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 B$_{12}$H$_x$(NF$_2$)$_{12-x}$ 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 B$_{12}$H$_x$(NF$_2$)$_{12-x}$ anions. The obtained results broaden the idea of aromaticity of B$_{12}$H$_{12}^{2-}$ anion and will be useful in synthesis of new B$_{12}$H$_{12}^{2-}$ derivatives.

1. Introduction

There are currently synthesized and investigated hundreds of compounds of dodecahydro-closododecaborate anions (B$_{12}$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 B$_{12}$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 B$_{12}$H$_{12}^{2-}$ anion, the vast majority of its compounds are difficult to ignite and burn poorly because of the formation of boron-oxycoumpounds 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 (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 B$_{12}$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 B$_{12}$H$_{12}^{2-}$. 
Figure 1. Structure of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion.

Of particular fundamental and practical interest is the investigation of $\text{B}_{12}\text{H}_{12}^{2-}$ 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 $\text{B}_{12}\text{H}_{12}^{2-}$ anion structure by fluoromethyl groups leads to the existence of stable anions [10]. Known is a number of nitrogen-substituted derivatives of $\text{B}_{12}\text{H}_{12}^{2-}$, for example, $\text{B}_{12}\text{H}_{11}\text{NO}^{2-}$, $\text{B}_{12}\text{H}_{11}\text{NH}_{3}^{-}$, $\text{B}_{12}\text{H}_{10}(\text{NH}_{3})_{2}$, 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 $\text{B}_{12}\text{H}_{12}^{2-}$ 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 $\text{B}_{12}\text{H}_{x}(\text{NF}_{2})_{12-x}^{2-}$ ($x = 9 – 12$) 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-$\text{closo}$-dodecaborate anion $\text{B}_{12}\text{H}_{12}^{2-}$ 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$1075 cm$^{-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 $\text{B}_{12}\text{H}_{12}^{2-}$ structure was formed with $I_{h}$ symmetry. Further optimization of $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{B}_{12}\text{H}_{x}(\text{NF}_{2})_{12-x}^{2-}$ ($x = 9 – 12$) was executed without symmetry constraints. Anion structures with substituted difluoramino groups $\text{B}_{12}\text{H}_{x}(\text{NF}_{2})_{12-x}^{2-}$, ($x = 9 – 12$) 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].
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 \( \text{B}_{12}\text{H}_{12}^{2-} \) anion. To be sure that the singlet is the most energetically stable structure, we also computed the \( \text{B}_{12}\text{H}_{12}^{2-} \) 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 \( \text{B}_{12}\text{H}_{12}^{2-} \) 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 \( \text{B}_{12}\text{H}_{12}^{2-} \) anion is \(-305.6596\) au. Analysis of the frequencies in the IR-spectrum of the icosahedral \( \text{B}_{12}\text{H}_{12}^{2-} \) anion reveals that the oscillation near \( 2490 \text{ cm}^{-1} \) 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 \( \text{B}_{12}\text{H}_{12}^{2-} \) 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: \( 2s^{0.65}2p^{5.0^{0.02}} \) and \( 1s^{0.99} \), respectively.

3.2. X = 11.

The \( \text{B}_{12}\text{H}_{11}\text{NF}_{2}^{2-} \) anion structure, shown in figure 3a have been found by replacing of one hydrogen atom of the optimized \( \text{B}_{12}\text{H}_{12}^{2-} \) 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 \( \text{B}_{12}\text{H}_{12}^{2-} \) 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 \( \text{B}_{12}\text{H}_{x}(\text{NF}_2)_{12-x}^{-2} \) (x = 9 – 12).

| Atom number | Mulliken charge \( x = 12 \) | Atom number | Mulliken charge \( x = 11 \) | Atom number | Mulliken charge \( x = 10 \) | Atom number | Mulliken charge \( x = 9 \) |
|-------------|----------------|-------------|----------------|-------------|----------------|-------------|----------------|
| 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         | H22         | -0.640         |
| H23         | -0.259         | H23         | -0.272         | H23         | -0.667         | H23         | -0.669         |
| H24         | -0.261         | N24         | -0.576         | N24         | -0.670         | N24         | -0.644         |
| F25         | -0.008         | F25         | 0.012          | F25         | 0.022          | F25         | 0.022          |
| F26         | -0.004         | F26         | 0.012          | F26         | 0.028          | F26         | 0.028          |
| F27         | 0.012          | F27         | 0.012          | F27         | 0.034          | F27         | 0.034          |
| F28         | 0.013          | F28         | 0.013          | F28         | 0.034          | F28         | 0.034          |

Figure 3. The most stable structures of \( \text{B}_{12}\text{H}_{x}(\text{NF}_2)_{12-x}^{-2} \): (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 \( \text{B}_{12}\text{H}_{12}^{2−} \) 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 positive charge while the closest to the substituted boron atoms of the upper layer have an excess negative charge (in comparison with the initial \( \text{B}_{12}\text{H}_{12}^{2−} \)).

The calculated features of the possible isomers of \( \text{B}_{12}\text{H}_{x}(\text{NF}_{2})_{12-x}^{2−} \) structures, \( x = 9 – 11 \).

| Label | Atom number | \( r(\text{B-B}) \) (Å) | \( r(\text{B-H}) \) (Å) | \( r(\text{B-N}) \) (Å) | \( r(\text{N-F}) \) (Å) |
|-------|-------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 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        | 1.7721-1.800             | 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    | 1.7721-1.814             | 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 \( \text{B}_{12}\text{H}_{x}(\text{NF}_{2})_{12-x}^{2−} \), 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 NF2 groups substituted on the adjacent boron atoms (connected by a common edge, e.g. B7 and B8) will be called ortho-, the position with NF2 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 NF2 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 \( \text{B}_{12}\text{H}_{x}(\text{NF}_{2})_{12-x}^{2−} \) with \( x = 9 – 11 \) show a large influence of the position of NF2 groups. As seen from the figure 3, where the most stable isomers of \( \text{B}_{12}\text{H}_{x}(\text{NF}_{2})_{12-x}^{2−} \) with \( x = 9 – 11 \) are shown, para-position with NF2 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 \( \text{B}_{12}\text{H}_{10}(\text{NF}_{2})_{2}^{2−} \) anion is observed when compared to the structure with one NF2 group (\( x = 11 \)). Thus, substitution of hydrogen atoms by NF2 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 NF2 groups are equal to \(-0.588\) and \(-0.644\) \( e \) (the average value), respectively. For other possible isomers of \( \text{B}_{12}\text{H}_{x}(\text{NF}_{2})_{12-x}^{2−} \) with \( x = 10 \) the total charges on NF2 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.

| Label | Atom number | ΔE, eV | d, D | ν(NF₂), cm⁻¹ | Δν(NF₂), 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 NF₂ 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 NF₂ groups on the vertices of the core. Among all the isomers that meet this condition, 3-6 isomer with three substituted NF₂ groups bonded to B10, B7 and B5 shown on the figure 3e has the lowest total energy.

Behaviour similar to the above-mentioned features was observed for this B₁₂H₁₀(NF₂)₃⁻ structure. Boron atoms related to the NF₂ group, and especially NF₂ 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 substitution of one or more hydrogen atoms with the appropriate number of NF₂ groups leads to the weakening of the bonds in the core, and the formation of strong ionic bond B–NF₂. This is indicated by the calculated bond distances and bond orders. With the increasing number of NF₂ groups bond lengths 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 NF₂ groups with the core for B₁₂H₄(NF₂)₁₂⁻ with x = 9 in comparison with the anion structures with x = 10 and 11.

Changes in the electron structure of B₁₂H₄(NF₂)₁₂⁻ reflect in the changes of its geometry. Thus, substitution of one or more hydrogen atoms with the appropriate number of NF₂ groups leads to the weakening of the bonds in the core, and the formation of strong ionic bond B-NF₂. This is indicated by the calculated bond distances and bond orders. With the increasing number of NF₂ groups bond lengths 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 NF₂ groups with the core for B₁₂H₄(NF₂)₁₂⁻ with x = 9 in comparison with the anion structures with x = 10 and 11.

In the infrared spectra of B₁₂H₄(NF₂)₁₂⁻ with x = 9 – 11 the most intense bands appear in the 1076 – 1156 cm⁻¹ region and are assigned to the vibrations of the difluoramino group. The calculated shifts compared to the vibrations of the free radical NF₂ are accompanied with the structural changes of B₁₂H₄(NF₂)₁₂⁻²⁻. Blue shifts in the IR spectrum compared to the vibrations of the free radical NF₂...
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 $\nu$(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 B$_{12}$H$_{12}^{2-}$ and its difluoramino-substituted derivatives. The results of quantum chemical calculations of the most stable isomers of B$_{12}$H$_x$(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 B$_{12}$H$_x$(NF$_2$)$_{12-x}^{2-}$ ($x = 9 - 12$) have been discussed. We hope that these results will aid in the investigation of B$_{12}$H$_{12}^{2-}$ derivatives and will broaden the idea of one of the most important features of B$_{12}$H$_{12}^{2-}$ anion – its aromaticity.

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References

[1] Ellis I A, Gaines D F and Schaeffer R 1963 J. Amer. Chem. Soc. 85 3885
[2] Miller H C, Miller N E and Muetterties E L 1964 Inorg. Chem. 3 1456-1463
[3] Mikhailov B M 1967 Chimiya borovodorodov (Moscow: Nauka) pp 419-424
[4] Kuznetsov N T 1988 Chimiya poliedricheskikh borovodorodnyh soedinenyi (Sbornik trudov IOIC) ed A Yu Civadze (Moscow: Nauka) pp 78-97
[5] Saldin V I and Sukhovey V V 2013 Sposob polucheniya borftorsoderzhashchej ehnergoemkoj kompozicii Russia Patent No. 2479560
[6] Kuznetsov N T, Ionov S P and Solntsev K A 2009 Razvitie koncepcii aromaticnosti: Poliedricheskie struktury (Moscow: Nauka) chapter 3 pp 264-395
[7] Kaczmarczyk A and Kolskiand G B 1965 Inorg. Chem. 4 665-671
[8] Hoffmann R and Lipscomb W N 1962 J. Chem. Phys. 37 520-523
[9] Allis D G and Hudson B S 2006 J. Phys. Chem. A 110 3474-9
[10] Koblova E A, Saldin V I and Ustinov A Yu 2016 AIP Conf. Proc. 1790 020014
[11] Kuznetsov N T, Ionov S P and Solntsev K A 2009 Razvitie koncepcii aromaticnosti: Poliedricheskie struktury (Moscow: Nauka) chapter 3 pp 296-306
[12] Schmidt M W et al. 1993 J. Comput. Chem. 14 1347-1363
[13] Becke A D 1993 J. Chem. Phys. 98 5648-5652
[14] Lee C, Yang W and Parr R G 1988 Phys. Rev. B 37 785-789
[15] Harmony M D, Myers R J, Schoen L J, Lide D R and Mann D E 1961 J. Chem. Phys. 35 1129-1130
[16] Andersson M P and Uvdal P 2005 J. Phys. Chem. A 109 2937-2941
[17] Glendening E D, Badenhoop J K, Reed A E, Carpenter J E, Bohmann J A, Morales C M, Landis C R and Weinhold F 2013 NBO Version 6.0
[18] Grundkotter-Stock B, Bezugly V, Kunstmann J, Cuniberti G, Frauenheim T and Niehaus T A 2012 J. Chem. Theory Comput. 8 1153-1163
[19] Muetterties E L, Merrifield R E, Miller H C, Knoth W H and Downing J R 1962 J. Am. Chem. Soc. 84 2506-2508