

Quantum chemical calculations of anion complex $[\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}]^{2-}$, $x = 9 - 12$

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Abstract. The geometric, energetic, spectral and electronic properties of various isomers of $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ anion complex with $x = 9 - 12$ have been studied using Density Functional Theory (B3LYP/6-311++G**). It was shown that the most stable isomers are characterized by the preference to form the most symmetric structures with uniformly distributed charge densities. However, when replacing a hydrogen atom with difluoramino group, an inductive effect occurs. NF_2 group pulls a part of electron density that leads to the polarization of the boron core. Blue shifts in the IR spectrum compared to the vibrations of the free radical NF_2 ranging from 5 to 69 cm^{-1} for the most stable isomers with the minimum total energy are characteristic and points to the stability of $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ anions. The obtained results broaden the idea of aromaticity of $\text{B}_{12}\text{H}_{12}^{2-}$ anion and will be useful in synthesis of new $\text{B}_{12}\text{H}_{12}^{2-}$ derivatives.

1. Introduction

There are currently synthesized and investigated hundreds of compounds of dodecahydro-*closo*-dodecaborate anions ($\text{B}_{12}\text{H}_{12}^{2-}$, figure 1) with simple (almost all metals of the Periodic Table), onium (alkyl-ammonium, -sulfonium, -phosphonium), and complex (transition metals with various organic ligands) cations [1-4]. The elemental composition of $\text{B}_{12}\text{H}_{12}^{2-}$ holds some promise for the preparation of compounds that can be used as energy-intensive components of energy-saturated materials for various purposes. However, because of the superior stability of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion, the vast majority of its compounds are difficult to ignite and burn poorly because of the formation of boron-oxycompounds on the surface of the burning particle melt. This fact does not allow the realization of the high energy intensity of these compounds. One of the ways to overcome this drawback is to incorporate the anions in mixed formulations with ultrafine polytetrafluoroethylene (UPTFE) [5]. Replacing the oxygen-containing oxidant (fully or partially) to UPTFE improves combustion of the borohydride fragment because the burning surface is constantly renewed by release of volatile boron trifluoride BF_3 or boron oxofluoride $(\text{BOF})_3$. In pure oxygen systems, boron release in the form of a boron oxide melt creates a protective film on the burning surface.

One of the most important features of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion is its aromaticity, i.e. the ability to replace the terminal hydrogen atoms with other atoms or groups of atoms without destroying the core. Therefore, another possible method of improving the flammability of the boron anion may be the introduction of fluorinated groups to the exo-environment of $\text{B}_{12}\text{H}_{12}^{2-}$.



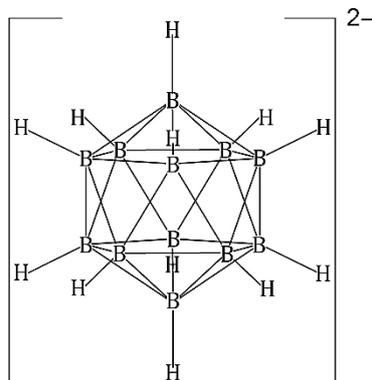


Figure 1. Structure of the $B_{12}H_{12}^{2-}$ anion.

Of particular fundamental and practical interest is the investigation of $B_{12}H_{12}^{2-}$ derivatives – structures with the hydrogen atoms replaced with other atoms or groups [1-9]. Previous quantum chemical calculations showed that the replacement of some hydrogen atoms in $B_{12}H_{12}^{2-}$ anion structure by fluoromethyl groups leads to the existence of stable anions [10]. Known is a number of nitrogen-substituted derivatives of $B_{12}H_{12}^{2-}$, for example, $B_{12}H_{11}NO^{2-}$, $B_{12}H_{11}NH_3^-$, $B_{12}H_{10}(NH_3)_2$, etc. [11]. Of particular theoretical interest is the substitution of oxygen and hydrogen atoms associated with a nitrogen atom to fluorine atoms. Nitrogen-fluorinated derivatives of $B_{12}H_{12}^{2-}$ anion can be practically valuable as a power-consuming fuel, the combustion of which will lead to the release of boron in the form of volatile fluorides. In this case the amount of combustion gas can be increased by 25% in comparison with carbon-fluorinated derivatives since nitrogen will be evolved in a gas form.

The aim of the present work is to characterize the stability and some physico-chemical properties of the anion complex $B_{12}H_x(NF_2)_{12-x}^{2-}$ ($x = 9 - 12$) with the use of quantum-chemical calculations.

2. Computational Details

All the calculations were carried out within the GAMESS-US package [12] using the hybrid functional B3LYP [13, 14] and the split-valence basis set 6-311++G** with diffuse and polarization functions. The choice of this computational method is based on the available literature data and our personal results. On the figure 2 we illustrated some of the results obtained with the use of various methods and split-valence basis sets. From these data it is well seen that even with the parallel computing, the computation time significantly increases with the addition of diffuse and polarization functions. But as far as we deal with the dodecahydro-*closo*-dodecaborate anion $B_{12}H_{12}^{2-}$ and its derivatives, the addition of diffuse functions is necessary for the correct description of the ionic nature, and the addition of polarization functions is important for the correct modeling of chemical bonds. Also, the calculated frequencies of the free radical NF_2 are in a better agreement with the known experimental value of $\sim 1075\text{ cm}^{-1}$ [15] when using DFT method of calculations. Furthermore, B3LYP/6-311++G** shows a good correlation between accuracy and computational time.

The initial geometry of the $B_{12}H_{12}^{2-}$ structure was formed with I_h symmetry. Further optimization of $B_{12}H_{12}^{2-}$ and $B_{12}H_x(NF_2)_{12-x}^{2-}$ ($x = 9 - 12$) was executed without symmetry constraints. Anion structures with substituted difluoramino groups $B_{12}H_x(NF_2)_{12-x}^{2-}$, ($x = 9 - 12$) were formed by replacing of one to three hydrogen atoms with the appropriate number of NF_2 groups. To find the most stable structures, we compared total energies of all possible isomers of the given size. Harmonic vibrational frequency analysis was used to confirm the true local minima of the potential energy surface. If no imaginary frequencies were found, the structure was considered to be a global minimum. All energies were corrected by their zero-point energies (ZPE), and scaled by a factor of 0.9877 [16]. Bond orders between atoms and valence electron configurations were computed using Natural Bond Orbital (NBO) analysis [17].

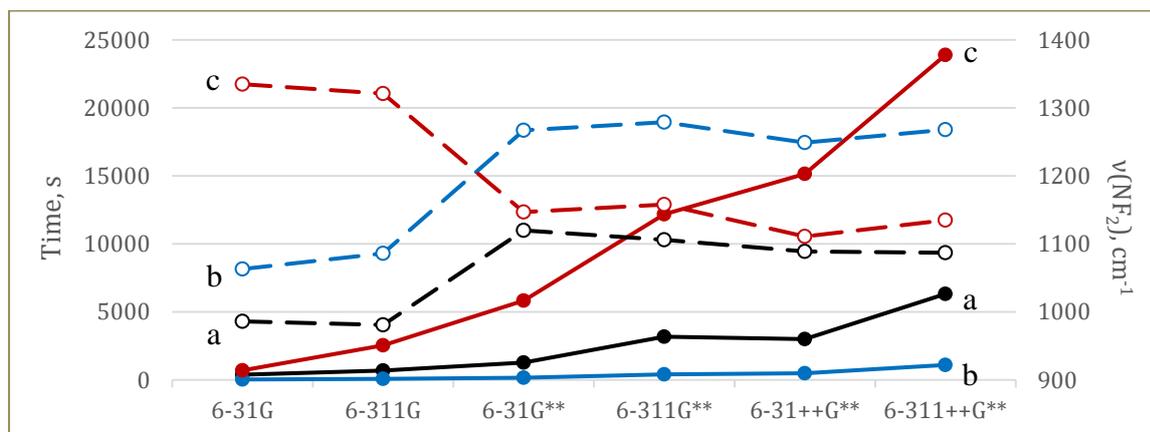


Figure 2. Time (s) needed for the optimization and IR frequency calculations of the $B_{12}H_{12}^{2-}$ anion structure (solid lines with filled circles); values of the stretching vibrations (cm^{-1}) of the free radical NF_2 (dashed lines with opened circles). The results obtained using DFT (a), HF (b) and MP2 (c) methods.

3. Results and Discussion

3.1. $X = 12$.

Before studying the anion structures with substituted difluoramino groups, it was necessary to analyse the electronic and geometric structure of the initial $B_{12}H_{12}^{2-}$ anion. To be sure that the singlet is the most energetically stable structure, we also computed the $B_{12}H_{12}^{2-}$ cluster in the triplet state. The results of the calculations confirmed the 0.2 eV preference in energy of the singlet over the triplet, so the singlet anion structures will be considered in further discussion.

In the initial $B_{12}H_{12}^{2-}$ cluster (figure 1) boron atoms are bonded to each other with the bond length of 1.787 or 1.789 Å, wherein the B-H bond length is equal to 1.203 Å. The formed B-B-B angles are equal to 60.0° and 108.0°, and B-B-H angles are equal to 121.7°. The total energy of the $B_{12}H_{12}^{2-}$ anion is -305.6596 au. Analysis of the frequencies in the IR-spectrum of the icosahedral $B_{12}H_{12}^{2-}$ anion reveals that the oscillation near 2490 cm^{-1} is characteristic of the nearly isolated B-H stretch. These given geometric and spectroscopic parameters are in a good agreement with the known experimental and theoretical results [3, 4, 6, 8, 11, 18, 19].

The calculated Mulliken charges of the boron and hydrogen atoms are listed in table 1. As seen, in the initial $B_{12}H_{12}^{2-}$ anion the charge is uniformly distributed in the core: boron atoms are positively charged, whereas negative charge is distributed over the hydrogen atoms. According to the NBO analysis, the valence electron configuration of B and H is: $2s^{0.65}2p^{2.50}3p^{0.02}$ and $1s^{0.99}$, respectively.

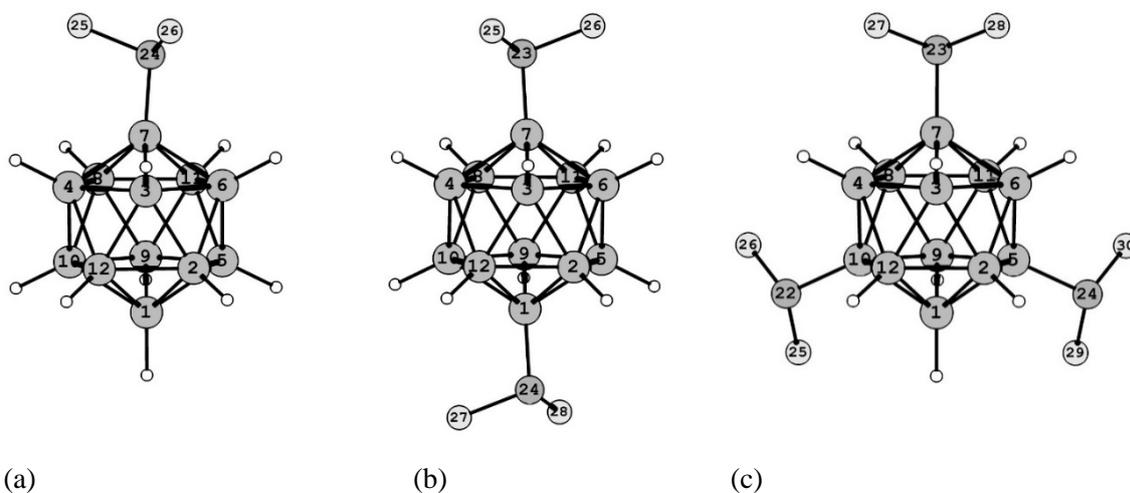
3.2. $X = 11$.

The $B_{12}H_{11}NF_2^{2-}$ anion structure, shown in figure 3a have been found by replacing of one hydrogen atom of the optimized $B_{12}H_{12}^{2-}$ structure by difluoramino group. The anion structure with one NF_2 group is seen to have decreased B-B and B-H bond distances near the B atom related to the NF_2 group, when compared to the initial $B_{12}H_{12}^{2-}$ anion and are in the range of 1.776 – 1.788 and 1.194 – 1.196 Å, respectively. The bond distances between boron atoms that are under the influence of fluorine atoms of NF_2 group change most of all. The optimized B-N and N-F bond distances are 1.558 Å and 1.450, 1.451 Å, respectively (table 2).

In any case, when replacing a hydrogen atom with an electron-withdrawing difluoramino group, an inductive effect occurs due to the transfer of electron density from the boron core. As a result, the charge on the boron atom related to the substituted NF_2 group (B7, figure 3a) and on the neighboring to the B7 boron atoms (connected by a common edge, i.e. B3, B4, B8, B11 and B6) increases. At the

Table 1. Calculated Mulliken charges of the most stable structures of $B_{12}H_x(NF_2)_{12-x}^{2-}$ ($x = 9 - 12$).

Atom number	Mulliken charge						
x = 12		x = 11		x = 10		x = 9	
B1	0.149	B1	0.538	B1	0.383	B1	0.521
B2	0.109	B2	0.060	B2	0.369	B2	0.356
B3	0.118	B3	0.124	B3	-0.083	B3	-0.424
B4	0.132	B4	0.133	B4	0.143	B4	0.514
B5	0.091	B5	-0.098	B5	0.123	B5	0.083
B6	0.086	B6	0.185	B6	-0.014	B6	0.467
B7	0.079	B7	0.231	B7	0.358	B7	0.241
B8	0.105	B8	0.227	B8	0.319	B8	0.224
B9	0.081	B9	-0.077	B9	-0.108	B9	-0.330
B10	0.076	B10	-0.031	B10	0.011	B10	0.038
B11	0.096	B11	0.479	B11	0.102	B11	0.186
B12	0.041	B12	-0.062	B12	0.056	B12	0.262
H13	-0.261	H13	-0.256	H13	-0.236	H13	-0.405
H14	-0.265	H14	-0.440	H14	-0.274	H14	-0.268
H15	-0.265	H15	-0.266	H15	-0.192	H15	-0.109
H16	-0.264	H16	-0.249	H16	-0.237	H16	-0.393
H17	-0.261	H17	-0.282	H17	-0.276	H17	-0.237
H18	-0.266	H18	-0.296	H18	-0.189	H18	-0.064
H19	-0.265	H19	-0.262	H19	-0.258	H19	-0.394
H20	-0.264	H20	-0.258	H20	-0.254	H20	-0.227
H21	-0.267	H21	-0.232	H21	-0.227	H21	-0.258
H22	-0.266	H22	-0.309	H22	-0.226	N22	-0.640
H23	-0.259	H23	-0.272	N23	-0.667	N23	-0.669
H24	-0.261	N24	-0.576	N24	-0.670	N24	-0.644
		F25	-0.008	F25	0.012	F25	0.022
		F26	-0.004	F26	0.012	F26	0.028
				F27	0.012	F27	0.034
				F28	0.013	F28	0.034
						F29	0.022
						F30	0.028

**Figure 3.** The most stable structures of $B_{12}H_x(NF_2)_{12-x}^{2-}$: (a) $x = 11$, (b) $x = 10$, (c) $x = 9$.

same time, the charge on the distant boron atoms (not connected by an edge, i.e. B2, B12, B10, B9 and B5) decreases (table 1). The total Mulliken charge on the boron atoms of the upper layer increases to 1.148, instead of 0.537 e for the initial $B_{12}H_{12}^{2-}$ anion, and the boron atoms of the bottom layer become charged negatively with the total Mulliken charge equal to -0.208 instead of 0.398 e (table 1). Herewith, the largest increase in the charge on the diagonally arranged boron atoms B1 and B11 is observed. These changes ultimately lead to the polarization of the boron core. As a result, boron atoms of the bottom layer have an excess negative charge while the closest to the substituted boron atoms of the upper layer have an excess positive charge (in comparison with the initial $B_{12}H_{12}^{2-}$). The electron configuration of $B_{12}H_{11}NF_2^{2-}$ according to the results of NBO analysis can be described as following: B $2s^{0.66}2p^{2.49}3p^{0.02}$, B* $2s^{0.58}2p^{2.22}3s^{0.01}3p^{0.03}$, H $1s^{0.98}$, N $2s^{1.53}2p^{3.31}3p^{0.02}3d^{0.01}$, F $2s^{1.90}2p^{5.40}$, where B* indicates the boron atom related to the NF_2 group (B7).

Table 2. Calculated bond lengths (Å) of $B_{12}H_x(NF_2)_{12-x}^{2-}$ structures, $x = 9 - 11$.

Label	Atom number	$r(B-B)$	$r(B-H)$	$r(B-N)$	$r(N-F)$
1	7	1.776-1.802	1.194-1.200	1.558	1.450, 1.451
2-1	7, 1	1.775-1.803	1.192-1.195	1.553, 1.553	1.447, 1.449
2-2	7, 2	1.772-1.800	1.191-1.198	1.553, 1.560	1.446-1.449
2-3	7, 8	1.770-1.801	1.189-1.198	1.555, 1.551	1.443-1.447
3-1	8, 2, 7	1.769-1.803	1.186-1.193	1.551, 1.547, 1.551	1.436-1.447
3-2	8, 7, 4	1.769-1.819	1.186-1.196	1.554, 1.544, 1.549	1.432-1.443
3-3	8, 12, 3	1.772-1.814	1.184-1.196	1.559, 1.549, 1.549	1.439-1.446
3-4	10, 4, 3	1.769-1.800	1.184-1.196	1.554, 1.548, 1.549	1.438-1.446
3-5	10, 4, 11	1.774-1.803	1.186-1.196	1.547, 1.547, 1.558	1.443-1.448
3-6	10, 7, 5	1.772-1.808	1.188-1.193	1.553, 1.548, 1.553	1.442-1.445

3.3. $X = 10$.

To find the most stable anion structures with two or three substituted difluoramino groups of $B_{12}H_x(NF_2)_{12-x}^{2-}$, various isomers fully optimized without symmetry constraint were obtained. Some of the results are summarized in tables 2, 3 and the energetically most favourable structures are shown in figure 3. By analogy with the disubstituted benzenes, the following prefixes indicating the positions of the substituent can be used: ortho-, meta-, para-. Thus, the position of NF_2 groups substituted on the adjacent boron atoms (connected by a common edge, e.g. B7 and B8) will be called ortho-, the position with NF_2 groups substituted on the boron atoms separated by one or two boron atoms of the same plane (not connected by an edge, e.g. B7 and B2) – meta-, and the position with NF_2 groups that are substituted at a maximum distance from each other (e.g. B7 and B1) – para-position.

The calculated features of the possible isomers of $B_{12}H_x(NF_2)_{12-x}^{2-}$ with $x = 9, 10$ show a large influence of the position of NF_2 groups. As seen from the figure 3, where the most stable isomers of $B_{12}H_x(NF_2)_{12-x}^{2-}$ with $x = 9 - 11$ are shown, para-position with NF_2 groups substituted on hydrogen atoms bonded to B7 and B1, is the most favourable one (table 3). The energy preference of this position over ortho- and meta-positions is 0.27 and 0.16 eV, respectively. A broader range of B-B and B-H bond lengths in the $B_{12}H_{10}(NF_2)_2^{2-}$ anion is observed when compared to the structure with one NF_2 group ($x = 11$). Thus, substitution of hydrogen atoms by NF_2 groups leads to the increase of the charge on the boron atoms conjugated with nitrogen atoms of difluoramino groups (table 1) and polarization of the boron atoms of the core. For the most stable isomers 1 and 2-1 the total charges on NF_2 groups are equal to -0.588 and $-0.644 e$ (the average value), respectively. For other possible isomers of $B_{12}H_x(NF_2)_{12-x}^{2-}$ with $x = 10$ the total charges on NF_2 groups are equal $-0.642 e$ for meta- and $-0.575 e$ for ortho-positions. As seen from the table 3, for the most stable isomer 2-1 the dipole moment is equal to 0.00 D while for others (less symmetric structures) the dipole moment is much higher. The difference in values of the dipole moments is the greater, the greater the difference in

energies among the energetically most favorable isomer with the energy taken as a zero, and other isomers.

Table 3. Calculated relative energies (ΔE), dipole moments (d), IR frequencies ($\nu(\text{NF}_2)$) and frequency shifts ($\Delta\nu(\text{NF}_2)$) of $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ structures, $x = 9 - 11$.

Label	Atom number	ΔE , eV	d , D	$\nu(\text{NF}_2)_i$, cm^{-1}	$\Delta\nu(\text{NF}_2)_i$, cm^{-1}
1	7	0.00	4.42	1092	5
2-1	7, 1	0.00	0.00	1092, 1120	5, 33
2-2	7, 2	0.16	2.78	1076, 1090	-11, 3
2-3	7, 8	0.27	4.66	1076, 1102	-11, 15
3-1	8, 2, 7	0.23	1.73	1092, 1103, 1129	5, 16, 42
3-2	8, 7, 4	0.65	4.24	1085, 1095, 1118	-2, 8, 31
3-3	8, 12, 3	0.38	2.40	1088, 1099, 1121	1, 12, 34
3-4	10, 4, 3	0.32	3.21	1099, 1120, 1130	12, 33, 43
3-5	10, 4, 11	0.41	2.32	1081, 1083, 1098	-6, -4, 11
3-6	10, 7, 5	0.00	1.01	1121, 1156, 1156	34, 69, 69

3.4. $X = 9$.

As the number of NF_2 groups increases the substituted groups prefer to occupy positions such that the electron density in the core is most uniformly distributed. This corresponds to the symmetrical arrangement of NF_2 groups on the vertices of the core. Among all the isomers that meet this condition, 3-6 isomer with three substituted NF_2 groups bonded to B10, B7 and B5 shown on the figure 3c has the lowest total energy.

Behaviour similar to the above-mentioned features was observed for this $\text{B}_{12}\text{H}_{10}(\text{NF}_2)_3^{2-}$ structure. Boron atoms related to the NF_2 group, and especially NF_2 groups itself, pull a part of electron density from the boron core. As a result, an excess positive charge appears around the boron atom related to the NF_2 group. The diagonally arranged boron atoms B3 and B9 have a negative charge that, presumably, partly compensate the large positive charge. The total charges on the NF_2 groups decrease with the increasing number of NF_2 groups and are equal to $-0.588 e$ for the anion structure with $x = 11$ and $-0.594 e$ for $x = 9$. The electron configuration of the most stable 3-6 isomer according to the results of NBO analysis can be described as following: B $2s^{0.67}2p^{2.48}3p^{0.02}$, B* $2s^{0.57}2p^{2.21}3p^{0.04}$, B** $2s^{0.57}2p^{2.21}3s^{0.01}3p^{0.03}$, H $1s^{0.95}$, N $2s^{1.52}2p^{3.32}3p^{0.02}3d^{0.01}$, F $2s^{1.90}2p^{5.39}$, where B* indicates the B5, B10 and B** – B7. In comparison with the electron configuration of the most stable structure of $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ with the larger x , there is a tendency of increasing electrons on 2s orbitals and decreasing of electrons on 2p orbitals of B atoms, wherein hydrogen atoms donate electrons, that reflects in the decreasing of electrons on its 1s orbitals.

Changes in the electron structure of $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ reflect in the changes of its geometry. Thus, substitution of one or more hydrogen atoms with the appropriate number of NF_2 groups leads to the weakening of the bonds in the core, and the formation of strong ionic bond B- NF_2 . This is indicated by the calculated bond distances and bond orders. With the increasing number of NF_2 groups bond length between the boron atoms of the core is increased, the length of the B-H, B-N and N-F decreases; and, on the contrary, the order of the B-B bond decreases, B-N and B-F – increases. These changes indicate to the better binding of NF_2 groups with the core for $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ with $x = 9$ in comparison with the anion structures with $x = 10$ and 11.

In the infrared spectra of $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ with $x = 9 - 11$ the most intense bands appear in the $1076 - 1156 \text{ cm}^{-1}$ region and are assigned to the vibrations of the difluoramino group. The calculated shifts compared to the vibrations of the free radical NF_2 are accompanied with the structural changes of $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$. Blue shifts in the IR spectrum compared to the vibrations of the free radical NF_2

are characteristic for the most stable isomers with the minimum total energy, namely, 1, 2-1 and 3-6 isomer, and points to a stronger bonding between NF_2 and the core. For $x = 9$ four isomers with blue shifts are observed but as it is seen from the table 3, the most stable isomer 3-6 is characterized by the greater values of $\nu(\text{NF}_2)$. The smaller values of frequency shifts and red shifts are typical for the less stable structures.

4. Conclusions

Within the present study, we examined the geometric, energetic, spectral and electronic features of the dodecahydro-closo-dodecaborate anion $\text{B}_{12}\text{H}_{12}^{2-}$ and its difluoramino-substituted derivatives. The results of quantum chemical calculations of the most stable isomers of $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ ($x = 9 - 12$) at the B3LYP/6-311++G** level of theory showed that as the number of NF_2 groups increases, they preferentially occupy symmetrical positions relatively to the core, such that the charge density in the complex achieves the most uniform distribution. The details of such distribution and the stability of the anion complex $\text{B}_{12}\text{H}_x(\text{NF}_2)_{12-x}^{2-}$ ($x = 9 - 12$) have been discussed. We hope that these results will aid in the investigation of $\text{B}_{12}\text{H}_{12}^{2-}$ derivatives and will broaden the idea of one of the most important features of $\text{B}_{12}\text{H}_{12}^{2-}$ anion – its aromaticity.

Acknowledgments

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