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Some nitroborazines – A DFT treatment

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Abstract

Borazine is an inorganic analogue of benzene and its nitro derivatives recently found some applications. Presently some nitro derivatives of borazine have been considered within the restrictions of density functional theory at the level of B3LYP/6-311++G(d,p) level. It has been found that all the structures of consideration have thermo chemically exothermic heat of formation and favorable G^o values at the standard states and energetically stable. Various structural and quantum chemical data have been collected and discussed, including UV-VIS spectra. Also the NICS (0) data have been obtained for the species which suggest that the structures are aromatic irrespective of whether nitro groups are linked to nitrogen or boron atoms.

1. Introduction

Organic compounds containing nitro (NO_2) substituents have high energy content and many of them are useful as explosive materials. Theoretical and experimental studies have suggested that some boron derivatives have some potential as new high energy materials [1-7]. On the other hand, borazine which is an inorganic analogue of benzene and its nitro derivatives recently have attracted attention as explosive materials [3]. However, nitroborazines although have higher thermodynamic stability, but lower detonation parameters compared to the corresponding nitrobenzenes [3]. These compounds usually have large negative heats of formation, and thus release energy, but the product B_2O_3 is a solid compound means that the number of moles of gaseous products is less [3,4]. The nitroborazines presently considered are either isoconjugate with an odd alternant or nonKekule' alternant hydrocarbon anions and the last group inherently should have some explosive character [8]. Note that having a nonKekule isoconjugate anion is a necessary but not a sufficient condition for being an explosive material [8].

2. Method of Calculations

In the present study, all the initial optimizations of the structures leading to energy minima have been achieved first by using MM2 method which is then followed by semi empirical PM3 self consistent fields molecular orbital method [9-11]. Afterwards, the structure optimizations have been achieved within the framework of Hartree-Fock and finally by using density functional theory (DFT) at the level of B3LYP/6-311++G(d,p) [12,13]. Note that 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 [14]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [15] and Lee, Yang, Parr (LYP) correlation correction functional [16]. In the present study, the normal mode analysis for each

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structure yielded no imaginary frequencies for the 3*N*–6 vibrational degrees of freedom, where *N* is the number of atoms in the system. This search has indicated that the structure of each molecule considered corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths have been thoroughly searched in order to find out whether any bond cleavage occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 [17]. Whereas the nucleus-independent chemical shift, NICS (0), calculations have been performed by using Gaussian 03 program [18].

3. Results and Discussion

In the present study, atoms of borazine are numbered as shown in Figure 1. Corresponding nitro derivatives are coded accordingly. The codes consisting of only odd numbers indicate that all the nitro groups are linked to nitrogen atoms (nitramines) of borazine skeleton. A code having an odd number and an even number is a mixed type which contains both N-NO_2 and B-NO_2 groups. Whereas all even numbered codes stand for the presence of B-NO_2 groups. Thus, code 13 indicates a dinitro derivative which possesses the nitro groups on nitrogens 1 and 3, whereas code 24 stands for a dinitro structure having NO_2 groups on boron atoms 2 and 4 (see Figure 2). On the other hand, structure having code 14 possesses nitro groups on nitrogen atom1 and boron atom 4.

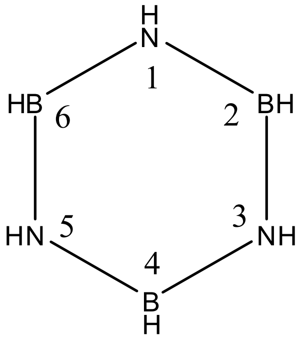
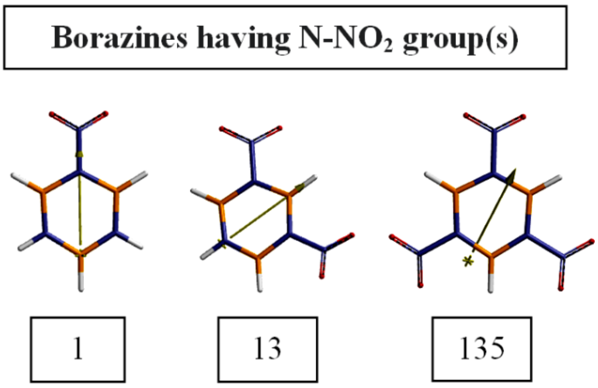


Figure 1. Numbering of ring atoms of borazine.

Nitroborazines considered contain isomer(s), such as structures 1 and 2; 13 and 24; 135 and 246 are pair wise isomeric and only the positions of the substituent(s) differ thus engendering positional isomers. Also 12, 13, 14 and 24 are isomeric dinitro structures.



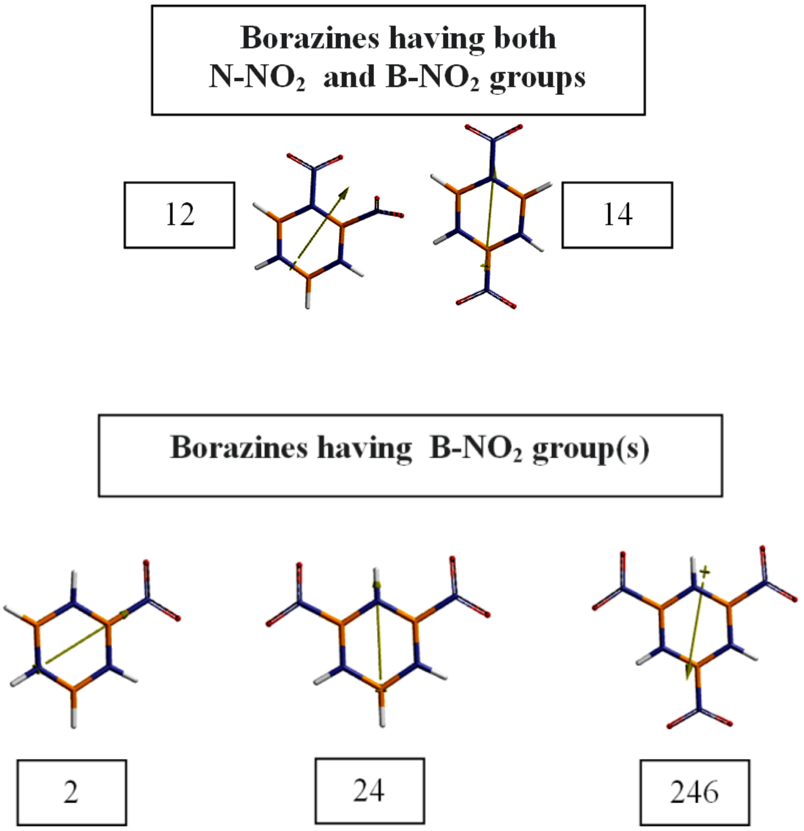


Figure 2. Optimized structures of the nitroborazines considered**.**

Table 1 lists some characteristics of the structures considered.

Table 1. Some characteristics of the structures considered.

Code	MW (amu)	Formula	Number of nitro groups
1	125.499	$H_5B_3N_4O_2$	1
13	170.496	$H_4B_3N_5O_4$	2
135	215.493	$H_3B_3N_6O_6$	3
12	170.496	$H_4B_3N_5O_4$	2
14	170.496	$H_4B_3N_5O_4$	2
2	125.499	$H_5B_3N_4O_2$	1
24	170.496	$H_4B_3N_5O_4$	2
246	215.493	$H_3B_3N_6O_6$	3

See Figures 1 and 2.

Table 2 displays some of the standard thermo chemical formation data of the species considered. The data reveal that the standard heat of formation (H^o) values of all the isomers are exothermic and they are favored according to their G^o values. Among the isomeric structures the algebraic order of H^o and G^o values is 24<14<12<13. Structures 1 and 2 constitute another type (mono nitro isomers) and when their H^o and G^o values are considered, B-NO_2 moiety results more exothermic and more favored structure compared to N-NO_2 having isomer. Note that C_v values progressively increase as the nitro groups increase in number. Moreover, the contribution of boron atom into C_v values seems to be positive.

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

Code	H°	S° (J/mol°)	G°	C_v (J/mol°)
1	-1174064.538	348.95	-1174168.577	98.20
13	-1711032.735	392.11	-1711149.645	120.06
135	-2247990.079	433.72	-2248119.397	142.27
12	-1711185.042	394.19	-1711302.571	120.98
14	-1711210.265	393.16	-1711327.487	120.44
2	-1174239.763	350.55	-1174344.28	98.70
24	-1711384.049	395.05	-1711501.833	120.63
246	-2248516.043	437.11	-2248646.369	142.42

See Figures 1 and 2. Energies in kJ/mol.

Table 3 shows some energies of the species considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. According to the data, they are all electronically stable structures.

Table 3. Some energies of the isomers considered.

Code	E	ZPE	E_C
1	-1174324.13	249.26	-1174074.87
13	-1711296.06	253.02	-1711043.04
135	-2248256.44	255.92	-2248000.52
12	-1711453.57	257.77	-1711195.80
14	-1711479.20	258.45	-1711220.75
2	-1174504.37	254.25	-1174250.12
24	-1711657.69	263.13	-1711394.56
246	-2248798.13	271.32	-2248526.81

See Figures 1 and 2. Energies in kJ/mol.

Note that the mixed type dinitro derivatives (12 and 14) are isomeric structures but the relevant data in Tables 2 and 3 reveal that 14 is more exothermic and more stable compared to the isomer 12. It seems B-NO_2 group at the 4-position results in more favorable isomer which could be due to the electronic π-topology. In general, replacement of N-NO_2 moiety by B-NO_2, keeping the relative positions of NO_2 groups in the molecule, results in more exothermic and more favorable structure (compare structures 1 and 2; 13 and 24; 135 and 246). In each pair of structures, the second one is more stable than the first. As for the ZPE values, the centric perturbation of N-NO_2 to B-NO_2 is accompanied by a more positive ZPE value. Even, isotopic exchange type perturbations results in some changes in ZPE values [19].

Figure 3 shows the ESP charges on atoms of the species 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 [17]. Electrostatic potential is the energy of interaction of a positive charge with a molecule. It represents a balance between repulsive interactions involving the positively charged nuclei and attractive interactions involving the negatively charged electrons.

The data in Figure 3 indicate that nitrogen atoms linked to a NO_2 group bear some negative partial charge whereas boron atoms of B-NO_2 moieties possess some positive partial charge in all the cases.

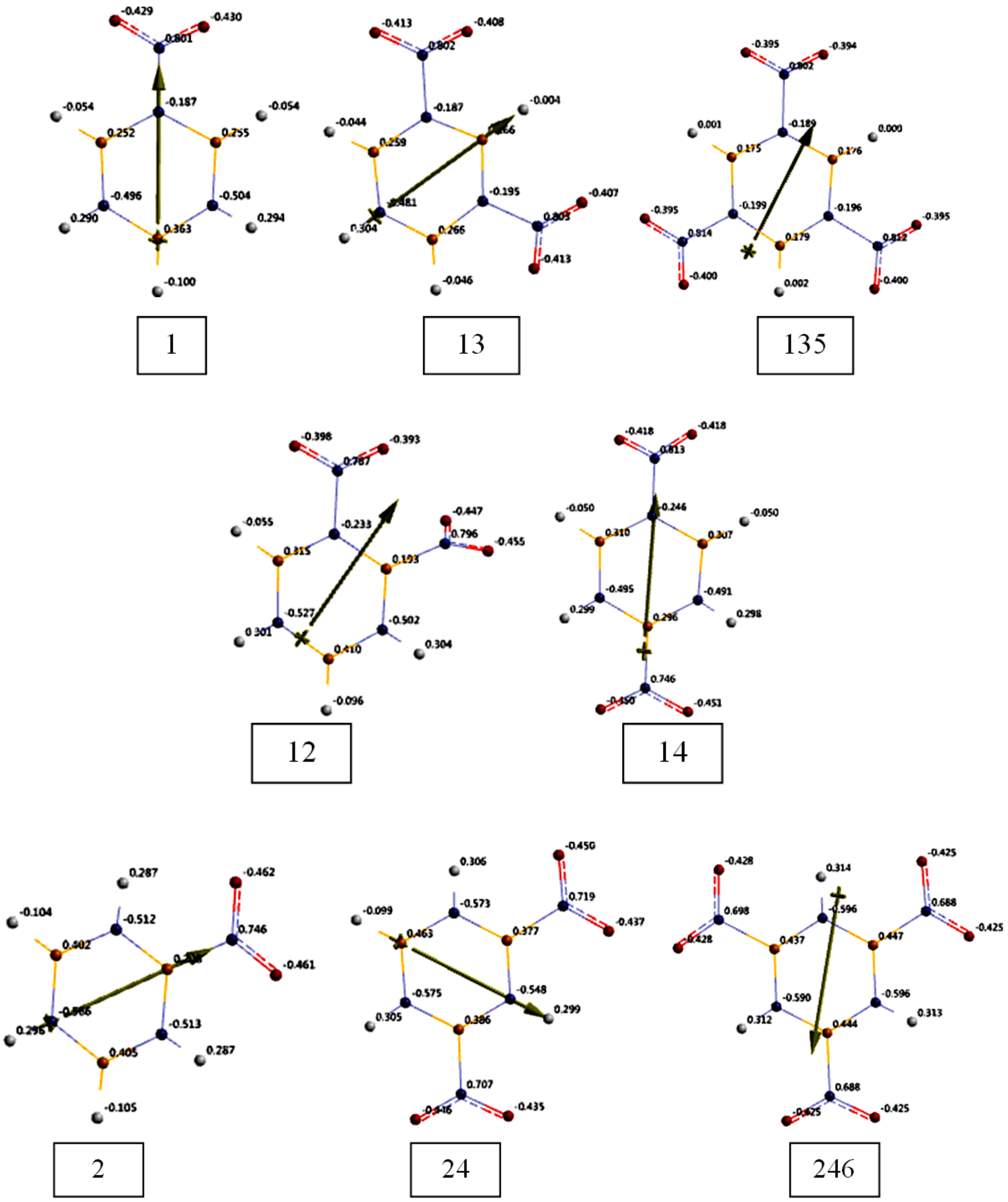
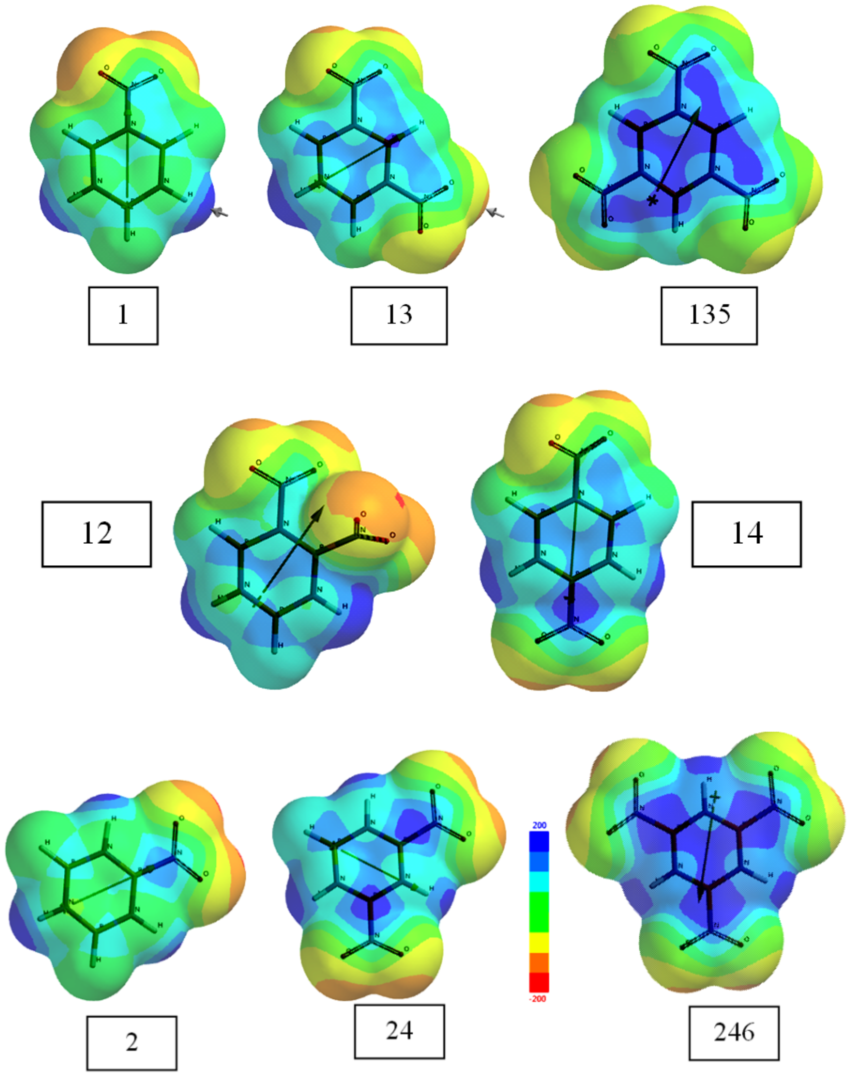


Figure 3. ESP charges on the atoms of the species considered.

Figure 4 stands for the electrostatic potential maps of the species where negative potential regions reside on red/reddish and positive ones on blue/bluish parts of the maps. Electrostatic potential map paints the value of electrostatic potential onto an electron density surface. As seen in Figure 4, as the number of nitro groups increases in the structures, blue areas on the boron atoms progressively get darker and darker.


1

13

135

12

14

2

24

246

Figure 4. ESP maps of the species considered.

Figure 5 shows the bond densities of the nitroborazines considered. The bond density contains fewer electrons in total and demarks atomic connectivity. In the figure the perturbation effect of boron atom in every case is clearly discernable. The bond density of N-NO_2 bond(s) seems to be higher than the respective values of B-NO_2 bond(s). It should arise from the difference(s) of electro-negativities of nitrogen and boron atoms in the ring. Additionally, electron attracting ability of nitro groups attracts some lone pair electrons of nitrogen atom which is not possible for boron atom case.

The local ionization potential maps of the species are shown in Figure 6, where conventionally red/reddish regions (if any exists) on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. It is worth remembering that the local ionization potential map is a graph of the value of the local ionization potential on an isodensity surface corresponding to a van der Waals surface.

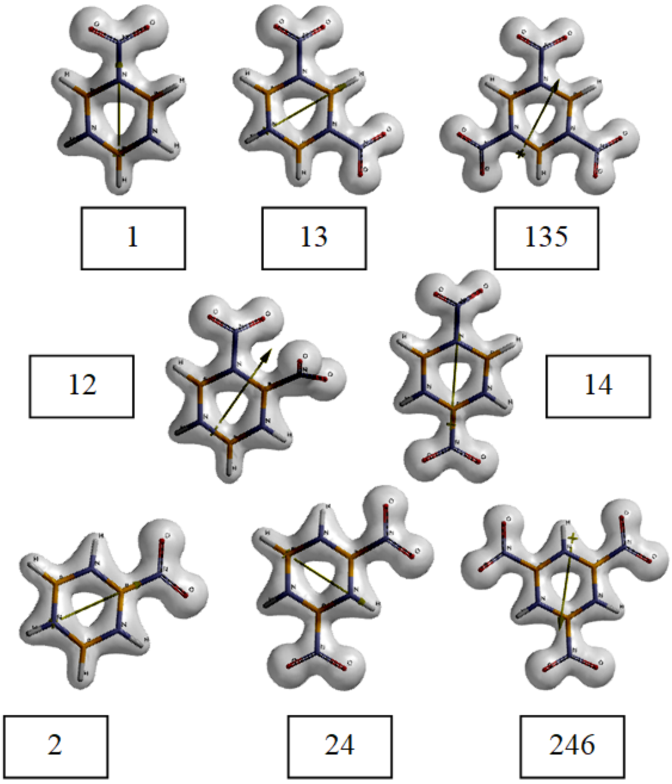


Figure 5. Bond densities of the species considered.

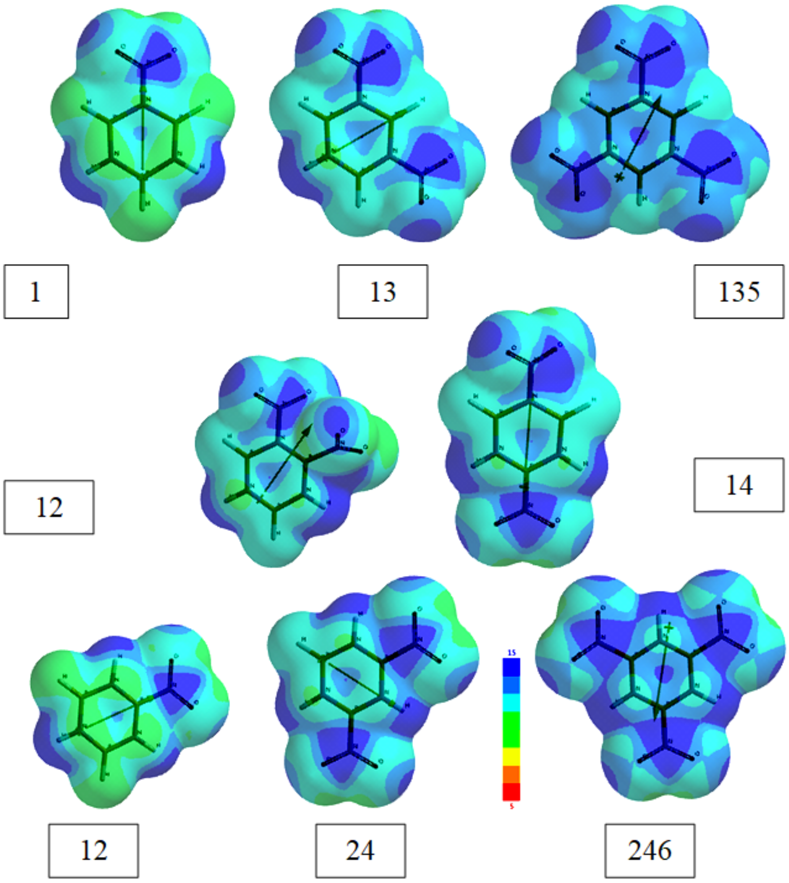


Figure 6. Local ionization potential maps of the species considered.

The LUMO maps of the isomers are shown in Figure 7. Note that a LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color (if any exists) stands for the maximum value of the LUMO and the red colored region, associates with the minimum value. Note that the LUMO and NEXTLUMO are the major orbitals directing the molecule towards of the attack of nucleophiles [17]. Positions where the greatest LUMO coefficient exists is the most vulnerable site in nucleophilic reactions.

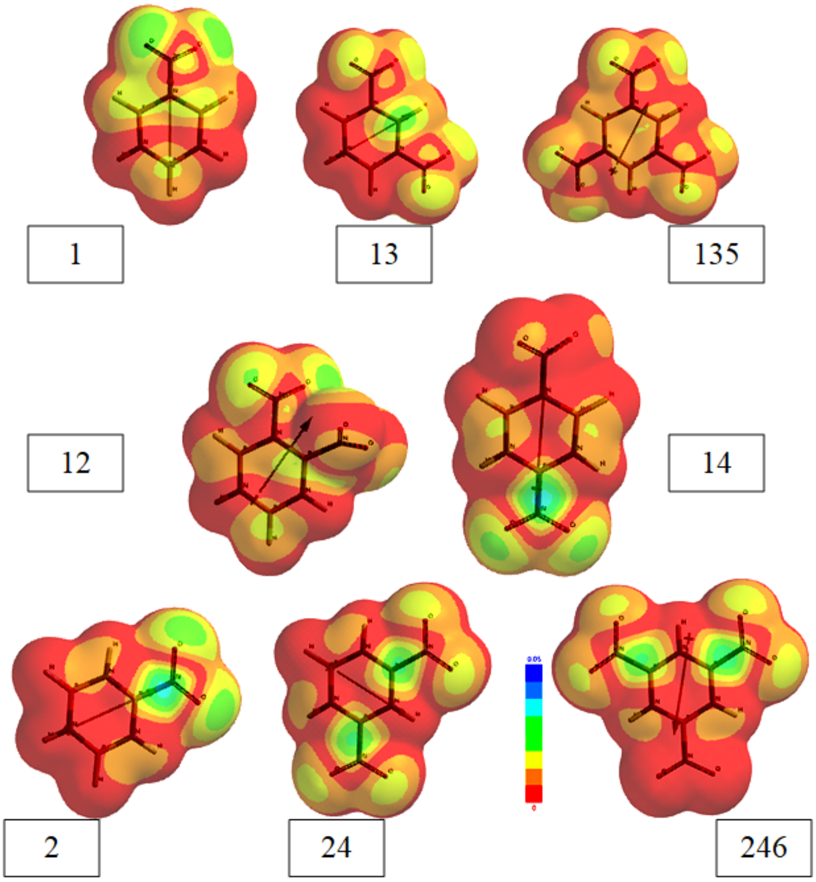
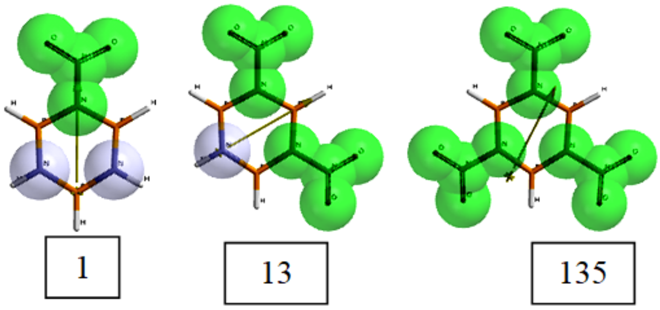


Figure 7. LUMO maps of the species considered.

The chemical function descriptors (CFD) of the nitroborazines considered are shown in Figure 8, where HBA and HBD stand for hydrogen bond acceptor and donor type properties, respectively. Note that CFDs are attributes given to a molecule in order to characterize or anticipate its chemical behavior. As seen in the figure the CFD characteristics change depending on the number of nitro groups as well as their positions.



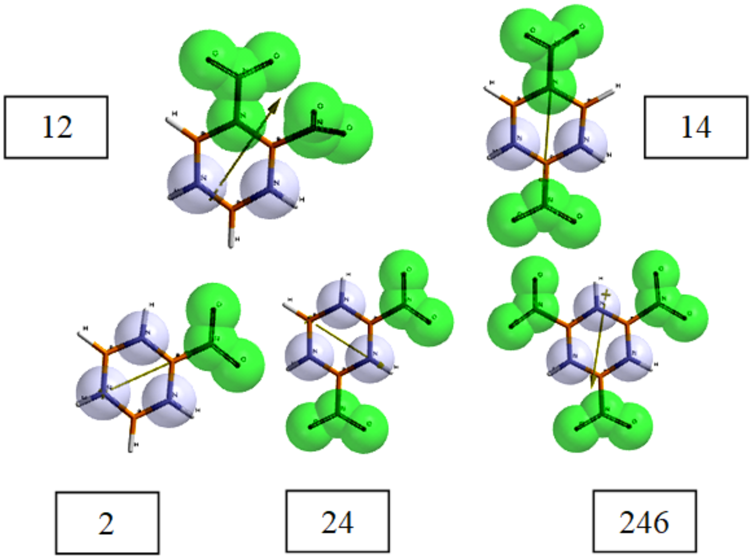


Figure 8. The CFD patterns of the nitroborazines considered. (Green: HBA, Purple: HBA, HBD, +ionizable).

Table 4 lists the HOMO, LUMO energies and the interfrontier molecular orbital energy gap, Δε, values (Δε = ε_{LUMO}-ε_{HOMO}) of the species considered. As expected, increase of the number of nitro groups lower both the HOMO and LUMO energies.

Table 4. The HOMO, LUMO energies and Δε values of the species considered.

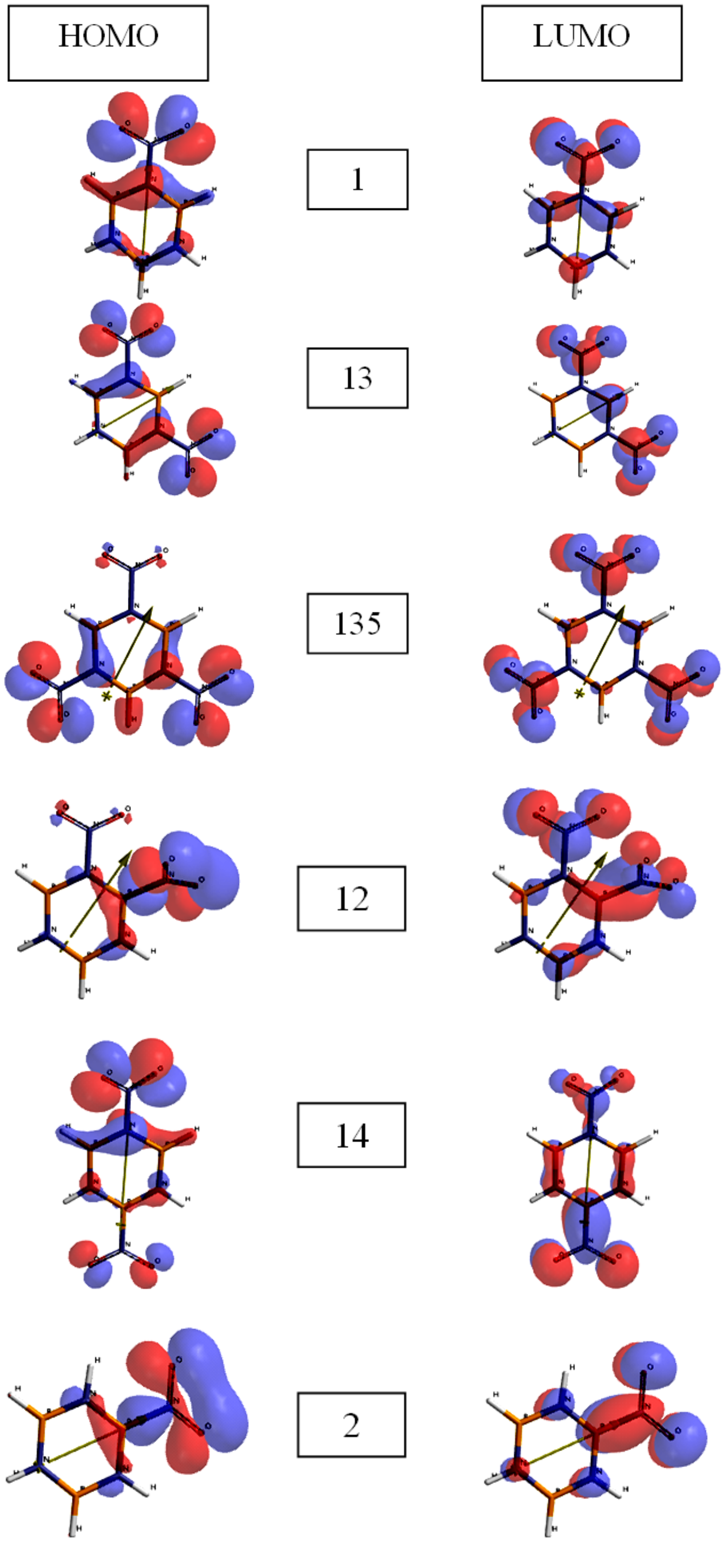
Code	HOMO	LUMO	Δε
1	-801.19	-229.13	572.06
13	-853.11	-282.21	570.90
135	-897.92	-323.58	574.34
12	-831.05	-284.26	546.79
14	-851.80	-335.59	516.21
2	-812.38	-278.45	533.93
24	-847.69	-336.59	511.10
246	-884.05	-381.67	502.38

See Figures 1 and 2. Energies in kJ/mol.

However, in the case of isomeric nitroborazines, there is no regularity on the lowering or raising of the frontier molecular orbital energies depending on the location of the nitro group(s). The order of Δε values is 246< 24<14 <2< 12< 13<1 <135. Some ballistic properties of explosives are correlated with the interfrontier molecular orbital gap values, for instance the impact sensitivity of explosives are related to the interfrontier molecular orbital energy gap values. That is narrower the gap, the explosive becomes more sensitive to an impact stimulus [20, 21].

The detonation velocity of the boron compounds is always superior to the all-carbon analogues at the corresponding densities. Nitro-substituted boron compounds bearing amino groups instead of hydrogen display even higher performance [7]. However, the calculated detonation velocity and pressure are relatively low for nitroborazines [3, 4]. Nitroborazines have higher thermodynamic stability and lower detonation parameters compared to the corresponding nitro benzenes. Presumably the problem with regard to the detonation properties is that the oxygen atoms in the molecules are used to form solid B_2O_3 [3, 4].

Figure 9 displays the HOMO and LUMO patterns of the isomers considered.



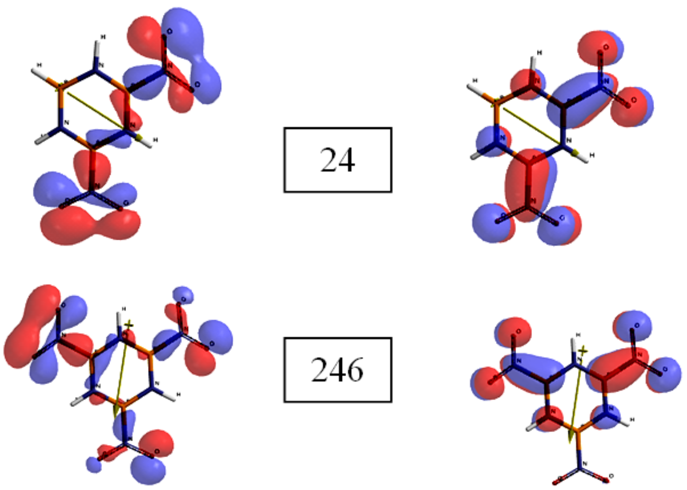


Figure 9. The HOMO and LUMO patterns of the species considered.

The calculated time dependent UV-VIS spectra (TDDFT) of the nitroborazines are shown in Figure 10.

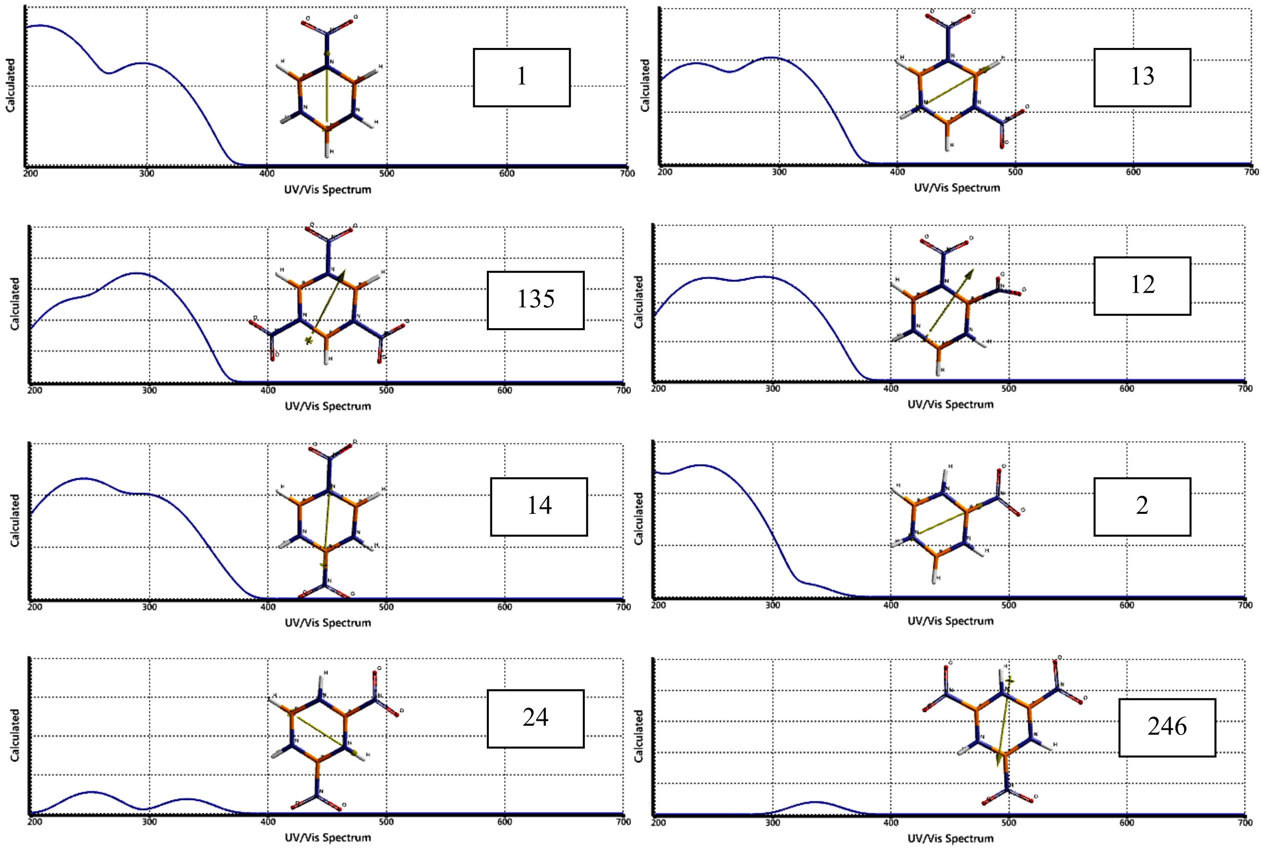


Figure 10. The calculated UV-VIS spectra (TDDFT) of the species considered.

As seen in the figure, all the spectra are confined into UV region having some shoulders which vary in shape, intensity and position depending on the molecular structures. The molecular structure dictates the extent of conjugation and value of the transition moment which is responsible for the excitations of nonbonding and/or π-electrons to unoccupied molecular orbitals [22, 23]. Table 5 lists the calculated λ_{max} values (nm) of the species considered.

Table 6 displays “nucleus-independent chemical shift” NICS (0) values of the rings of the nitroborazines considered. The calculated data so far have piled in the literature [24-35], have indicated that negative NICS values are associated with aromaticity. On the contrary, positive NICS values are associated with antiaromaticity while small NICS values are indicative of non-aromaticity [24-26,33-35].

Table 5. The calculated λ_{max} values (nm) of the species considered.

Species considered							
1	13	135	12	14	2	24	246
189.69	228.17	238.16	244.65	248.52	237.76	250.71	337.27
212.30	293.10	289.20	289.99	296.29		332.28	
296.02							

The data presented in Table 6 reveal that as the number of nitro groups increases, the NICS values get more and more negative indicative of increased aromaticity. However this effect is more pronounced in the series of nitramine type nitroborazines (1, 13 and 135). The nitro group on the boron atom(s) produces relatively less aromatic structures. Since, a cyclic π-electron delocalization is necessary for the aromaticity, the values in the table give some idea about the effectiveness of the cyclic conjugation and symmetric distribution of π-electrons in the ring of nitroborazines considered.

Table 6. NICS (0) values of the ring of the species considered.

Species							
1	13	135	12	14	2	24	246
-3.202	-5.009	-6.906	-4.253	-4.144	-2.684	-3.572	-4.465

4. Conclusion

In the present computational study, within the restrictions of DFT study at the level of B3LYP/6-311++G(d,p), some nitroborazines have been considered. They include some positional isomers having N-NO_2 and or B-NO_2 moieties. The present results indicate that in the vacuum conditions, all the structures are characterized with exothermic heat of formation and favorable Gibbs free energy of formation values and they are electronically stable. The nitrogen atoms linked to a NO_2 group bear some negative partial charge whereas boron atoms of B-NO_2 moieties possess some positive partial charge in all the cases. The bond density of N-NO_2 bond(s) seems to be higher than the respective values of B-NO_2 bond(s). The results reveal that increase of the number of nitro groups lower both the HOMO and LUMO energies. However, in the case of isomeric nitroborazines, there is no regularity on the lowering or raising of the frontier molecular orbital energies depending on the location of the nitro group(s). All the UV-VIS spectra of the nitroborazines considered are confined into UV region having some shoulders which vary in shape, intensity and position depending on the molecular structures.

On the other hand, as the number of nitro groups increases, the NICS (0) values get more and more negative which is indicative of increased aromaticity. However this effect is more pronounced in the series of nitramine type nitroborazines. The nitro group on the boron atom(s) produces relatively less aromatic structures.

The present study, comparatively considers the nitroborazines, having N-NO_2 and /or B-NO_2 bonds thus enlightens some properties of these potential high energy compounds at the molecular level.

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