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Charged forms of some nitroborazines – A DFT treatment

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Abstract

Spark sensitivity of explosives is an important subject**.** One of the causes of accidental explosion of explosives is due to static electricity. The present study deals with the development of static electric charge on nitroborazines resulting ionic charges eventually. In the present study, mono ionic forms of various nitroborazines are considered within the restrictions of unrestricted density functional theory at the level of UB3LYP/6-311++G(d,p) level. All the ionic systems of present interest are thermally favored and electronically stable at the standard states. Various structural and quantum chemical data have been collected and discussed, including UV-VIS spectra.

1. Introduction

Impressive recent advances in the synthesis of novel boron-containing molecules and the diverse materials derived there from, combined with a significantly improved understanding of the properties of these boron based molecules and materials, have been published [1]. Nitrogen enriched boron-based heterocyclic high energy density materials (HEDMs) have received a considerable interest because of their remarkable explosive properties [2,3]. In recent decades, various articles on boron compounds or borazine have piled up in the literature [4-12].

A spark is a discrete discharge that leaks through a gap between two conductors in the form of an ionization path in which the stored energy is transferred swiftly. The spark is triggered when the breakthrough field strength is reached at a certain point in the gap. Also, sufficiently high field strength is required in the whole space between the electrodes so that the discharge can travel through that space. A homogeneous electrical field between the electrodes is an important requirement [13].

A solid material in an electric field acts as a dielectric material and when the field strength is sufficient, electric and/or electro-thermal breakdown occurs. An electric breakdown develops as a result of interaction of free charged particles (electrons and/or ions) accelerated by an electric field with the particles of a dielectric, or as a result of inelastic displacement of bound charges in a dielectric under the action of an external electric field [14-16].

Whatever the discharge type is, organic molecules exposed to an electric field should be affected due to polarization depending on the field strength. It is known that the polarizability increases with the size of the atom and with the number of electrons it possesses [15-18]. Note that polarization effects eventually may lead to ionic charge development.

The spark sensitivity of various explosive molecules has been the subject of very many articles in the literature [19-28]. In the present study, mono ionic forms of nitroborazines have been subjected to density

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functional (DFT) treatment. Up to the best knowledge of the author there is no work in the literature on the charged forms of borazine or nitroborazines.

2. Method of Calculation

In the present study, the initial structural optimizations of all the monoionic structures leading to energy minima have been achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [29,30] at the restricted level [31,32]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, the structural optimizations were managed within the framework of density functional theory (DFT) [33,34] at the (unrestricted, doublet state) level of UB3LYP/6-311++G(d,p) [35,36]. 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 [34,37]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [38] and Lee, Yang, Parr (LYP) correlation correction functional [39]. Also, the vibrational analyses have been done and 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 [40].

3. Results and Discussion

In the present study, numbering of ring atoms of borazine is 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 of borazine skeleton yielding certain nitramines. 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 the 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 atom-1 and boron atom-4. The capital letters A or C after the code numbers indicates that the ion concerned is a mono valent anion or cation, respectively.

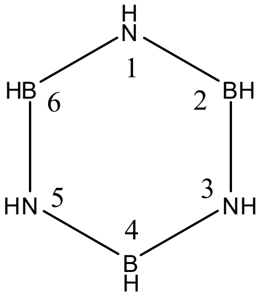


Figure 1. Numbering of ring atoms of borazine.

Figure 2 shows the optimized structures and the direction of the dipole moment vectors of the mono ionic nitroborazines of present consideration. The starting and end points of the dipole moment vector in each case is structure dependent. There is no particular chose for boron or nitrogen atom. In that sense relative position(s) of the nitro groups should be more effective rather than they are on the nitrogen or boron atom.

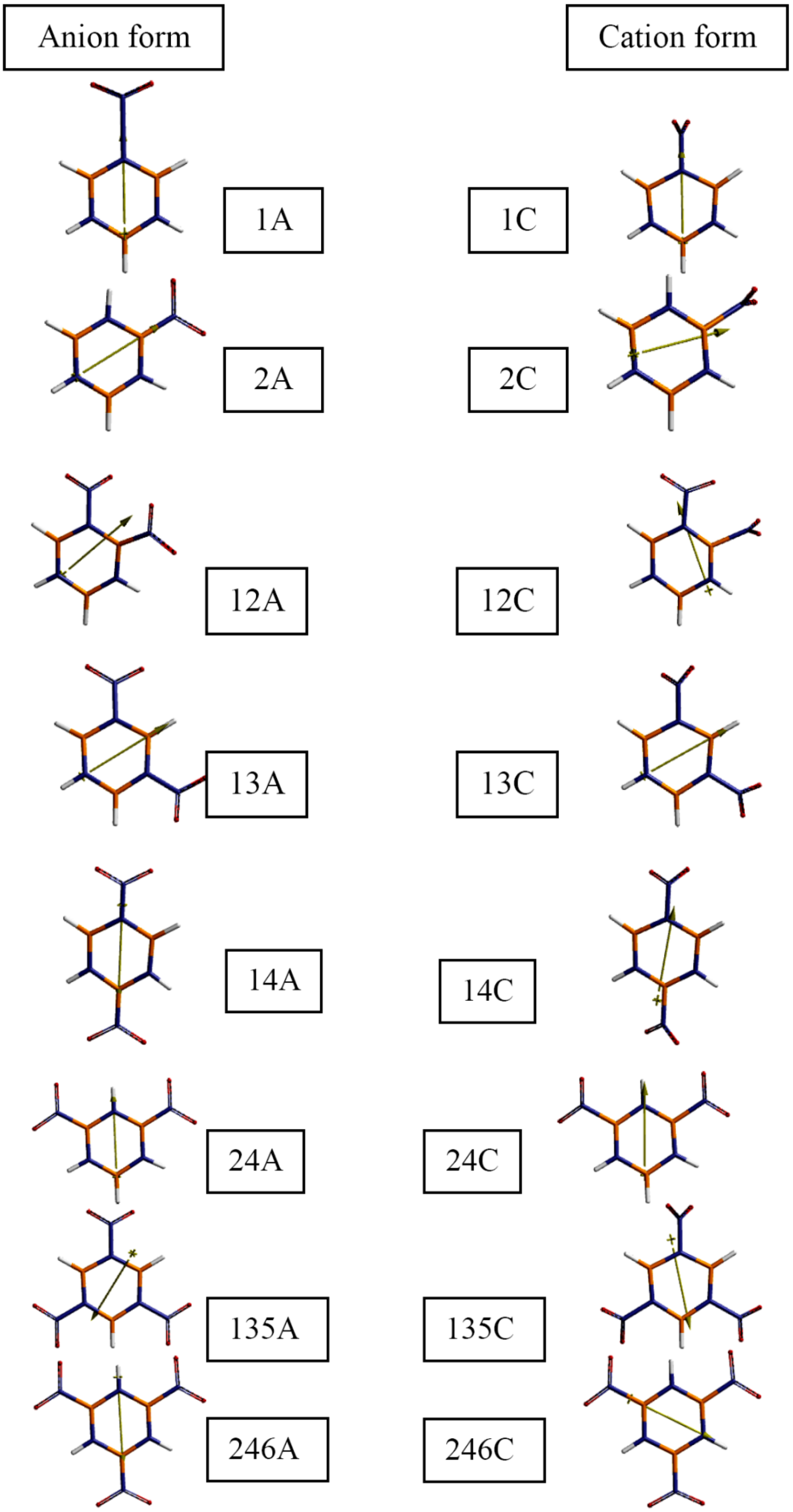


Figure 2. Optimized structures of the mono ions of nitroborazines presently considered.

The figure reveals that the optimization is accompanied mostly by some small bond length changes except in 1A which contains highly elongated $N\text{-}NO_2$ bond length/distance (possibly a bond rupture, see below text). Although in the anions the nitro group(s) is coplanar with the borazine ring, in the case of the cations some rotations about the $N\text{-}NO_2$ or $B\text{-}NO_2$ (1C, 2C, etc.) bonds happen. Also in some cations the ring bond angles deviate from the internal angles of a regular hexagon.

Table 1 lists some of the standard thermo chemical formation data of the nitroborazines considered. The data reveal that the standard heat of formation (H^o) values of all of them is exothermic and they are favored according to their G^o values. The relevant entropy values are all positive. As seen in the table the cations possess less exothermic H^o values compared to the relevant isomeric anion forms. In the case of mixed type nitroborazines which contains the same number(s) of nitro groups (e.g., dinitro group 12,13 and 14, or trinitro group 135 and 246) nitro group on boron atom yields more exothermic H^o value, thus the algebraic order becomes 24<14<12<13 and 246<135. The same order holds for the G^o values. As for the cations, the orders of H^o and G^o values are the same, namely 2<1 (mono nitro isomers), 24<14<12<13 (dinitro isomers) and 246<135 (trinitro isomers).

Table 1. Some thermo chemical properties of the nitroborazine ions considered.

Anionic form				Cationic form		
H^o	S^o (J/mol°)	G^o	Ions	H^o	S^o (J/mol°)	G^o
-1174166.18	369.99	-1174276.49	1	-1173090.36	361.25	-1173198.07
-1174361.05	354.13	-1174466.63	2	-1173260.66	359.67	-1173367.90
-1711355.04	394.86	-1711472.77	12	-1710185.28	403.78	-1710305.67
-1711170.91	400.70	-1711290.38	13	-1710021.80	400.10	-1710141.09
-1711405.01	395.01	-1711522.77	14	-1710202.09	401.10	-1710321.68
-1711580.00	397.61	-1711698.55	24	-1710380.51	401.96	-1710500.36
-2248183.08	441.42	-2248314.69	135	-2246942.64	444.16	-2247075.07
-2248763.96	442.28	-2248895.83	246	-2247489.23	443.40	-2247621.43

Energies in kJ/mol.

Table 2 shows some energies of the nitroborazines 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 table, the stability order of the anion forms of isomeric nitroborazine considered are 246>135, 24>14>12>13, and 2>1. The same orders hold for the cation forms of the nitroborazines considered. Note that 1A is less stable than its isomeric 2A, although in the previous structure (1A) $N\text{-}NO_2$ bond rupture occurs (entropically more favored but still less favored by G^o value compared to 2A). Note that in the table E_C for 1A stand for the decomposed system.

Table 2. Some energies of the nitroborazine ions considered.

Anionic form				Cationic form		
E	ZPE	E_C	Ions	E	ZPE	E_C
-1174410.57	231.58	-1174178.99	1	-1173341.51	239.21	-1173102.30
-1174618.96	246.87	-1174372.09	2	-1173516.78	244.39	-1173272.39
-1711616.45	250.41	-1711366.04	12	-1710444.76	247.32	-1710197.44
-1711423.83	241.02	-1711182.81	13	-1710276.25	242.87	-1710033.38
-1711667.27	251.37	-1711415.9	14	-1710461.42	247.68	-1710213.74
-1711845.88	254.82	-1711591.06	24	-1710645.05	252.76	-1710392.29
-2248438.57	243.55	-2248195.02	135	-2247196.59	241.88	-2246954.71
-2249035.14	259.36	-2248775.78	246	-2247759.91	258.66	-2247501.25

Energies in kJ/mol.

Table 3 lists some properties of the nitroborazine ions considered. It is worth mentioning that the polar surface area (PSA) is defined as the amount of molecular surface area arising from polar atoms (N,O) together with their attached hydrogen atoms. Although some of these ions are isomeric, their PSA values differ from each other meaning that the same kind of atoms might be influenced by electronic factors differently at different positions.

Table 3. Some properties of the nitroborazine ions considered.

Anionic form					Cationic form			
Area (Å^2)	Volume (Å^3)	PSA (Å^2)	Ovality	Ions	Area (Å^2)	Volume (Å^3)	PSA (Å^2)	Ovality
158.39	126.42	71.28	1.30	1	148.32	122.36	62.38	1.24
145.58	120.35	70.63	1.23	2	145.97	119.91	71.89	1.24
170.72	142.96	99.56	1.29	12	170.56	142.39	100.27	1.29
171.70	144.02	93.88	1.29	13	173.94	144.58	93.16	1.31
171.30	142.70	101.17	1.30	14	173.35	142.82	102.69	1.31
171.95	141.66	110.03	1.31	24	172.71	141.43	111.82	1.32
197.27	166.28	124.59	1.35	135	199.70	166.94	124.13	1.36
198.68	163.09	149.84	1.38	246	197.78	162.67	149.49	1.37

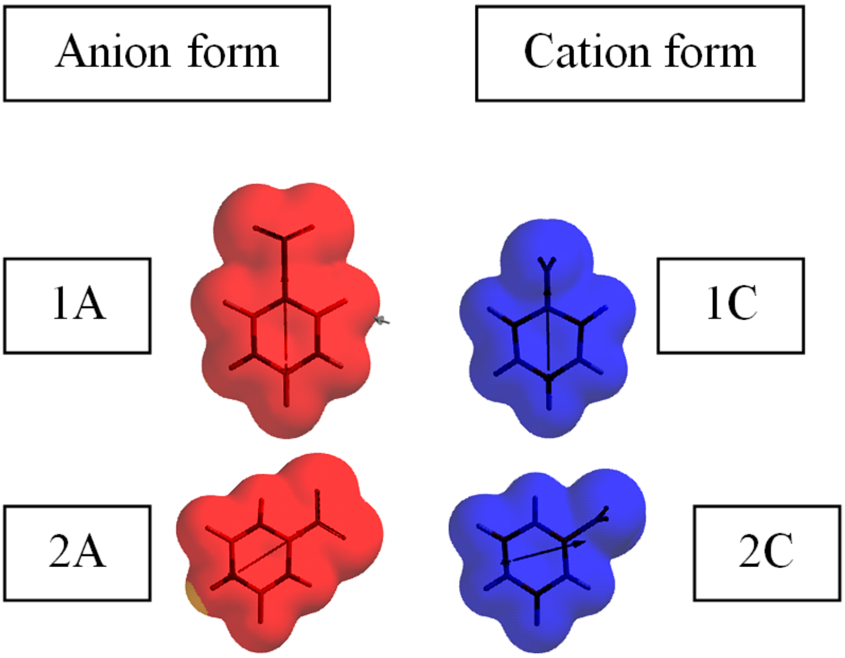
Table 4 lists dipole moment values of nitroborazine ions considered. As the data reveal, in general anions have much greater dipole moment values compared to the relevant cations. The dipole moment provides a measure of the extent to which charge distributed in a molecule and the resultant value is the vectorial sum of individual bond dipoles in a molecule. The magnitude of the dipole moment also depends on the extent to which charge is separated. All these factors dictate the magnitudes and the direction of the resultant dipole moments.

Table 4. Dipole moment values of nitroborazine ions presently considered.

Anionic form	Ions	Cationic form
8.32	1	1.14
11.16	2	0.39
11.42	12	3.84
7.85	13	1.95
4.05	14	0.95
6.48	24	1.17
0.03	135	1.55
2.38	246	0.61

In debye units.

Typical electrostatic potential (ESP) maps of the anions and cations are depicted in Figure 3. Electrostatic potential map paints the value of electrostatic potential onto an electron density surface. The maps based on the ESP charges which are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [40]. In an electrostatic potential map colors towards red depict negative potential while colors towards blue depict positive potential and colors in between (orange, yellow, and green) depict intermediate values of the potential. As seen in the figure the anions and cations are characterized with all red and all blue painted maps, respectively. The net charge of the ions spread over the whole system except 12A and 13A in which some inhomogeneity is discernable in the map (yellowish region).



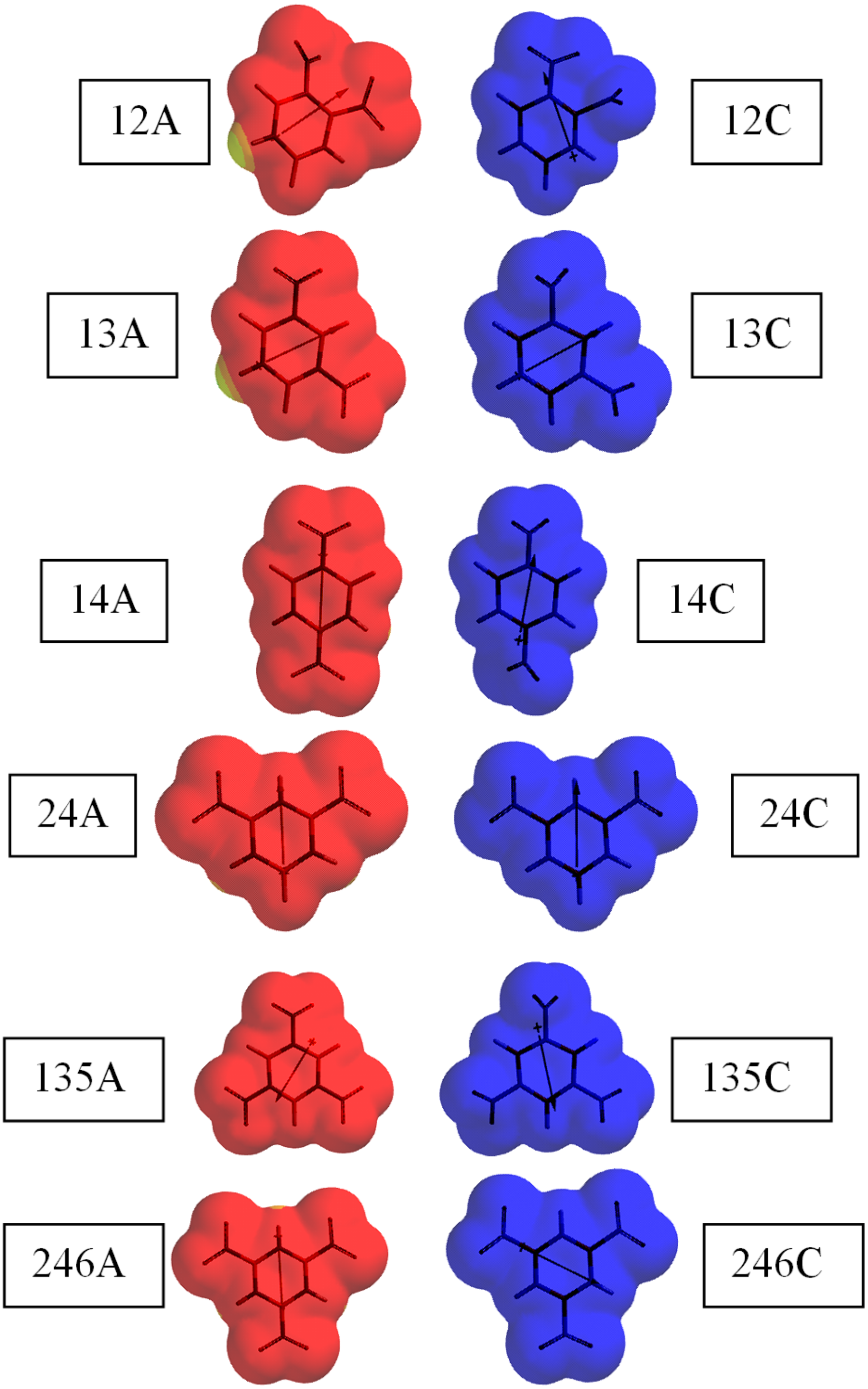


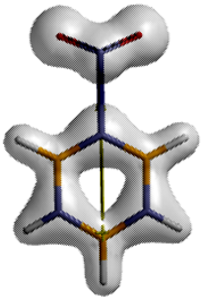
Figure 3. ESP maps of the nitroborazine ions considered.

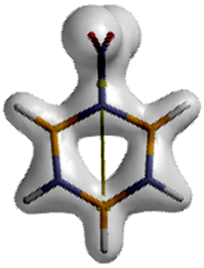
Figure 4 shows the bond densities of the nitroborazine ions of the present concern. The bond density contains fewer electrons in total and demarks atomic connectivity. Note that in 1A case no bond density present between the ring nitrogen atom and the nitro group. The distance between them is 2.276 Å which indicates a bond rupture (see also Figure 2). On the other hand, in the cation (1C) the bond density seems to be very high and the ring has some bond elongations and contractions. The nitro group attracts π-electrons of the ring to the nitramine moiety. Such kind of electronic effects should be occurring in the other ions considered depending on the π-topology of the ions.

Anion form

Cation form

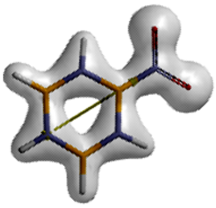
1A

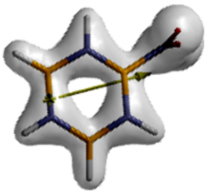




1C

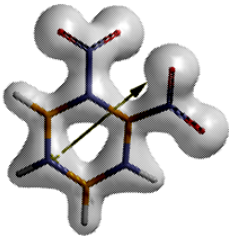
2A

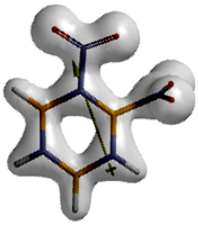




2C

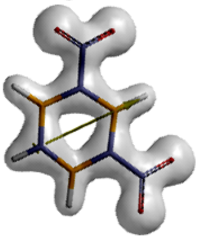
12A

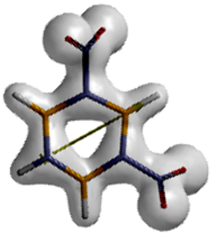




12C

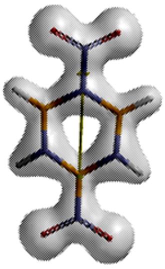
13A

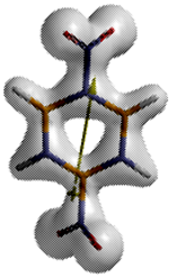




13C

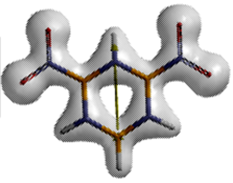
14A

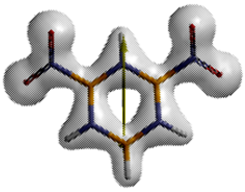




14C

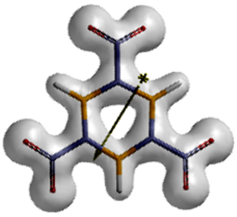
24A

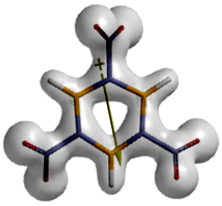




24C

135A





135C

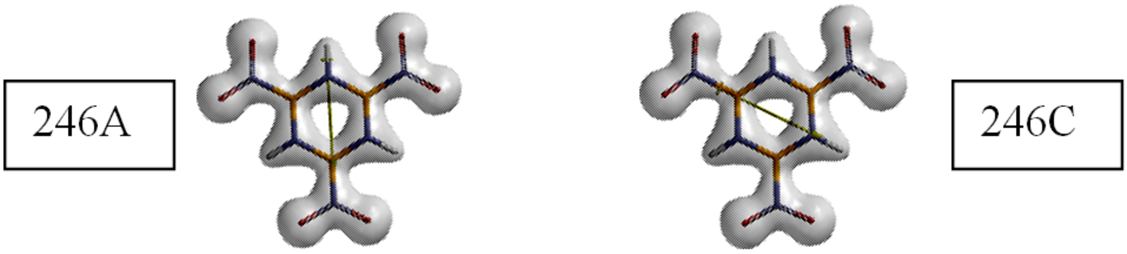
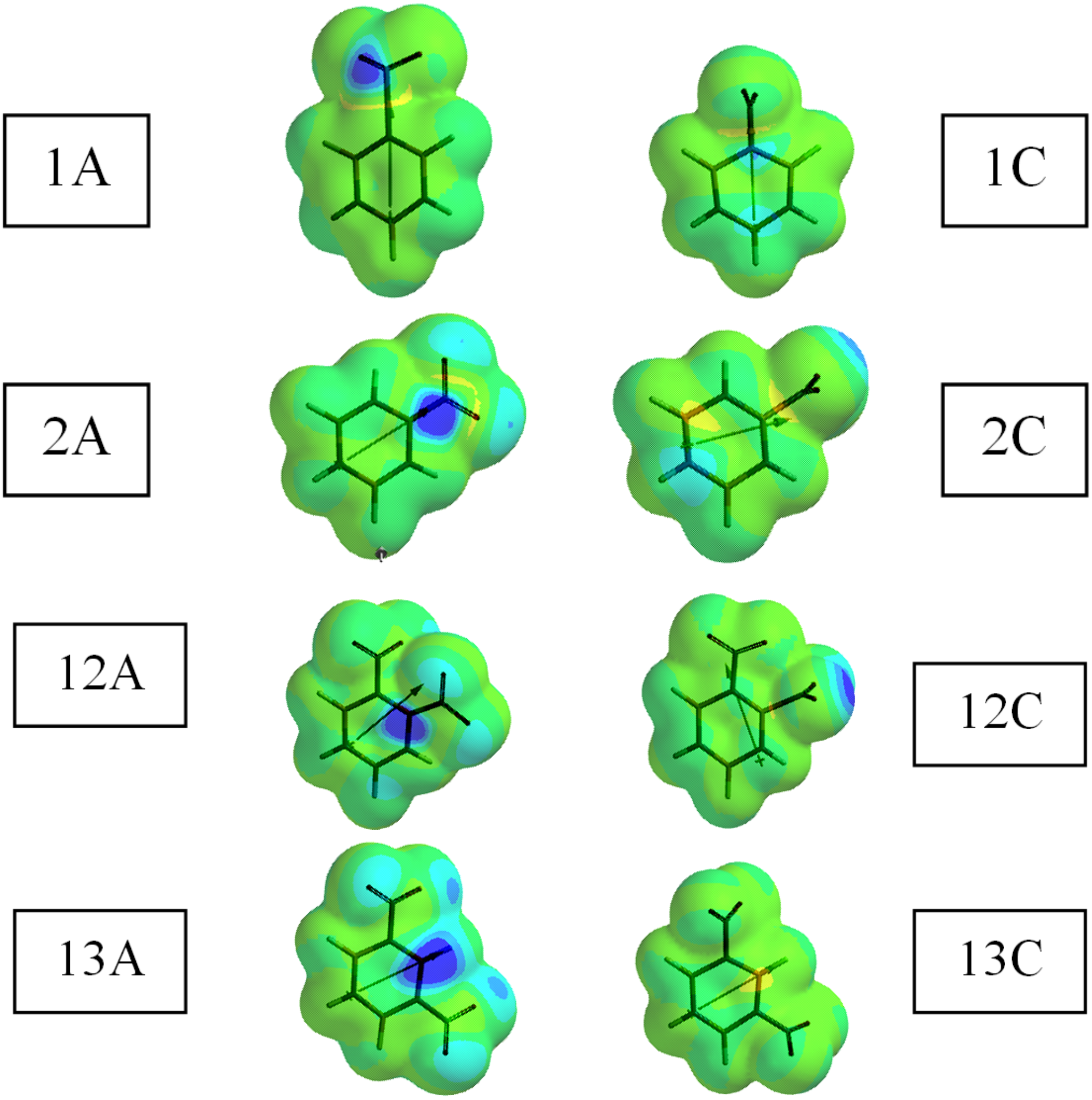


Figure 4. Bond densities of the nitroborazine ions of the present concern.

Figure 5 shows the spin density maps of the ions considered which indicate the distribution of the unpaired electron over the system. A spin density map is a graph that shows the value of the spin density on an electron density isosurface corresponding to a van der Waals surface. On the other hand, spin density is the difference in number of electrons of α and β spins at a point in space. It indicates the location of the unpaired electron in radical or unpaired electrons in triplet or higher multiplicity state in units of electrons/au^3.



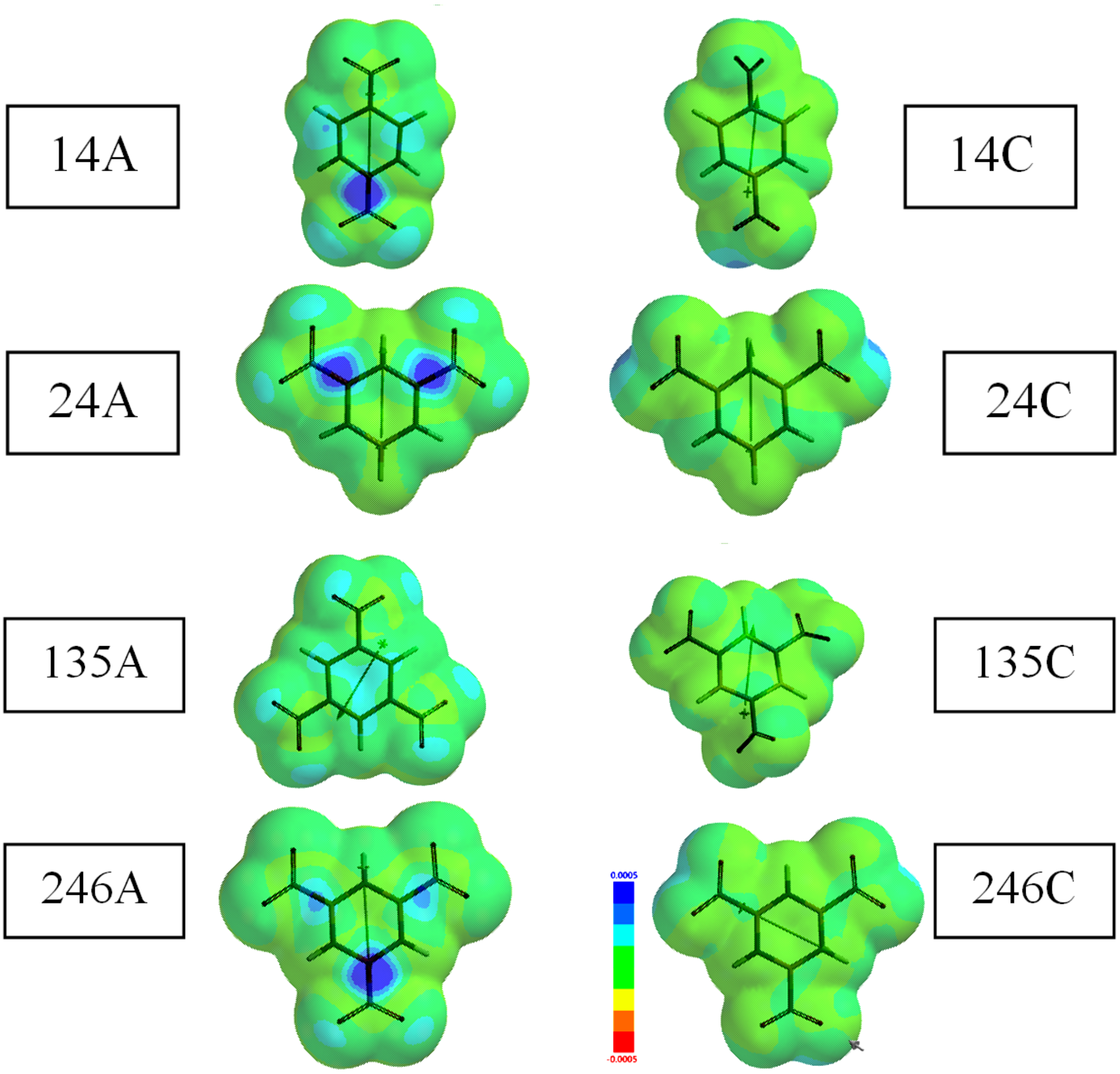
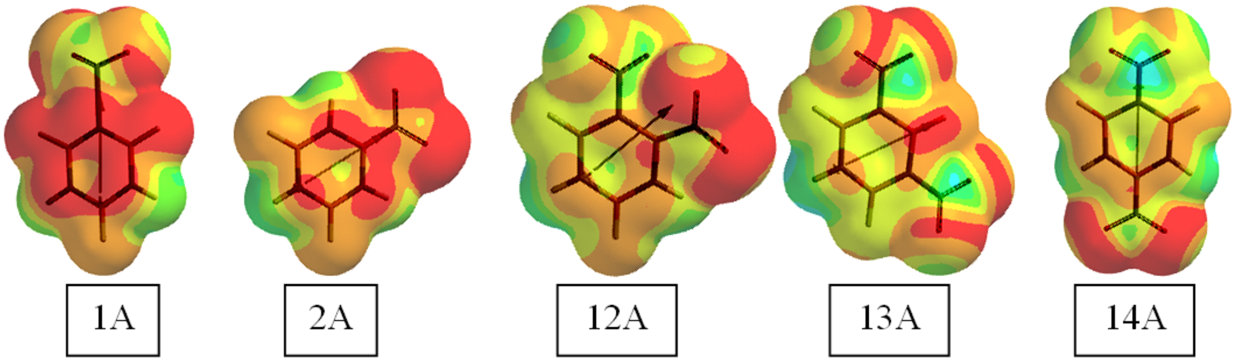


Figure 5. The spin density maps of the nitroborazine ions considered.

Figure 6 shows the local ionization maps of the nitroborazine anions considered. 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 are subject to electrophilic attack.



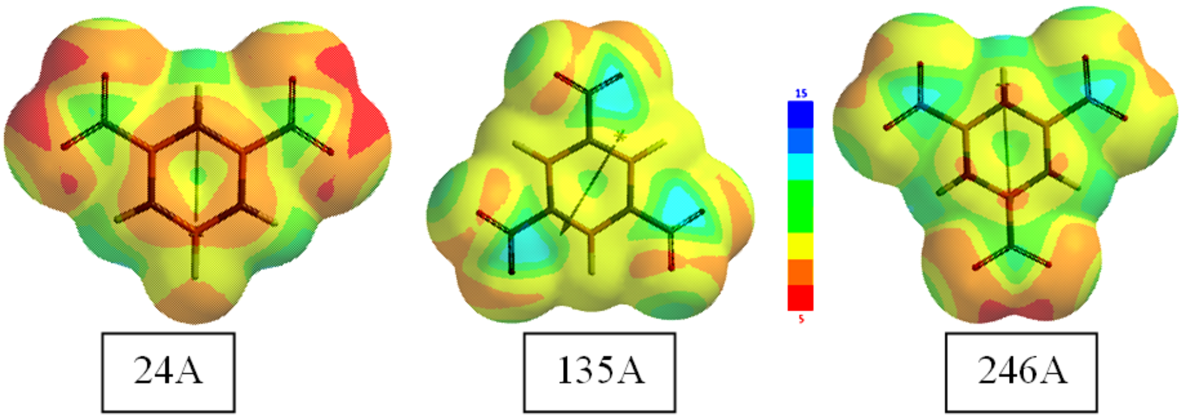


Figure 6. Local ionization maps of the nitroborazine anions considered.

Table 5 shows the HOMO, LUMO energies and the interfrontier molecular orbital energy gap (Δε) values, ($\Delta\varepsilon=\varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of the species considered.

Table 5. The HOMO, LUMO energies and Δε values of the nitroborazine ions considered.

Anionic form				Cationic form		
HOMO	LUMO	Δε	Ions	HOMO	LUMO	Δε
-127.62	241.47	369.09	1	-1356.27	-813.68	542.59
45.92	221.91	175.99	2	-1353.26	-798.97	554.29
-20.57	144.37	164.94	12	-1320.09	-841.92	478.17
22.02	100.39	78.37	13	-1370.66	-777.18	593.48
-42.89	86.92	129.81	14	-1339.58	-788.74	550.84
-41.13	48.08	89.21	24	-1338.59	-793.56	545.03
-42.22	30.95	73.17	135	-1343.51	-803.38	540.13
-94.01	-31.76	62.25	246	-1312.63	-804.93	507.70

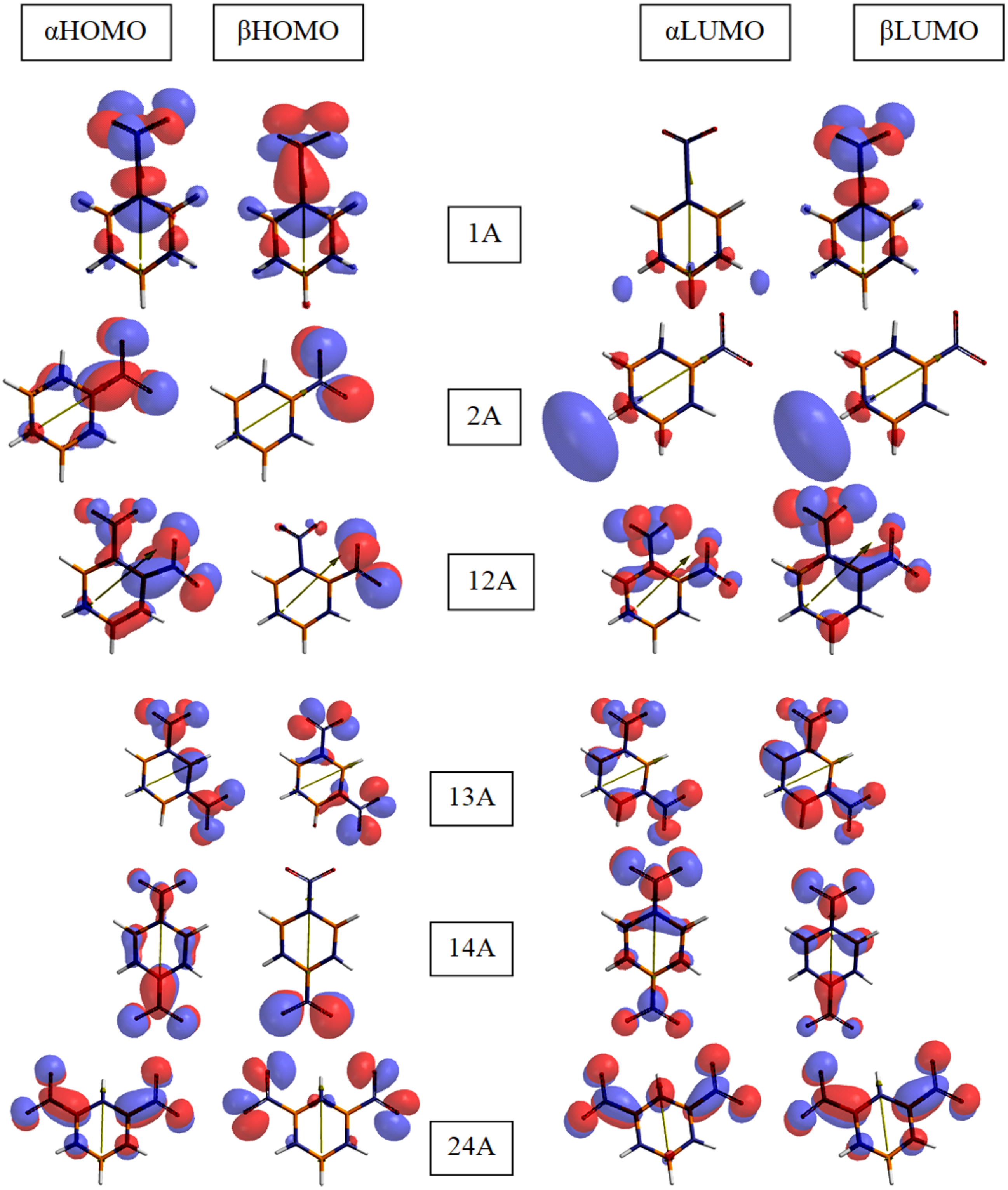
Energies in kJ/mol.

Note that the algebraic HOMO energy order for mono nitro borazines is 1A<2A and remember that 1A has a broken N-NO_2 bond. In the case of dinitro derivatives, in which one of the nitro group is on the boron atom, the algebraic order of the HOMO energies is 14A <24A <12A <13A, hence the order is dependent on the location of the NO_2 group as well as π-topology of the system. In the trinitro case, the order happens as 246A <135A. Thus, the nitro groups on the boron atoms lower the HOMO energy level more effectively compared to the case of all on the nitrogens. The LUMO energy order for the anions is 246A<135 A <24A <14A <13A <12A <2A <1A. In isomeric structures the order can be grouped as 246A<135 A; 24A <14A <13A <12A and 2A <1A, respectively for the tri, di and mono nitro anions. Thus, nitro groups all on the boron atoms lower the LUMO energy of the anions more effectively than all on the nitrogen atoms. In the case of dinitro borazine, 24A, has much lower LUMO energy than all the mixed types (such as 14A, 13A, etc.).

As for the cations, the HOMO and LUMO energy orders are 3C<1C <2C <135C <14 C <24C <12C <246C and 12C <1C <246C <135C <2C <24C <14C <13C, respectively. The LUMO energy order for isomeric cations is, 246C <135C; 12C <24C <14C <13C and 1C <2C, respectively for the tri, di and mono nitro anions.

The narrowest interfrontier molecular orbital gap values (Δε) for the anions follow the order of 246A<135A<13A whereas for the cations it is 12C<246C etc.

Figure 7 shows the HOMO and LUMO patterns of nitroborazine anions considered. Because of the unrestricted treatment, the α and β orbitals arise for the ions of nitroborazines.



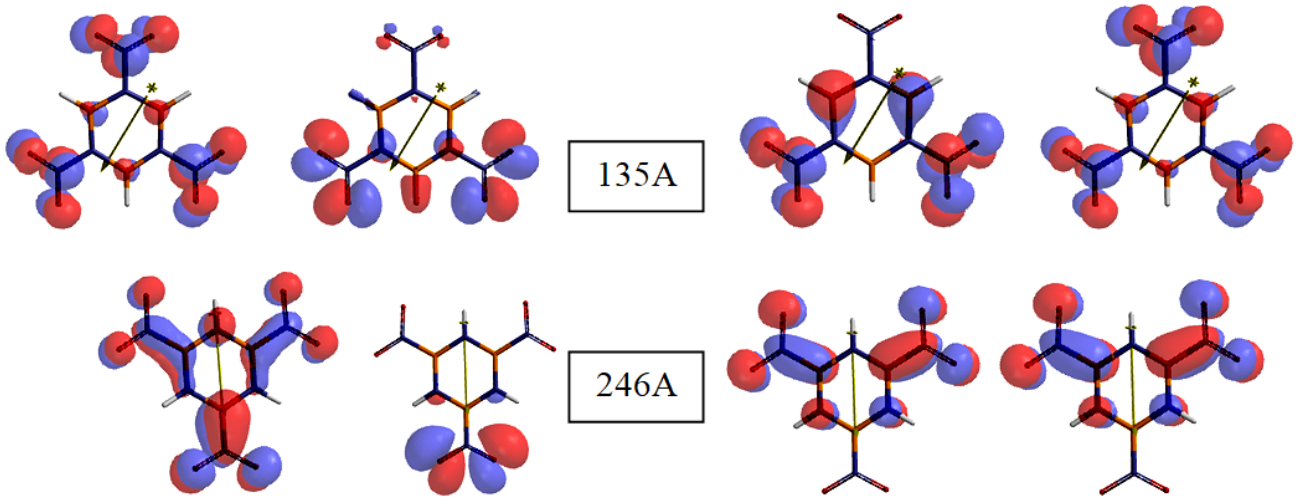
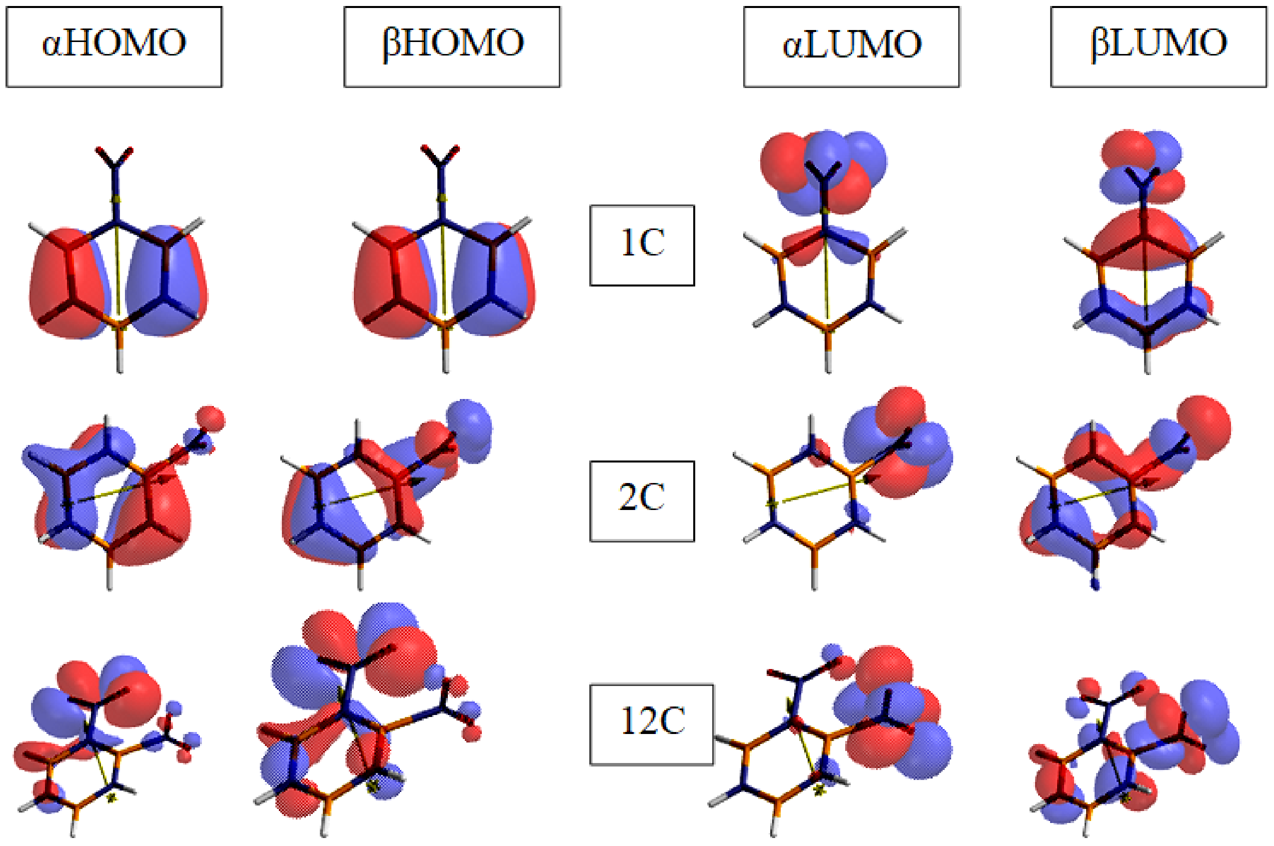


Figure 7. The HOMO and LUMO patterns of nitroborazine anions considered.

Figure 8 displays the HOMO and LUMO patterns of nitroborazine cations considered.



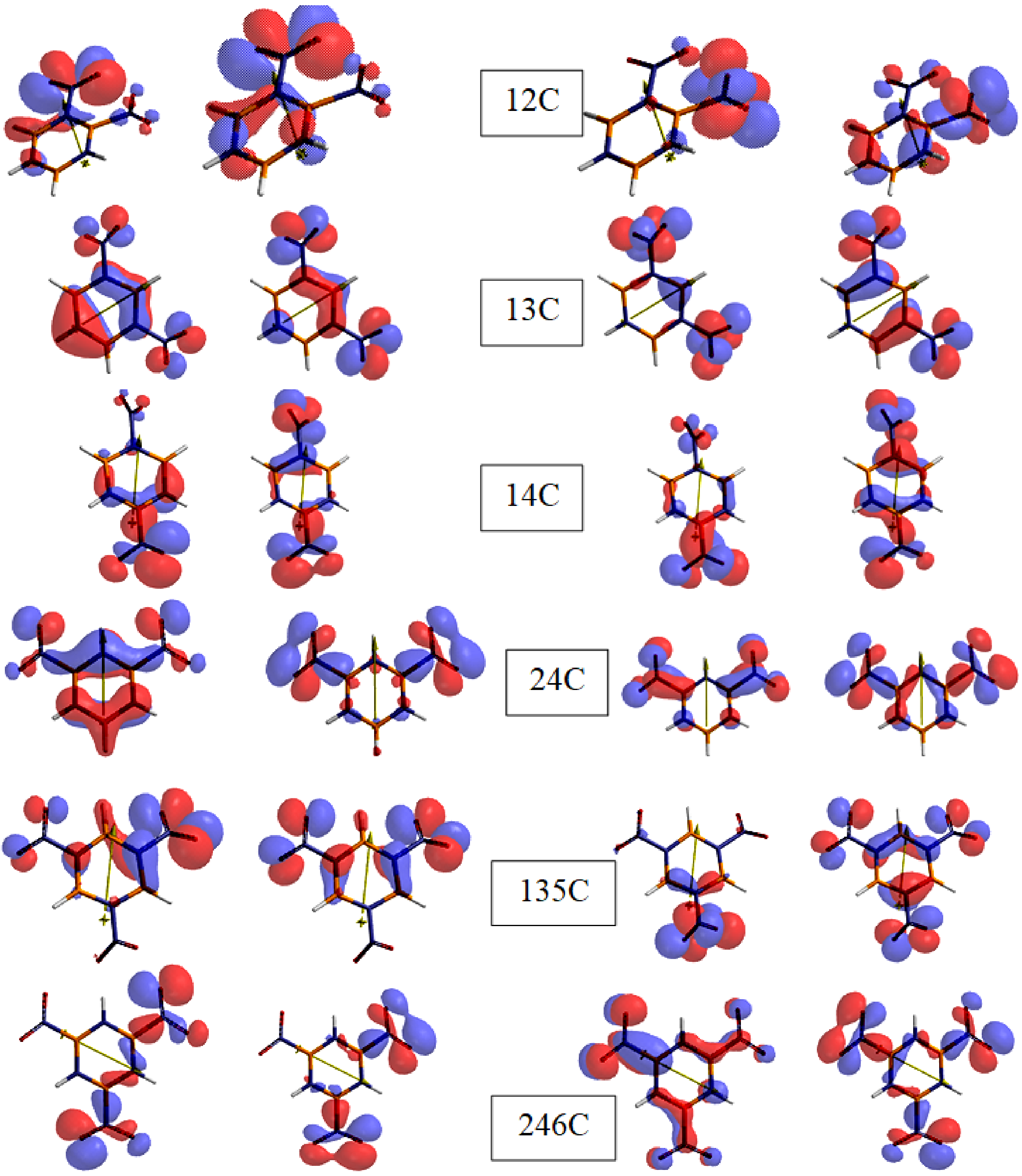
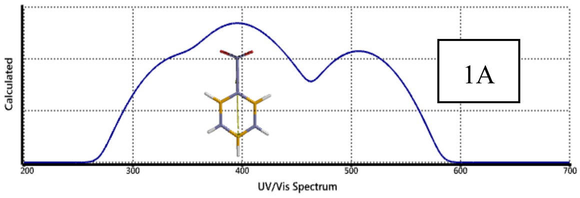


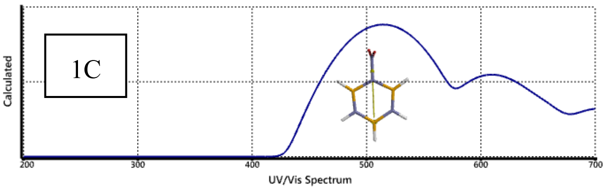
Figure 8. The HOMO and LUMO patterns of nitroborazine cations considered.

The calculated UV-VIS spectra (time dependent DFT, TDDFT) of the nitroborazine ions considered are shown in Figure 9. In the figure, the missing spectra of the nitroborazine cations; 24C, 135C and 246C do not have any appreciable absorption in the range. From the inspection of the spectra of the anions, one may get the impression of that as the nitro group(s) bind to boron atom(s) some sort of bathochromic effect [41,42] is observed, such as 2A,12A etc., but not always. However, the cations usually absorb at longer wavelengths compared to the corresponding anion forms. Note that the calculated spectra obtained from not only the HOMO-LUMO transition but some other transitions as well. Therefore, λ_{max} values may not directly follow the order of $\Delta\varepsilon$ values in all the cases considered.

Anion form

Cation form


1A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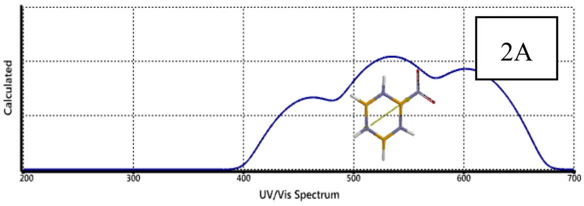
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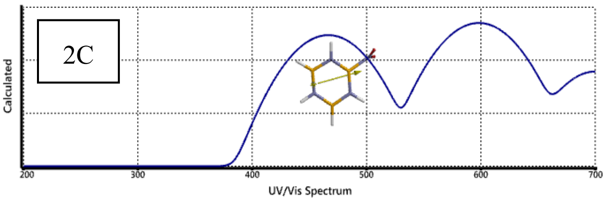
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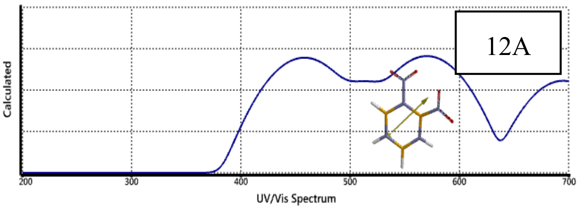
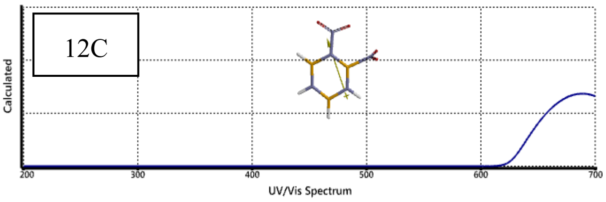

12A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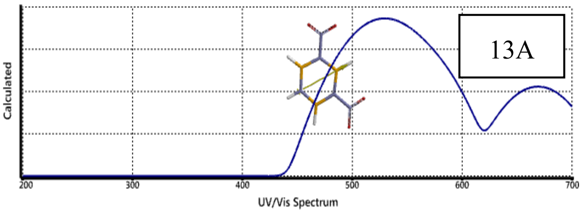
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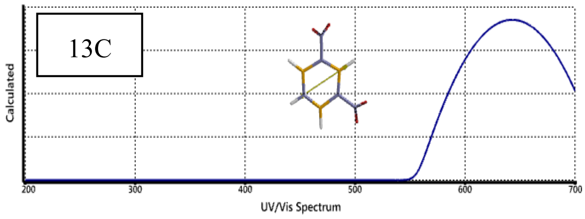
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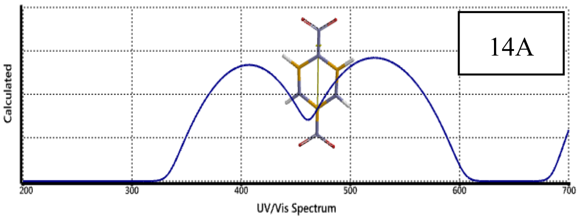
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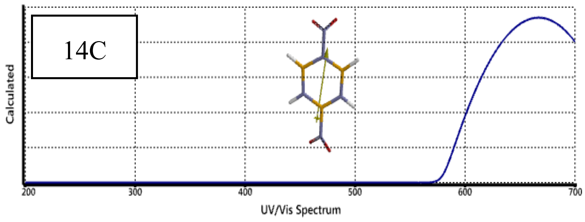
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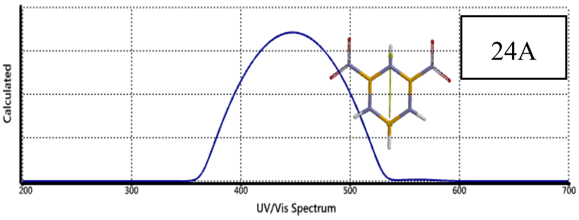
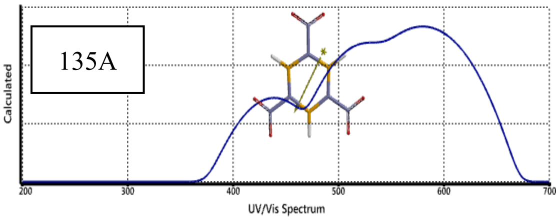

24A


135A

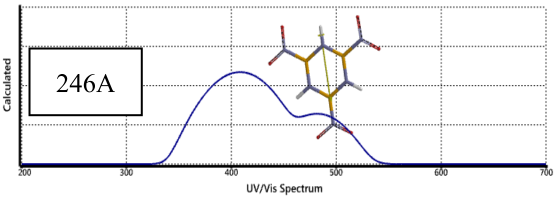


Figure 9. The calculated UV-VIS spectra of the nitroborazine ions considered.

4. Conclusion

In the present computational study, some nitroborazine ions are considered within the restrictions of density functional theory and the applied basis set. In the vacuum conditions, all of the ionic systems are characterized with exothermic heat of formations and favorable Gibbs free energy of formation values and they are all electronically stable (except 1A). Depending on the position of the nitro group(s) and the extend of conjugation of them with the ring, the HOMO and LUMO energies vary. Consequently, the UV-VIS spectra show variations, even among the isomeric ions considered. The stability of these mono ions implies that the relevant parent systems should resist to static charging (no bond cleavage happens) unless during the process in which some other initiation reactions occur due to certain factors arising from individual identity of the structures.

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