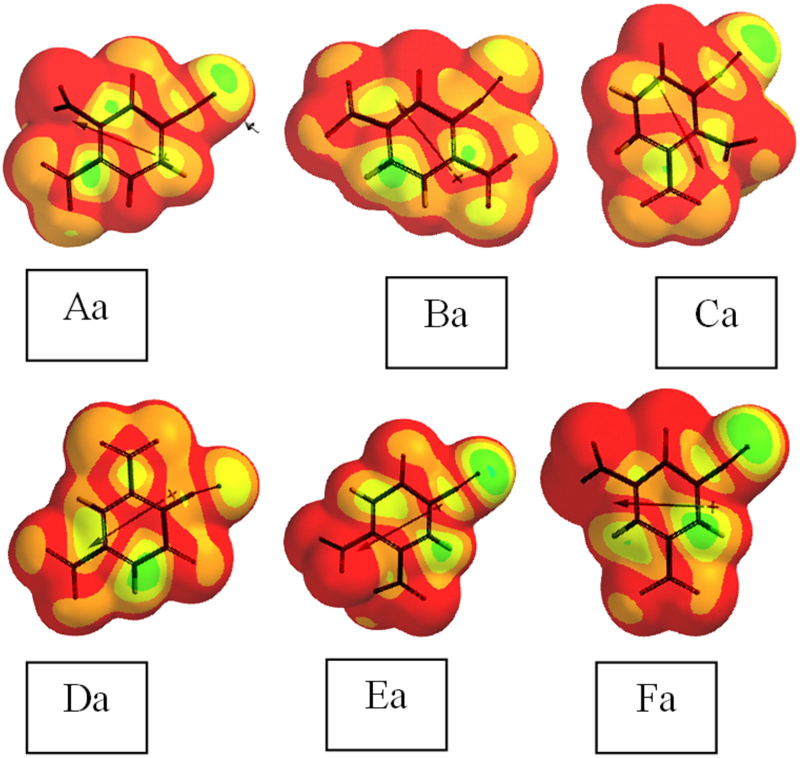


Figure 10. The LUMO maps of the azides considered.

NICS

Although aromaticity arises by a combination of various properties in cyclic delocalized systems, in the literature, generally aromaticity has been discussed in terms of energetic, structural and magnetic criteria [26-31]. A simple but efficient probe has been introduced for aromaticity that is "nucleus-independent chemical shift" (NICS) [32]. It is the computed value of the negative magnetic shielding at some selected point in space (generally, at a ring or cage center). Through the years the calculated data piled in the literature indicate that negative NICS values denote aromaticity (-11.5 for benzene, -11.4 for naphthalene) whereas positive NICS values denote antiaromaticity (28.8 for cyclobutadiene) while small NICS values indicate non-aromaticity (-2.1 for cyclohexane, -1.1 for adamantane). It has been generally accepted that NICS may be a useful indicator of local aromaticity that usually correlates successfully with the other energetic, structural and magnetic criteria for aromaticity [33-36]. Note that resonance energies and magnetic susceptibilities measure the overall aromaticity of a polycycle, but do not provide any information about the individual rings, whereas NICS has been proved to be an effective probe for local aromaticity of individual rings of polycyclic systems although couple of contradictory results exist [32].

Table 4 shows the NICS(0) values of the rings of the bicyclic isomers considered.

Table 4. NICS(0) values of the bicyclic isomers considered.

Structure	6-membered ring	5-membered ring
A	-2.5806	-3.7554
B	-3.0282	-4.4458
C	-2.5815	-8.2405
D	-0.9647	-4.1662
E	-3.2813	-5.1749
F	-4.2927	-4.2482

The data reveal that in each case the 5-membered ring is more aromatic than the corresponding 6-membered one, except in structure F in which the NICS values are comparable for both rings but 6-membered ring being slightly more aromatic. It should be due to positional effects of the nitro substituents.

Table 5 lists the NICS(0) values of the ring in phenolate azides considered. In this case the aromaticity order should be Fa>Ea>Ca>Ba>Da>Aa. The azido and nitro groups are electron attractors. The ring electrons are withdrawn meanwhile the phenolate oxygen supplies electrons. Depending on the position of the substituents, electron distribution over the ring varies which affects the ring current which is an indispensable factor for aromaticity.

Table 5. The NICS(0) values of the phenolate azides considered.

Structure	NICS
Aa	-15.6717
Ba	-16.6621
Ca	-19.0270
Da	-15.4628
Ea	-19.4803
Fa	-20.1372

See Figure 2 for the structures.

4. Conclusion

The present study within the restrictions of density functional theory and the level of basis set employed has revealed that like DDNP, the other positional isomers arising from the nitro groups prefer to be in the phenolate azide form rather than the bicyclic (dinitrobenzoxadiazole) isomers. The NICS(0) values obtained have indicated that 5-membered ring in the bicyclic isomers is more aromatic than the 6-membered ring except DDNP (Structure F). Whereas in the azide form DDNP is the most aromatic within the series of azide isomers in which all the electron attracting groups are crossly conjugated with each other.

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