Russian Chemical Bulletin, International Edition, Vol. 52, No. 3, pp. 519—525, March, 2003

Full Articles

Tetra- and hexaatomic cyclic clusters of main-group elements $(XY)_2$ and $(XY)_3$: an *ab initio* and density functional study

V. I. Minkin,* T. N. Gribanova, A. G. Starikov, and R. M. Minyaev*

Institute of Physical and Organic Chemistry, Rostov State University,
194/2 ul. Stachki, 344090 Rostov on Don, Russian Federation.
E-mail: minkin@ipoc.rsu.ru

The electronic and molecular structure of planar (cyclic and linear) tetra- and hexaatomic clusters $(XY)_n$ (XY = CC, BN, BeO, LiF; n = 2, 3) was studied using the *ab initio* CCD(full)/6-311+G** method and density functional approach (B3LYP/6-311+G**). The stability of cyclic clusters C_6, B_3N_3, and Be_3O_3 with D_{3h} symmetry is mainly determined by the aromaticity of their π-electron systems.

Key words: *ab initio* quantum-chemical calculations, density functional theory, atomic clusters, linear and cyclic clusters, main-group elements, aromaticity.

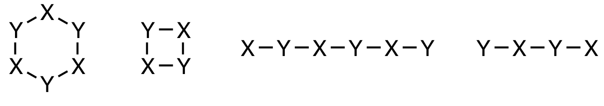
Research into the structure and unusual properties of fullerenes[1—3] has given a strong impetus to further progress of one of the most topical avenues of modern experimental and theoretical investigations, namely, studies of the stability and nature of self-organization of the main-group element clusters. Most of stable carbon clusters C_n (n = 2—139) are formed at such n values which provide for a particular cluster the possibility to have a closed π-electron shell and a sufficiently wide energy gap between the frontier orbitals; for cyclic and polyhedral structures this implies manifestation of the properties of an aromatic system.[4] It is attaining an optimum correspondence (a specific kind of balance) between the chemical composition and structure that is the driving force of the assembly of carbon clusters upon vaporization of graphite (both in flames and plasma) in inert gases at temperatures ranging from 1500 to 5000 °C. Various mechanisms of formation of polyatomic and polyhedral carbon clusters have been proposed.[2,3,5,6] All of them are based on the assumption that polyhedral structures are formed from cyclic and polycyclic structural fragments which, in turn, are formed from initial (generic) chain-type units. In this connection particular emphasis has been placed on the studies of the structure and relative stability of small carbon rings C_n (n = 3—20) in different electronic and charge states.[7—10] However, not only the carbon atoms but also atoms of other main-group elements of the periodic table can form stable cyclic cluster structures.[1] Of considerable interest are the boron—nitrogen analogs of carbon clusters, in which diatomic CC groups are replaced by isoelectronic BN units. Semiempirical MNDO calculations

---

* Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 497—503, March, 2003.

of a fullerene derivative BNC_{58} and polyhedral clusters $C_{12}B_{24}N_{24}$ and $B_{30}N_{30}$ suggested high stability of these structures.[11] The properties and stability of polyatomic and polyhedral clusters are known to depend on the characteristics of cyclic constituents. In this work we report on the results of a theoretical study of simple six- and four-membered cyclic heteroatomic structures **1** and **2** formed by eight-electron XY groups and isoelectronic to the carbon clusters C_6 and C_4, respectively. The stability of the cyclic clusters was estimated relative to the corresponding chain isomers **3** and **4**.



1a—d **2a—d** **3a—d** **4a—d**

XY = CC (**a**), BN (**b**), BeO (**c**), LiF (**d**)

Calculation Procedure

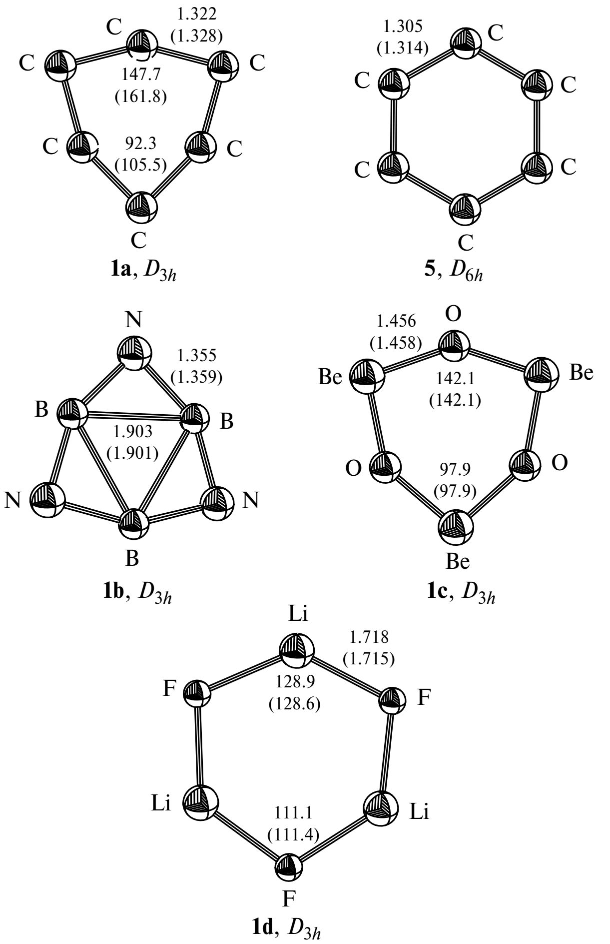
Quantum-chemical calculations were carried out in the framework of the *ab initio* computational scheme by the CCD(full)/6-311+G** coupled cluster method[12] and using the density functional approach (DFT) by the B3LYP/6-311+G** method using the *GAUSSIAN*-98 program suite.[13] Clusters C_4 and C_6 were calculated with the 6-311G** basis set. Obtaining reliable data for clusters C_n ($n > 4$) requires the inclusion of electron correlation effects.[14—18] Full optimization of the geometry of the molecular structures corresponding to the stationary points on the potential energy surfaces (PES) was carried out in the "tight" mode (with more rigorous convergence criteria). Stationary points were identified using analytical calculations of the force constant matrix. According to calculations, for all cyclic systems the triplet states lie higher than the singlet states on the energy scale. Because of this, they are left out of consideration.

Results and Discussion

Our calculations showed that all six-membered (**1**) and four-membered (**2**) clusters correspond to minima ($\lambda = 0$, hereafter λ is the number of negative eigenvalues of the Hessian at a given stationary point) on their PES. All chain systems, except for the carbon system (**3a**) and lithium—fluorine cluster (**4d**) treated as second-order stationary points ($\lambda = 2$) in the CCD calculations, also correspond to minima on the PES.

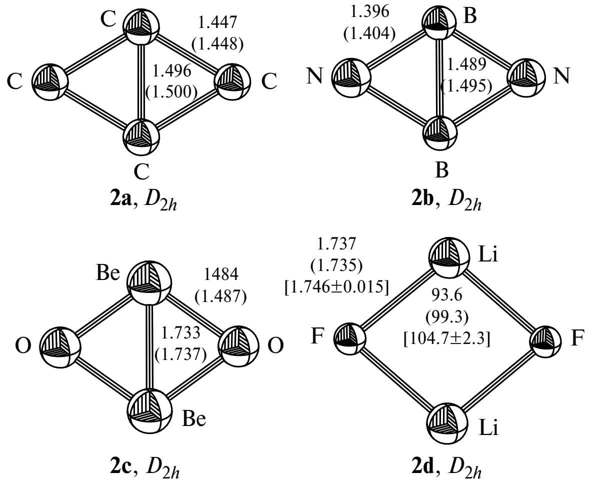
The calculated geometric parameters and energy characteristics of these structures are shown in Figs. 1 and 2 and listed in Tables 1 and 2.

According to the CCD(full)/6-311G** calculations, cyclic structure **1a** with D_{3h} symmetry is the most stable for carbon cluster C_6. This is in agreement with the results of earlier *ab initio* calculations.[14—16] The geometric pa-



1a, D_{3h} **5**, D_{6h} **1b**, D_{3h} **1c**, D_{3h} **1d**, D_{3h}

Fig. 1. Geometric parameters of structures **1a—d** and **5** calculated by the DFT and CCD methods (figures in parentheses). The bond lengths are given in Å and the bond angles are given in degrees.



2a, D_{2h} **2b**, D_{2h} **2c**, D_{2h} **2d**, D_{2h}

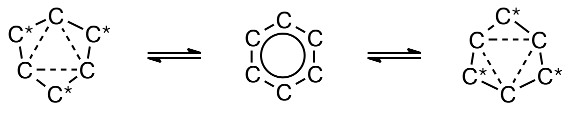
Fig. 2. Geometric parameters of structures **2a—d** obtained from DFT and CCD calculations (figures in parentheses), experimental data (figures in brackets) for structure **2d** (see Ref. 19). The bond lengths are given in Å and the bond angles are given in degrees.

Table 1. Results of the CCD and DFT calculations of compounds **1**, **3**, and **5** [a]

Structure, symmetry, state	Computational method	$-E_{total}$	λ	ΔE	ZPE	ΔE_{ZPE}	$\omega_1/i\omega$
1a, D_{3h}	CCD(full)/6-311G**	227.728587	0	0.0	0.027674	0.0	451
	B3LYP/6-311G**	228.303693	0	0.0	0.027407	0.0	431
5, D_{6h}	CCD(full)/6-311G**	227.714307	0	9.1	0.030185	10.5	504(e)
	B3LYP/6-311G**	228.279450	2	15.2	0.025650	14.1	*i*613
1b, D_{3h}	CCD(full)/6-311+G**	238.344957	0	0.0	0.026742	0.0	514(e)
	B3LYP/6-311+G**	238.918994	0	0.0	0.026326	0.0	506(e)
1c, D_{3h}	CCD(full)/6-311+G**	269.705070	0	0.0	0.021148	0.0	364(e)
	B3LYP/6-311+G**	270.331798	0	0.0	0.020769	0.0	360(e)
1d, D_{3h}	CCD(full)/6-311+G**	321.902637	0	0.0	0.011651	0.0	156(e)
	B3LYP/6-311+G**	322.592338	0	0.0	0.011385	0.0	150(e)
3a, $D_{\infty h}$	CCD(full)/6-311G**	227.716680	2	7.5	0.021410	3.5	*i*425(e)
${}^3\Sigma_g$	B3LYP/6-311G**	228.313458	0	−6.1	0.023315	−8.7	102
3b, $C_{\infty v}$	CCD(full)/6-311+G**	238.223826	0	76.0	0.022770	73.5	67
${}^3\Sigma$	B3LYP/6-311+G**	238.807672	0	69.8	0.022493	67.5	78
3c, $C_{\infty v}$	CCD(full)/6-311+G**	269.569438	0	85.1	0.016669	82.3	24
${}^3\Sigma$	B3LYP/6-311+G**	270.197212	0	84.4	0.017047	82.1	48
3d, $C_{\infty v}$	CCD(full)/6-311+G**	321.828595	0	46.5	0.009524	45.1	12(e)
${}^1\Sigma_g$	B3LYP/6-311+G**	322.52199	0	44.1	0.009625	43.0	17(e)

[a] E_{total}/a.u. is the total energy (1 a.u. = 627.5095 kcal mol^{-1}); λ is the number of negative eigenvalues of the Hessian; ZPE/a.u. is the zero-point vibrational energy correction; ΔE (kcal mol^{-1}) and ΔE_{ZPE} (kcal mol^{-1}) are the relative energies of isomeric structures calculated without and with inclusion zero-point vibrational energy correction; and $\omega_1/i\omega$ (cm^{-1}) is the lowest or imaginary harmonic frequency.

rameters of the planar cluster obtained from the CCD calculations (Fig. 1) virtually coincide with those found earlier in the calculations carried out at relevant level of theory.[14] However, our CCD(full)/6-311G** calculations revealed an energy minimum for yet another cyclic structure **5** with D_{6h} symmetry, lying 10 kcal mol^{-1} higher on the energy scale. Earlier,[8,14,15] this structure was identified as a first-order saddle point. The B3LYP calculations also predict that structure **1a** is more preferable than **5**; however, in this approximation structure **5** is located at the top of a flattened hill on the PES of the C_6 cluster (two imaginary vibrational frequencies). Flattening of the PES of the C_6 system in the vicinity of the point corresponding to highly symmetric structure **5** implies that characterization of this stationary point strongly depends on the computational method employed. It seems to be highly probable that structure **5**, irrespective of whether it corresponds to a transition state or intermediate, lies on the pathway of a low-barrier topomerization of **1a**, which leads to the position exchange between two different types of carbon atoms in the structure with D_{3h} symmetry.


1a, D_{3h} **5a**, D_{6h} **1a′**, D_{3h}

As can be seen in Fig. 1, the C—C*—C angles in molecule **1a** are close to 90°. Both computational methods predict that system **1a** has three occupied π-orbitals. This allows one to describe the electronic configuration of the valence shell of the C* atom as $(s,p_\sigma,p_\sigma,p_\pi)$. For the carbon atoms occupying the vertices of the C*—C—C* angles (~150 °C) the valence shell configuration can be written as $(sp^{1.4},sp^{1.4},sp^{3.2},p_\pi)$. Ring distortion causes the three positively charged C atoms to bring closer together so that the distances between them approach the longest carbon—carbon bond lengths. These atoms can be treated as a three-membered pseudoring within the molecule, bearing a positive charge of 0.2—0.3 e. This structural situation closely resembles the conditions for the so-called planar, or radial, aromaticity[4,20] and favors an increased stability of cyclic system **1a** compared to structure **5**. This is in agreement with the aromaticity estimates obtained for **1a** and **5** based on the structural aromaticity criteria HOMA and HOMAS.[21,22] The aromaticity calculated based on the carbon—carbon bond lengths obtained from CCD calculations is 0.529 for **1a** and 0.319 for **5**.

According to our (and earlier[8]) DFT calculations, the energy of the ground triplet electronic state ${}^3\Sigma_g{}^-$ of linear carbon cluster **3a** is nearly 6 kcal mol^{-1} lower than the energy of the singlet electronic state ${}^1A_{1g}$ of the system **1a** with D_{3h} symmetry. This was also confirmed by the *ab initio* CASSCF calculations.[14] However, most of the *ab initio* calculations,[10,14–16] as well as the coupled cluster

Table 2. Results of the CCD and DFT calculations of compounds **2** and **4**[a]

Structure, symmetry, state	Computational method	$-E_{\text{total}}$	λ	ΔE	ZPE	ΔE_{ZPE}	$\omega_1/i\omega$
2a, D_{2h}	CCD(full)/6-311G**	151.745946	0	0.0	0.013129	0.0	379
	B3LYP/6-311G**	152.102840	0	0.0	0.012459	0.0	308
2b, D_{2h}	CCD(full)/6-311+G**	158.691988	0	0.0	0.013085	0.0	426
	B3LYP/6-311+G**	159.086307	0	0.0	0.013476	0.0	575
2c, D_{2h}	CCD(full)/6-311+G**	179.691585	0	0.0	0.012348	0.0	532
	B3LYP/6-311+G**	180.118073	0	0.0	0.012267	0.0	531
2d, D_{2h}	CCD(full)/6-311+G**	214.571658	0	0.0	0.007212	0.0	289
	B3LYP/6-311+G**	215.033241	0	0.0	0.007079	0.0	287
							287 [b]
4a, $D_{\infty h}$	CCD(full)/6-311G**	151.685500	0	37.9	0.019855	42.1	250
$^3\Sigma_g^-$	B3LYP/6-311G**	152.128365	0	−16.0	0.012953	−15.7	170(e)
							172.4 [b]
4b, $C_{\infty v}$	CCD(full)/6-311+G**	158.733936	0	−26.3	0.013540	−22.8	163
$^3\Sigma$	B3LYP/6-311+G**	159.120548	0	−21.5	0.013322	−21.6	175
4c, $C_{\infty v}$	CCD(full)/6-311+G**	179.633801	0	36.3	0.009732	38.2	61
$^3\Sigma$	B3LYP/6-311+G**	180.050910	0	42.1	0.009899	40.7	104
4d, $C_{\infty v}$	CCD(full)/6-311+G**	214.525638	2	28.9	0.005635	27.9	*i*16(e)
$^3\Sigma_g^-$	B3LYP/6-311+G**	214.989233	0	27.6	0.005823	26.8	40(e)
C_2, $D_{\infty h}$	CCD(full)/6-311G**	75.739929	0	—	0.004308	—	1891
$^3\Sigma_g^+$	B3LYP/6-311G**	75.900548	0	—	0.004267	—	1873
							1854.78 [b]
BN, $C_{\infty v}$	CCD(full)/6-311+G**	79.249090	0	—	0.003884	—	1705
$^3\Pi$	B3LYP/6-311+G**	79.437784	0	—	0.003570	—	1567
							1514.6 [b]
BeO, $C_{\infty v}$	CCD(full)/6-311+G**	89.716606	0	—	0.003562	—	1564
$^1\Sigma_g$	B3LYP/6-311+G**	89.934005	0	—	0.003496	—	1334
							1487.32 [b]
LiF, $C_{\infty vg}^-$	CCD(full)/6-311+G**	107.234512	0	—	0.002060	—	904
$^3\Sigma^-$	B3LYP/6-311+G**	107.468220	0	—	0.002046	—	898
							910.25 [b]

[a] See note to Table 1.

[b] Experimental values.[19]

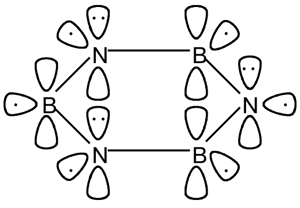
calculations carried out in this work, lead to the reverse. The fact that in these calculations the linear isomer of cluster **3a** with the cumulene-type geometry found from the B3LYP and RCCSD(T)/204cGTO calculations[23] does not correspond to a PES minimum can be rationalized by some bending and flexibility of the linear structure, as follows from the experimental IR and EPR spectra of the isotopomers of the C_6 cluster.[10] The experimental normal mode frequencies of linear cluster C_6 with $D_{\infty h}$ symmetry are in reasonable agreement with the results of our DFT calculations (*cf.*, the calculated value, 102 cm^{-1}, obtained for the lowest harmonic frequency in **3a** and the corresponding experimental[24] value for the π_u-mode, 97 cm^{-1}).

Both DFT and CCD calculations of heteroatomic clusters **1** and **3** predict that for all trimers $(XY)_3$ the cyclic structure with D_{3h} symmetry is highly stable toward dissociation into the XY monomers. Analysis of the total energies (CCD calculations, see Tables 1 and 2) shows that the endothermicity of the reaction $(XY)_3 \rightarrow 3XY$ for compounds **1a—c** changes in the series XY = CC, BN, BeO and equals 319, 375, and 348 kcal mol^{-1}, respectively. It should be noted that the hexagonal structure of the N_6 clusters is unstable toward dissociation into three N_2 molecules.[25] Much smaller (125 kcal mol^{-1}) is the energy gain corresponding to the formation of trimer **3d** from LiF molecules, which is due to essentially ionic type of chemical bonding owing to high polarity of the bonds in these molecules.

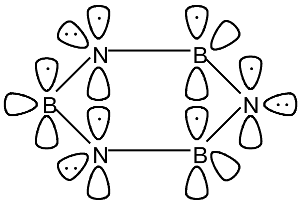
Six-membered heteroatomic clusters **1b—d** are energetically favorable as compared with the corresponding linear isomers **3b—d**. This can be due to higher aromaticity of these systems compared to the carbon cluster C_6.

The energy difference between the cyclic and linear structures increases in the series XY = CC, BN, BeO and then decreases on going to LiF. A possible reason can be a decrease in the overlap of the p_π-orbitals of the Li and F atoms due to a greater elecrtonegativity difference between these atoms. Going from the linear to cyclic structure causes changes in the electron occupancy of the π-orbitals and in steric strain (sp-hybridization corresponds to the least sterically strained linear system). Therefore, estimation of the aromaticity of cyclic systems **3** as the total energy difference (ΔE) between structures **1** and **3** seems to be too simplified; however, this difference can serve as a qualitative characteristic of the aromaticity of structures **1**. The ΔE values listed in Table 1 suggest that the formation of an aromatic π-electron sextet in structures **1** makes the largest contribution to stabilization of the cyclic structure of the boron—nitrogen (**1b**) and beryllium—oxygen (**1c**) clusters. Figure 3 presents the correlation diagram of π-MO energy levels for system **1b**, which exhibits a completely analogy with the π-MOs of the aromatic system of benzene molecule. Stability of the cyclic π-system is also characterized by a rather wide energy gap between the highest occupied and lowest unoccupied MOs. The HOMA structural index for **1b** is 0.867 (calculated using the B—N bond parameters calibrated[26] against the borazine molecule, $B_3N_3H_6$), which is much larger than the corresponding value for carbon clusters **1a**.

Of particular interest is to answer the question as to which electronic configuration of the cluster, namely, **6a** or **6b**, is the determining factor for the formation of the π-MO of the cyclic structure **1b**. The former configuration is analogous to the electronic configuration of the borazine molecule ($B_3N_3H_6$, or "inorganic benzene"), which is characterized by high degree of π-electron localization on the nitrogen atoms.[26] In the latter configuration (**6b**) the π-electron sextet is formed due to donation of one π-electron by each atom of the six-membered ring. For isolated B and N atoms the corresponding electronic configurations are energetically unfavorable; however, they can be realized in the molecule if π-electron delocalization over all centers is more preferable than σ-electron delocalization in the molecular plane. It is this effect that determines the formation of aromatic π-electron sextet in the borazine molecule, where the electronic configuration of the B atom, $(sp^2)^2(sp^2)^0(p_\pi)^1$, is similar to **6b**.[27]



6a



6b

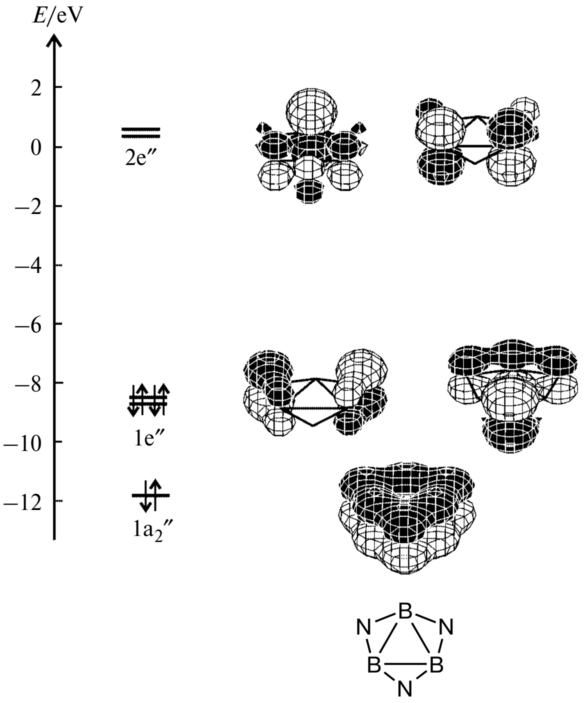


Fig. 3. Correlation diagram of π-MO energy levels for system **1b** according to RHF/6-311+G** calculations.

Clusters **1c** and **1d** can build up an aromatic electron shell only following the "**6a**"-way, where the π-electron sextet is formed due to the two-electron contribution from each of the three electronegative centers. High degree of charge separation in system **1d** indicates a large contribution of ionic bonding. The geometric parameters of clusters **1d** found in this work virtually coincide with those obtained from B3LYP/6-311+G* calculations[28] of cyclic clusters $(LiF)_n$ with n = 1—4. Atomic charge estimation based on the populations calculated using the natural bonding orbital (NBO) approach[29] gives +0.96 a.u. (Li) and –0.96 a.u. (F) for both the monomer and all types of associates,[28] thus indicating the ionic type of chemical bonding in these structures.

Similarly to structure **1a**, the bond lengths between the atoms of the six-membered ring correspond to double bonds. The experimental B=N double bond length in the $(Pr^i{}_2)N{=}B{=}C(SiMe_3)_2$ molecule is 1.363 Å.[30] At the same time, in clusters **1c** and **1d** with more ionic bonds the Be—O and Li—F distances between the closest centers much exceed the bond lengths in the BeO and LiF molecules (1.33 and 1.55 Å, respectively).[19] The geometric parameters of linear structures **3** and **4** are presented in Fig. 4. The carbon—carbon bonds in structure **3a** with cumulene geometry are much shorter than in the cyclic system, which is in agreement with the results of earlier calculations.[10]

Cluster C_4 has been the subject of numerous theoretical studies (see Refs. 10, 31, 32, and references cited therein). Different computational methods have led to

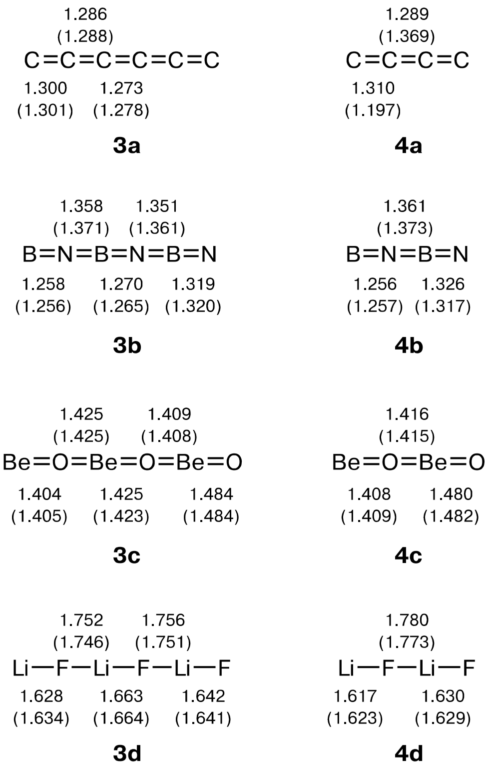


Fig. 4. Geometric parameters of structures **3a—d** and **4a—d** calculated by the DFT and CCD methods (figures in parentheses). The bond lengths are given in Å and the bond angles are given in degrees.

contradictory results and it is still to be clarified which structure is the most stable, namely, a singlet structure **2a** with D_{2h} symmetry or a linear triplet structure **4a** with $D_{\infty h}$ symmetry. Both methods employed in this work also reproduce this contradiction (see Table 2). From the results of our CCD(full)/6-311G** calculations, which are qualitatively similar to those of the most precise CCSD(T)aug-cc-pVDZ//B3LYP/6-31G* calculations,[31] it follows that rhombic cyclic structure **2a** is more preferable. This structure was also found to be the most stable for the BeO (**2c**) and LiF (**2d**) dimers (in the latter case this is in good agreement with the experimental data[19] and the results reported in Ref. 28). However, linear structure **4b** of the boron—nitrogen cluster is more energetically favorable than rhombic structure **2b** (the energy difference between them is 20 kcal mol^{-1}).

All cyclic dimers **2a—d** are stable toward dissociation into diatomic monomers. The dissociation energies obtained from our CCD calculations are as follows: 167 (**2a**), 122 (**2b**), 162 (**2c**), and 64 (**2d**) kcal mol^{-1}. They are approximately halved compared to the dissociation energies of trimers **1**.

Analysis of the MOs of cyclic heteroatomic clusters **2** revealed the presence of two filled π-levels, which allows these compounds to be formally treated as antiaromatic systems. The reason for stability of systems **2** can be rationalized by comparing the π-MO structure of these systems and the classical antiaromatic 4π-electron system of cyclobutadiene (Fig. 5).

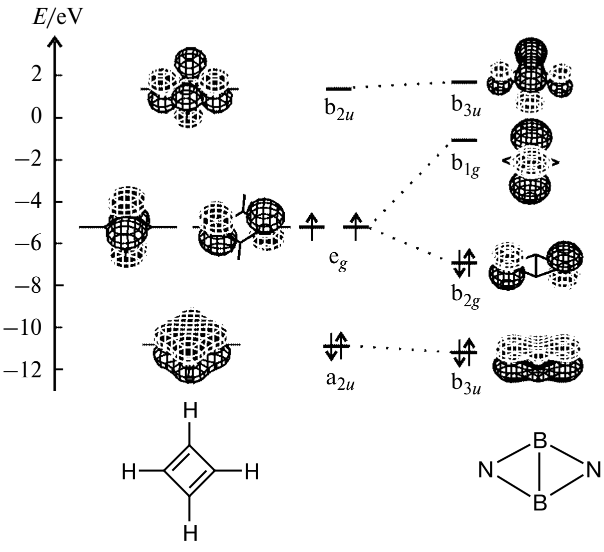


Fig. 5. Correlation diagram of π-MO energy levels for system **2b** and cyclobutadiene molecule obtained from RHF/6-311+G** calculations.

The presence of two inequivalent pairs of atoms in the four-membered ring causes splitting of the degenerate π-levels (e_g) responsible for antiaromatic destabilization of cyclobutadiene and filling of only one energy level, namely, that associated with the pair of more electronegative atoms. The antibonding interaction between these atoms is compensated by rhombic distortion in systems **2**, which leads to large separation of the interacting centers and eliminates antiaromatic destabilization, thus providing conditions for the formation of stabilized π-system of cyclic clusters **2** and being an important factor determining their stability.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project Nos. 01-03-32546, 02-03-33227, and 00-15-97320) and the U.S. Civilian Research and Development Foundation (CRDF, Grant No. RC1-2323-RO-02).

References

1. I. V. Stankevich, *Chemistry Reviews*, Harwood Academic Publishers, Basel, 1994, **20**, Part 1.
2. W. Weltner and R. J. van Zee, *Chem. Rev.*, 1989, **89**, 1713.
3. A. Hirsch, *The Chemistry of Fullerenes*, G. Thieme, Stuttgart, 1994.
4. V. I. Minkin, M. N. Glukhovtsev, and B. Ya. Simkin, *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*, Wiley-Interscience, New York, 1994.

5. H. Schwarz, *Angew. Chem.*, *Int. Ed.*, 1993, **32**, 1412.
6. B. M. Bulychev and I. A. Udod, *Ross. Khim. Zh.* (*Zh. Ross. Khim. Obshch. im. D. I. Mendeleeva)*, 1995, **39**, 9 [*Mendeleev Chem. J.*, 1995, **39** (Engl. Transl.)].
7. F. Zerbetto, *J. Am. Chem. Soc.*, 1999, **121**, 10958.
8. J. Hutter, H. P. Lüthi, and F. Diederich, *J. Am. Chem. Soc.*, 1994, **116**, 750.
9. M. C. McCarthy and P. Thaddens, *Chem. Soc. Rev.*, 2001, **30**, 177.
10. A. Van Orden and R. J. Saykally, *Chem. Rev.*, 1998, **98**, 2313.
11. X. Xia, D. A. Jelski, J. R. Bowser, and T. F. George, *J. Am. Chem. Soc.*, 1992, **114**, 6493.
12. J. B. Foresman and E. Frisch, *Exploring Chemistry with Electronic Structure Methods. 2nd ed.*, Gaussian, Inc., Pittsburgh (PA), 1996, 302.
13. *GAUSSIAN 98*, *Revision A.9*, Gaussian, Inc., Pittsburgh (PA), 1998.
14. J. Hutter and P. J. Zuthi, *J. Chem. Phys.*, 1994, **101**, 2213.
15. V. Pless, H. U. Suter, and B. Engels, *J. Chem. Phys.*, 1994, **101**, 4042.
16. J. M. L. Martin and P. R. Taylor, *J. Phys. Chem.*, 1996, **100**, 6047.
17. G. Kaupp and J. Boy, *Angew. Chem.*, *Int. Ed.*, 1997, **36**, 48.
18. I. V. Komarov, *Usp. Khim.*, 2001, **70**, 1123 [*Russ. Chem. Rev.*, 2001, **70** (Engl. Transl.)].
19. K. S. Krasnov, N. V. Filippenko, V. A. Bobkova, N. L. Lebedeva, E. V. Morozov, T. I. Ustinova, and G. A. Romanova, *Molekulyarnye postoyannye neorganicheskikh soedinenii* [*Molecular Constants of Inorganic Compounds*], Khimiya, Leningrad, 1979, 446 pp. (in Russian).
20. A. B. McEwen and P. v. R. Schleyer, *J. Org. Chem.*, 1986, **51**, 4357.
21. T. M. Krygowski, *J. Chem. Int. Comput. Sci.*, 1993, **33**, 70.
22. T. M. Krygowski and M. K. Cyranski, *Chem. Rev.*, 2001, **101**, 1385.
23. S. Schmatz and P. Botschwina, *Chem. Phys. Lett.*, 1995, **235**, 5.
24. D. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos, and D. N. Neumark, *J. Chem. Phys.*, 1991, **95**, 8753.
25. M. N. Glukhovtsev and P. v. R. Schleyer, *Chem. Phys. Lett.*, 1992, **198**, 547.
26. P. v. R. Schleyer, H. Jiao, N. J. R. van E. Hommes, V. G. Malkin, and O. L. Malkina, *J. Am. Chem. Soc.*, 1997, **119**, 12699.
27. J. Cioslowski and P. J. Hay, *J. Am. Chem. Soc.*, 1990, **112**, 1707.
28. N. Haketa, K. Yokoyama, H. Tanaka, and H. Kudo, *J. Mol. Struct. (Theochem)*, 2002, **577**, 55.
29. A. E. Reed, Z. A. Curtiss, and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
30. J. D. Madura, T. M. Krygowski, and M. K. Cyranski, *Tetrahedron*, 1998, **54**, 14913.
31. S. J. Blanksby, D. Schroder, J. H. Bowie, and H. Schwarz, *J. Am. Chem. Soc.*, 2000, **122**, 7105.
32. Z. Slanina and R. Zahradnik, *J. Phys. Chem.*, 1977, **81**, 2252.

Received May 15, 2002;
in revised form November 5, 2002