Induced aromaticity

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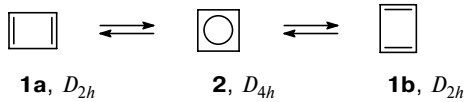
The influence of counterions on the stabilization of three-, five-, and six-membered cyclic organic and organoboron systems was studied by the *ab initio* (MP2(full)/6-311+G**) and density functional (B3LYP/6-311+G**) methods. The structures of molecular charge-transfer molecular complexes formed by the interaction with counterions are predicted. A crucial role of counterions in the stabilization of aromatic systems that are unstable in themselves was revealed. Stabilization of these systems involves both charge transfer and covalent bonding.

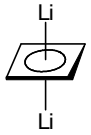
Key words: organoboron compounds, aromaticity, induced aromaticity, nonempirical quantum-chemical calculations.

The concept of induced aromaticity is associated with the stabilization of a conjugated cyclic system, which involves coordination to a counterion or the formation of a charge-transfer complex (CTC) with an electron donor (acceptor) species. Here, we imply that the system under study either exhibits no aromatic properties or is unstable in the absence of such species. Induced aromaticity is characteristic of, for instance, the complexes of antiaromatic systems with $4n$ π-electrons. In this case, counterions donate two electrons to complete the π-electron shell and obtain an aromatic shell with $4n + 2$ π-electrons. The molecule of cyclobutadiene adopts a rectangular conformation **1** with strongly different ordinary and double carbon—carbon bond lengths (*cf.* ~1.53 and ~1.35 Å, respectively).[1—3] Both the experimental data[1—3] and results of *ab initio* calculations[1,4] show that the classical antiaromatic square structure **2** corresponds to the transition state (TS) of a double bond migration along the ring perimeter (Scheme 1). Upon attachment of two Li atoms, cyclobutadiene forms a stable bipyramidal complex **3** [4—6] with D_{4h} symmetry and an aromatic shell with six π-electrons. The tetrakis(trimethylsilyl)cyclobutadienyl dianion obtained recently in the form of dilithium salt[7] was postulated to have this structure in the gas phase.

Scheme 1



1a, D_{2h} **2**, D_{4h} **1b**, D_{2h}

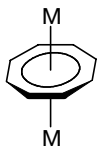


3, D_{4h}

The molecule of cyclooctatetraene adopts[8] a "boat" conformation (**4**). Both the experimental data[9—11] and results of *ab initio* calculations[12] show that antiaromatic planar structure **5** with D_{8h} symmetry corresponds to the TS of a topologically complex reaction, which involves a concerted migration of the double bond along the perimeter of the eight-membered ring and inversion of the ring (Scheme 2). The interaction with two alkali metal atoms M (M = Li, Na, K, Rb, and Cs) that donate two electrons to complete the π-electron shell of the cyclooctatetraene molecule and obtain an aromatic π-electron decet leads to a "bipyramidal" complex **6**,[13] in which the cyclooctatetraene molecule adopts a planar conformation.

Scheme 2

4a, D_{2d} **5**, D_{8h} **4b**, D_{2d}



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Previously, it was commonly accepted that the effect of the counteratom is reduced to transfer of an electron to the acceptor molecule and that the position of the

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counteratom is insignificant for manifestation of many properties of the entire system. However, experimental data[14—17] and the results of calculations[6,17—22] performed in the last two decades provide clear evidence for a strong effect of the position of the counterion on the stability and structural parameters of both the acceptor (donor) molecule and the entire complex. Recently,[17] it was shown that the molecular conformation of DNA changes in the presence of a cation and depends on its nature. In the tight ion pair, not only electrostatic interaction, but also relatively strong covalent ion—ion bonding occurs, which is mainly determined by the overlap of the frontier orbitals of the partners. For instance, the cyclobutadienyl dianion has a nonplanar boat-like geometry in the absence of counterions (structure **7**) and adopts a square-planar configuration in complex **3**.[5—7] Low degree of charge transfer from the lithium atoms to the cyclobutadiene fragment (<1e), rather short C...Li distance (~2.0 Å), which is close to the covalent C—Li bond lengths (*cf.* 1.961(5) Å for $LiCH_3$),[20] and lengthened carbon—carbon bonds (~1.47 Å, *cf.* ~1.40 Å for aromatic systems[1]) indicate that complex **3** can be placed between tight ion pairs and covalently bound systems that obey the decet rule for nonclassical bipyramidal structures.[23]

7, D_{2d}

Thus, the nature of the counterion has a strong effect on the stability and electronic properties of conjugated systems. It is thought that low-barrier migrations of Cl atoms[24] and the N_3,[25] NCS,[26] and SCN [26] groups along the perimeter of the cyclopropenyl ring also involve the formation of metastable tight ion pairs whose nature and structure are still to be clarified.

Currently, intensive research on tight ion pairs (CTC) in which one or both partners are aromatic systems has been carried out. This is due to their possible applications as molecular conductors or molecular electronic devices.[27—29]

In this work we studied the influence of the nature of counterions on the aromatic properties of three-, five-, and six-membered cyclic organic and organoboron systems by the *ab initio* (MP2(full)/6-311+G**)[30] and density functional theory (DFT, B3LYP/6-311+G**)[30] methods and predicted the geometries and electronic structure of molecular CTC.

Calculation Procedure

Calculations were carried out using the DFT approach with the B3LYP exchange-correlation functional and by the restricted Hartree—Fock method with inclusion of electron correlation at the second-order Møller—Plesset level (MP2) of perturbation theory for all (valence and core) electrons in the split-valence 6-311+G** basis set using the GAUSSIAN-94 [31] and GAMESS program packages.[32] Full optimization of the geometry of the molecular structures corresponding to the energy minima ($\lambda = 0$; hereafter, λ is the index of a stationary point, which is equal to the number of negative eigenvalues of the Hessian at a given stationary point)[33] and to the saddle points ($\lambda = 1$) on the potential energy surfaces (PES) was carried out using the "tight" convergence criterion (GAUSSIAN-94) and up to a gradient magnitude of 10^{-5} hartree $bohr^{-1}$ (GAMESS). The structures corresponding to the energy minima on the PES were found by the steepest descent method (movement along the gradient line) from the saddle point to the neighboring stationary point (a saddle point or a minimum).[33] The initial direction of the gradient line was specified by minor displacement (1/10 of the length of the normalized transition vector) along the transition vector. Graphic images of the molecular structures were obtained using the ORTEP program[34] for which the corresponding Cartesian atomic coordinates taken from the *ab initio* calculations served as input parameters.

Results and Discussion

Three-membered aromatic rings. The cyclopropenyl cation, $C_3H_3^+$, is the simplest aromatic system and has much been studied both theoretically[1,21,35—37] and experimentally.[1,35,38] According to calculations, there is only one stationary point ($\lambda = 0$) on the PES of the singlet ground state of $C_3H_3^+$ (the triplet PES lies higher on the energy scale), which corresponds to cyclic aromatic structure **8** with D_{3h} symmetry. The calculated energy and geometric characteristics of this structure (Fig. 1, Table 1) are in good agreement with experimental data[38] and the results of earlier calculations.[36,37] The calculated carbon—carbon bond length in cation **8** (1.363 (DFT) and 1.371 Å (MP2)) is close to the average bond length (1.373 Å), determined by X-ray diffraction analysis for various salts.[38]

The effect of the counterion on the geometric parameters and electronic structure of cation **8** was studied taking complex **11** formed from by the cyclopropenyl cation and BF_4^- anion as an example. According to

Table 1. Total energies (E_{tot}), zero-point vibrational energy corrections (*ZPE*), and the lowest harmonic vibrational frequencies (ω_1) of structures **8—11** calculated by the DFT and MP2 (figures in parentheses)* methods

Structure, symmetry	$-E_{tot}$	*ZPE*	ω_1 /cm^{-1}
	au		
$C_3H_3^+$ (**8**), D_{3h}	115.761072	0.045036	775
	(115.463339)	(0.045323)	(775)
C_3FH_3 (**9**), C_s	215.933112	0.048452	436
	(215.456336)	(0.049029)	(446)
$C_3FH_3 \cdot BF_3$ (**10**), C_1	540.604271	0.061336	19
	(539.549974)	(0.062393)	(24)
$C_3H_3^+ \cdot BF_4^-$ (**11**), C_s	540.601682	0.060898	96
	(539.546036)	(0.061833)	(81)
BF_4^-, T_d	424.679695	0.013657	337
	(423.918822)	(0.013974)	(347)
BF_3, D_{3h}	324.66414	0.012113	102.4
	(324.083767)	(0.012299)	(103.7)

* 1 au = 627.5095 kcal mol^{-1}; for all systems, the number of negative eigenvalues of the Hessian (λ) is zero.

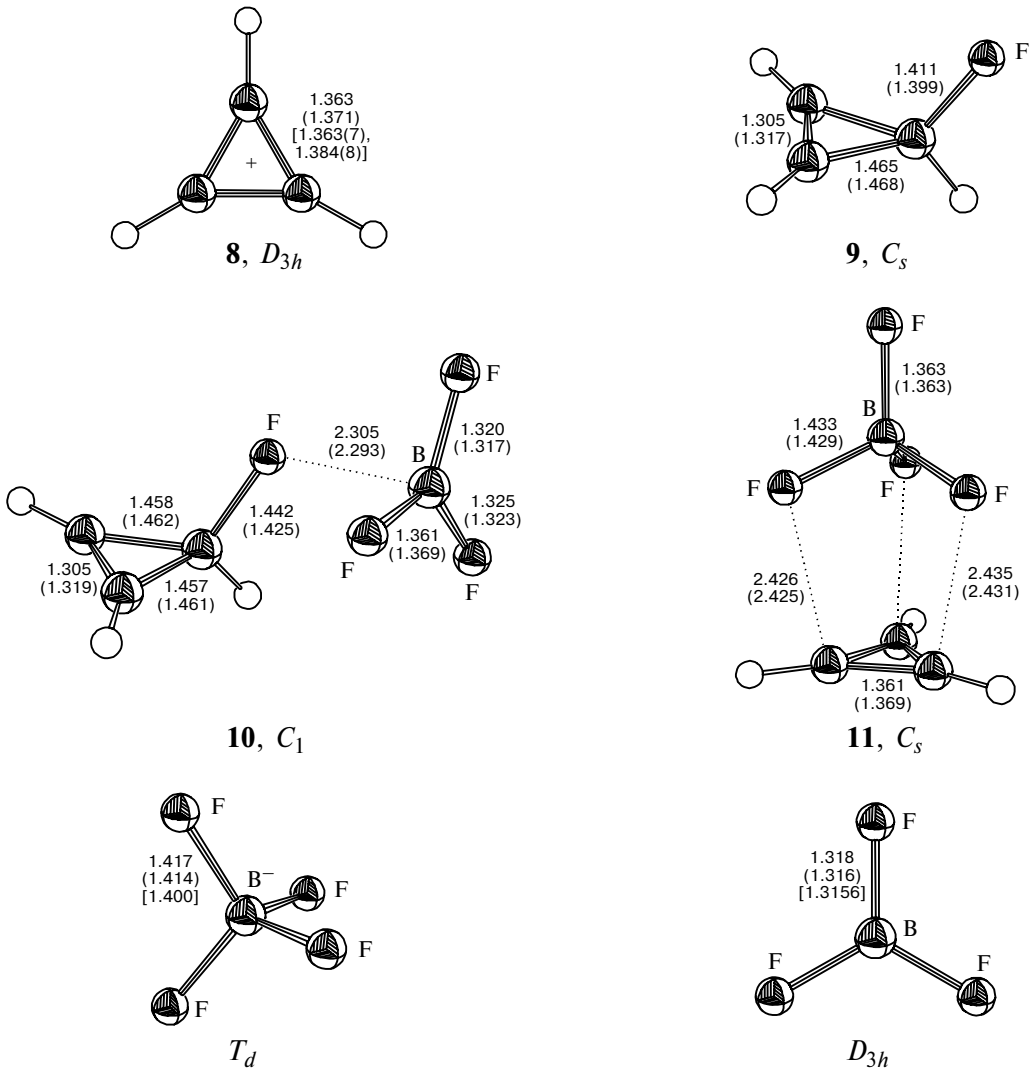
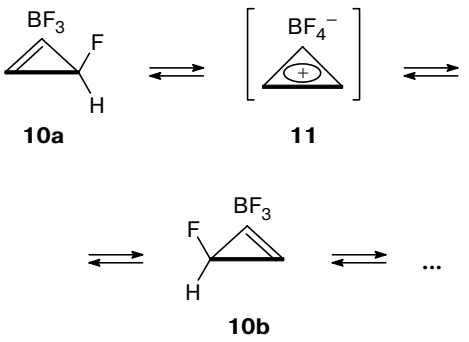


Fig. 1. Geometric characteristics of structures **8—11**, BF_4^- anion, and BF_3 corresponding to minima on the PES and calculated by the DFT (B3LYP/6-311+G**) and MP2(full)/6-311+G** (figures in parentheses) methods and the experimental data (figures in brackets) for structure **8** (see Ref. 38), BF_4^- anion, and BF_3 (see Refs. 39 and 40). Here and in Figs. 2—6 the bond lengths are given in Å and the bond angles are given in degrees.

calculations, complex **11** corresponds to a minimum on the PES ($\lambda = 0$) and has the structure of a tight ion pair $C_3H_3^+ \cdot BF_4^-$ in which the distance to the BF_4^- anion (~2.4 Å) is much shorter than the sum of the van der Waals radii of C and F atoms (3.1 Å).[41] The carbon—carbon bonds in molecule **11** are 0.002 Å shorter than in free cation **8**. The degree of charge transfer from the BF_4^- anion to the $C_3H_3^+$ cation is rather high, *viz.*, 0.73 (DFT) and 0.78 e (MP2), which is responsible for the large dipole moment of complex **11** (~10 D). The formation energy of complex **11** from the $C_3H_3^+$ cation and BF_4^- anion (101.0 and 105.3 kcal mol^{-1} according to DFT and MP2 calculations, respectively) is close to the experimentally determined C—F bond cleavage energy in the fluorine-substituted saturated hydrocarbons (~105 kcal mol^{-1}).[42] The total energy difference between complex **10** formed by fluorocyclopropene **9** and BF_3 and the tight ion pair **11** is only 1.6 (DFT) and 2.5 kcal mol^{-1} (MP2). The inclusion of zero-point vibrational energy correction reduces this value down to 1.3 (DFT) and 2.3 kcal mol^{-1} (MP2). The energy of the interaction of BF_3 with fluorocyclopropene in complex **10** is 4.4 (DFT) and 5.6 (MP2) kcal mol^{-1}, which is comparable with the energy of a rather strong hydrogen bond. One can expect that the formation of tight ion pair **11** is facilitated in solutions in the presence of BF_3, which must lead to low-barrier migrations of the F atom along the perimeter of the three-membered ring (Scheme 3) *via* intermediate **11** by dissociative mechanism.

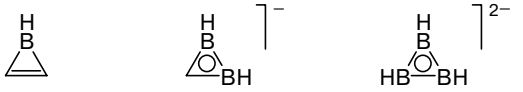
The inclusion of solvation energy in the framework of the PCM model[31] showed that in solvents complex **11** becomes thermodynamically more stable than **10** by 4.5, 9.5, and 10.8 kcal mol^{-1} for benzene, DMSO, and

Scheme 3



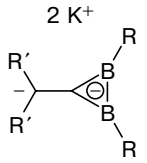
water, respectively (the estimates were obtained using the DFT approach). Thus, according to our calculations, an increase in the solvent polarity must lead to stabilization of the ion pair **11** relative to complex **10**. Mention may be made that the formation of the tight ion pair **11** as intermediate on the pathway of a low-barrier migration of the Hal atom along the perimeter of the cyclopropenyl ring was postulated earlier.[26,43]

Three-membered boron-containing cyclic systems BC_2H_3, $B_2CH_3^-$, and $B_3H_3^{2-}$ are isoelectronic to the cyclopropenyl cation and also represent aromatic systems.



12, C_{2v} **13**, C_{2v} **14**, D_{3h}

The possibility for the molecule of borirene, BC_2H_3 (**12**), to exist was first predicted[44] in 1962 and confirmed computationally in 1981;[45] however, the first triarylborirene was synthesized only after a lapse of nearly three decades.[46] Recently, matrix isolation spectroscopic studies of unsubstituted molecule **12** were reported.[47,48] The system with the cyclic fragment **13** was first obtained[49] in the form of salt **15** and structurally characterized by X-ray diffraction analysis.[49—51]



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According to calculations, cyclic systems **12—14** correspond to minima ($\lambda = 0$) on the PES of the singlet ground state. Their geometric parameters are presented in Figs. 2 and 3 and the corresponding energy characteristics are listed in Table 2.

The calculated geometric parameters are in reasonable agreement with the results of earlier calculations[36,45,47] and X-ray diffraction studies.[44,48] It should be noted that the corresponding carbon—carbon, boron—carbon, and boron—boron bond lengths in systems **8**, **12**, and **13** vary only slightly, which points to minor differences between the electronic characteristics of these structures.[1] The boron—carbon and boron—boron bonds in anion **12** and dianion **13** are much shorter than the corresponding ordinary bonds (B—C, ~1.57 Å;

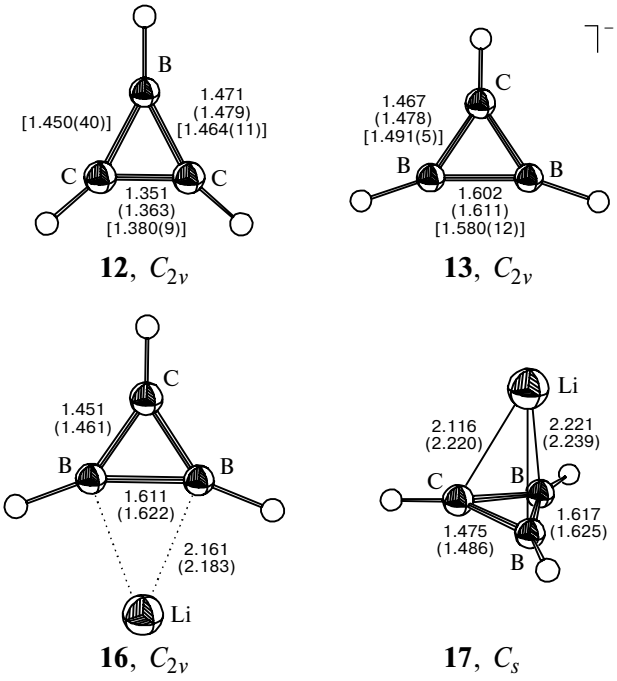


Fig. 2. Geometric characteristics of structures **12**, **13**, **16**, and **17** corresponding to minima on the PES and calculated by the DFT (B3LYP/6-311+G**) and MP2(full)/6-311+G** (figures in parentheses) methods and the experimental data (figures in brackets) for structure **12** (see Ref. 46) and anion **13** (see Refs. 50 and 51).

Table 2. Total energies (E_{tot}), zero-point vibrational energy corrections (*ZPE*), and the lowest real (ω_1) or imaginary harmonic vibrational frequencies ($i\omega$) of structures **12—14** and **16—21** calculated by the DFT and MP2 (figures in parentheses) methods

Structure, symmetry	$-E_{tot}$	*ZPE*	λ*	ω_1/cm^{-1} or $i\omega/cm^{-1}$
	au			
BC_2H_3 (**12**), C_{2v}	102.828267	0.041680	0	674
	(102.538472)	(0.042134)	0	(667)
$B_2CH_3^-$ (**13**), C_{2v}	90.607903	0.036568	0	586
	(89.230486)	(0.038392)	0	(608)
$B_2CH_3^- \cdot Li^+$ (**16**), C_{2v}	97.132746	0.039385	0	147
	(96.812851)	(0.039648)	0	(137)
$B_2CH_3^- \cdot Li^+$ (**17**), C_s	97.114868	0.039234	0	129
	(96.795940)	(0.049197)	0	(111)
B_3H_3 (**18**), C_s	76.256444	0.035304	0	306
	(76.004549)	(0.035759)	0	(266)
B_3H_3 (**19**), C_{2v}	76.249357	0.032429	1	i349
	(75.991693)	(0.032675)	1	(i545)
$B_3H_3^{2-}$ (**14**), D_{3h}	76.170441	0.030115	0	498
	(75.901966)	(0.030509)	0	(455)
$B_3H_3^{2-} \cdot Li_2^{2+}$ (**20**), C_s	91.400230	0.036990	0	115
	(91.053853)	(0.037674)	0	(112)
$B_3H_3^{2-} \cdot Li_2^{2+}$ (**21**), C_{2v}	91.414672	0.037590	0	149
	(91.066613)	(0.037817)	0	(149)

* The number of negative eigenvalues of the Hessian.

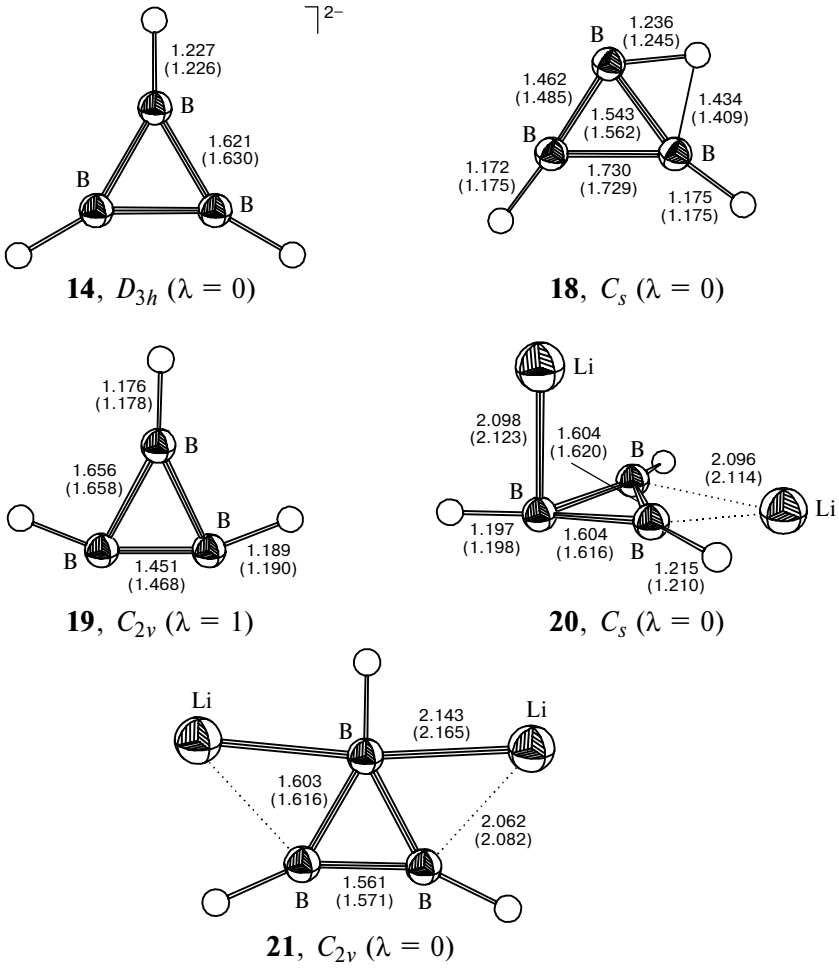


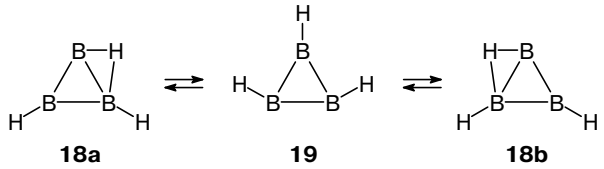
Fig. 3. Geometric characteristics of structures **14**, **18**, **20**, and **21** corresponding to minima and structure **19** corresponding to a saddle point on the PES calculated by the DFT (B3LYP/6-311+G**) and MP2(full)/6-311+G** (figures in parentheses) methods.

B—B, ~1.71 Å).[39,51,52] They are close to or shorter than the "sesqui"-bonds in organoboron compounds (B=C, ~1.50 Å; B=B, ~1.61 Å).[39,51,52] The interaction of cyclic anions **13** and **14** with lithium cations leads to two pairs of complexes, **16** and **17** for the former anion and **20** and **21** for the latter. The boron—boron bonds in complexes **16** and **17** are somewhat longer than in anion **13**, whereas in the second pair of complexes they are much shorter than in anion **14**. This can be explained by different electron density distribution in structures **16**, **17** and **20**, **21**. The atomic charge of Li is 0.26 (DFT) and 0.37 e (MP2) for complex **16**, 0.34 (DFT) and 0.43 e (MP2) for complex **17**, and 0.15 (DFT) and 0.27 e (MP2) for complex **21**. An analogous situation was also observed for complex **20** in which the degree of charge transfer from each Li atom to the three-membered ring is at most 0.4 e. Thus, the destabilizing electrostatic interactions in the three-membered rings of complexes **20** and **21** are much weaker than in dianion **14**. As can be seen in Figs. 2 and 3, the distances between the Li and B (C) atoms in complexes **16**, **17** and **20**, **21** differ insignificantly from the sum of the corresponding covalent radii (2.13 Å for Li—B and 2.0 Å for Li—C).[20,53] They are close to the experimentally found distances in various salts.[39,52] There results indicate that complexes **16**, **17**, **20**, and **21** are tight ion pairs and that their geometric characteristics are to a great extent determined by the contribution of covalent bonding to the ion—ion interaction.

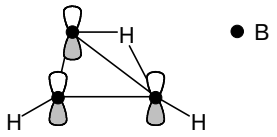
Unusual structure of neutral system B_3H_3 (**18**, see Fig. 3) represents a special case. Here, two boron—boron bonds are rather short and their lengths approach those of the double B=B bonds (formally, all bonds formed by the trivalent B atom in system **18** must be ordinary). This situation in structure **18** is due to the filling of the highest occupied π-MO (HOMO), which is a bonding orbital (**22**). The formation of an aromatic system with two π-electrons is favored by the rehybridization of two B atoms and filling of nonhybridized p_z-orbitals oriented perpendicular to the molecular plane (Scheme 4).

Molecule **18** can undergo a low-barrier topomerization (see Scheme 4) *via* TS **19**. The calculated barrier height is only 4.4 (DFT) and 8.1 (MP2) kcal mol^{-1}.

Scheme 4

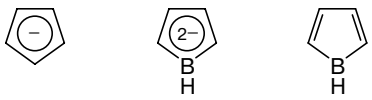


18a **19** **18b**



22

Borole, borole dianion, and borole complex with two lithium atoms. Borole dianion **24** is isoelectronic to the cyclopentadienyl anion **23** and also represents an aromatic system with six π-electrons, whereas the molecule of borole **25** is an antiaromatic system with four π-electrons.[54] Correspondingly, substituted borole and borole dianion exhibit different spectral properties. For instance, crystals of pentaphenylborole, Ph_5C_4B, are blue (λ = 540—605 nm), while those of an adduct $Ph_5C_4B^{2-} \cdot 2K^+$ are dark red (λ = 330 nm).[54]



23 **24** **25**

According to calculations, the π-electron structure of the borole dianion **24** is similar to that of the cyclopentadienyl anion **23**. It is also characterized by equalization of the carbon—carbon bonds (Fig. 4). In contrast to this, the antiaromatic structure of borole **25** exhibits substantial alternation of the carbon—carbon bonds (*cf.* ~1.51 Å for ordinary and ~1.34—1.35 Å for double bonds).

It should be noted that the borole molecule has two energetically less favorable isomers (nonclassical pyramidal structures **26** and **27**) which obey the octet rule[23] and correspond to relatively deep minima on the PES. The energy difference between (i) structures **25** and **26** is 21.4 (DFT) and 9.5 (MP2) kcal mol^{-1} and (ii) structures **25** and **27** is 39.1 (DFT) and 28.2 (MP2) kcal mol^{-1}.

The interaction of the borole molecule with one and two Li atoms leads to a pyramidal complex **28** and a strong bipyramidal complex **29**, respectively (no stationary points corresponding to other complexes were located on the PES of these systems). The formation energy of complex **29** is 108.8 (DFT) and 121.8 (MP2) kcal mol^{-1}, which points to a large covalent contribution to the bonding between the Li atoms and the five-membered ring. This is also supported by the relatively low degree of charge transfer from the Li atoms to the five-membered ring (at most 0.4 e for each

Table 3. Total energies (E_{tot}), zero-point vibrational energy corrections (*ZPE*), and the lowest real (ω_1) or imaginary harmonic vibrational frequencies (iω) of structures **23—29** calculated by the DFT and MP2 (figures in parentheses)* methods

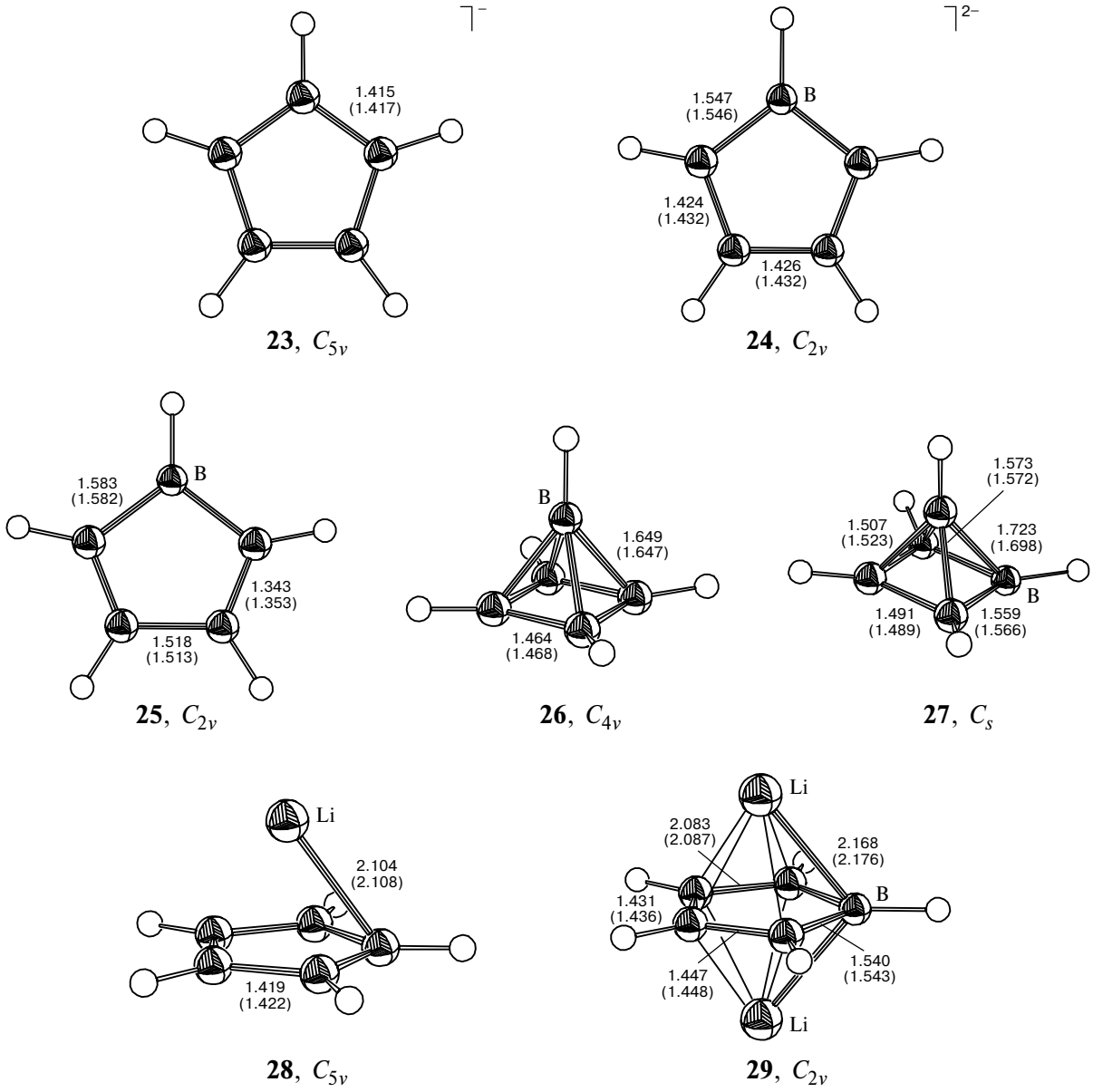
Structure, symmetry	$-E_{tot}$ (au)	*ZPE* (au)	ω_1/cm^{-1} or iω/cm^{-1}
$C_5H_5^-$ (**23**), C_{5v}	193.580770	0.078179	621
	(193.076447)	(0.077314)	(475)
$BC_4H_5^{2-}$ (**24**), C_{2v}	180.155178	0.070336	413
	(179.660546)	(0.068961)	(209)
BC_4H_5 (**25**), C_{2v}	180.266767	0.076443	195
	(179.779628)	(0.076719)	(1148)
BC_4H_5 (**26**), C_{4v}	180.232621	0.076090	448
	(179.764455)	(0.076506)	(484)
BC_4H_5 (**27**), C_s	180.204292	0.075630	394
	(179.734599)	(0.076241)	(434)
$C_5H_5^- \cdot Li^+$ (**28**), C_{5v}	201.138310	0.083704	409
	(200.597852)	(0.084501)	(410)
$BC_4H_5^{2-} \cdot Li_2^{2+}$ (**29**), C_{2v}	195.456068	0.082372	332
	(194.889494)	(0.083180)	(349)
Li_2, $D_{\infty v}$	15.015837	0.000781	343**
	(14.915748)	(0.000781)	(343)

* See Note to Table 1.
** The experimental frequency is 351.43 cm^{-1}, and the experimental Li—Li bond length is 2.672 Å (see Ref. 41).

Table 4. Total energies (E_{tot}), zero-point vibrational energy corrections (*ZPE*), and the lowest real (ω_1) or imaginary harmonic vibrational frequencies (iω) of structures **30—36** calculated by the DFT and MP2 (figures in parentheses)* methods

Structure, symmetry	$-E_{tot}$ (au)	*ZPE* (au)	λ	ω_1/cm^{-1} or iω/cm^{-1}
$BC_5H_6^-$ (**30**), C_{2v}	219.089639	0.093168	0	363
	(218.497881)	(0.092067)	0	(255)
BC_5H_6 (**31**), C_{2v}	218.386353	0.0846693	0	384
	(217.808491)	(0.084161)	0	(350)
$BC_5H_6^- \cdot Li^+$ (**32**), C_s	226.626804	0.098246	0	367
	(226.000552)	(0.099146)	0	(373)
$BC_5H_6^- \cdot Li^+$ (**33**), C_s	226.595146	0.097038	1	i74
	(225.964650)	(0.096623)	1	(i84)
$B_2C_4H_6^{2-}$ (**34**), D_{2h}	205.690377	0.085080	0	335
	(205.108495)	(0.083123)	0	(150)
$B_2C_4H_6$ (**35**), C_s	205.774397	0.092889	0	496
	(205.230994)	(0.093872)	0	(509)
$B_2C_4H_6$ (**36**), D_{2h}	205.743921	0.089553	1	i39
	(205.167942)	(0.089262)	2	(i202)
$B_2C_4H_6^{2-} \cdot Li^{2+}$ (**36**), D_{2h}	220.954707	0.096876	0	335
	(220.304063)	(0.097404)	0	(350)
LiH, $C_{\infty v}$	8.086268	0.003217	0	1412**
	(8.022098)	(0.003271)	0	(1436)

* See note to Table 2.
** The experimental frequency is 1405.65 cm^{-1} and the experimental Li—H bond length is 1.5953 Å (see Ref. 41).



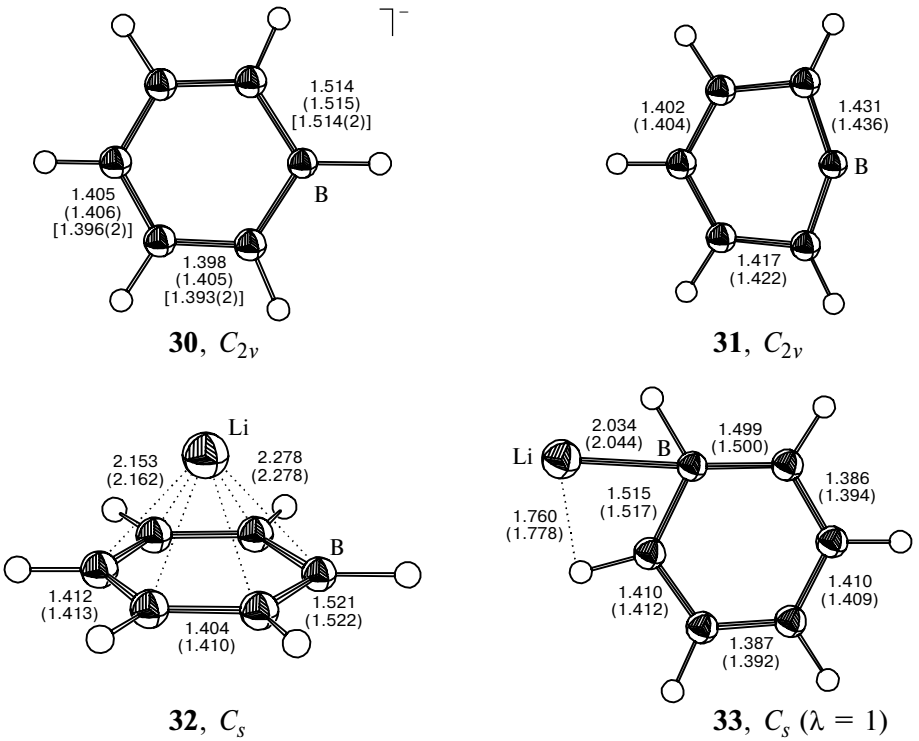
23, C_{5v} **24**, C_{2v} **25**, C_{2v} **26**, C_{4v} **27**, C_s **28**, C_{5v} **29**, C_{2v}

Fig. 4. Geometric characteristics of structures **23—29** corresponding to minima on the PES and calculated by the DFT (B3LYP/6-311+G**) and MP2(full)/6-311+G** (figures in parentheses) methods.

Li atom). The geometric characteristics of the pyramidal (**28**) and bipyramidal (**29**) complexes are very close to those of the ions **23** and **24**, which points to similarity of their electronic structures. It should be noted that the carbon—carbon bond lengths in anion **23** and complex **28** lie within the known limits for the carbon—carbon bond lengths in metallocenes (1.41—1.43 Å).[39] This emphasizes that the electronic characteristics of the five-membered rings in the systems considered above and in metallocenes are close.

Borabenzene and boratabenzene anion. The boratabenzene anion **30**, containing an electron-deficient B atom, is a heteroatomic system isoelectronic to benzene. Boratabenzene derivatives represent a large class of ligands in coordination chemistry of transition metals.[55—59] Similarly to the preceding system, boratabenzene exhibits interesting photophysical properties.[57] According to our calculations (Table 4), structure **30** corresponds to a minimum on the PES ($\lambda = 0$) and its geometric characteristics (Fig. 5) are reasonably close to the experimental data obtained[58] in the X-ray diffraction study of the lithium salt of boratabenzene.

The molecular geometry of borabenzene **31** and the structure of complex **32** formed by boratabenzene and a lithium atom is shown in Fig. 5. Despite the fact that the borabenzene molecule has two electrons less than the pyridine molecule, it is also an aromatic system with

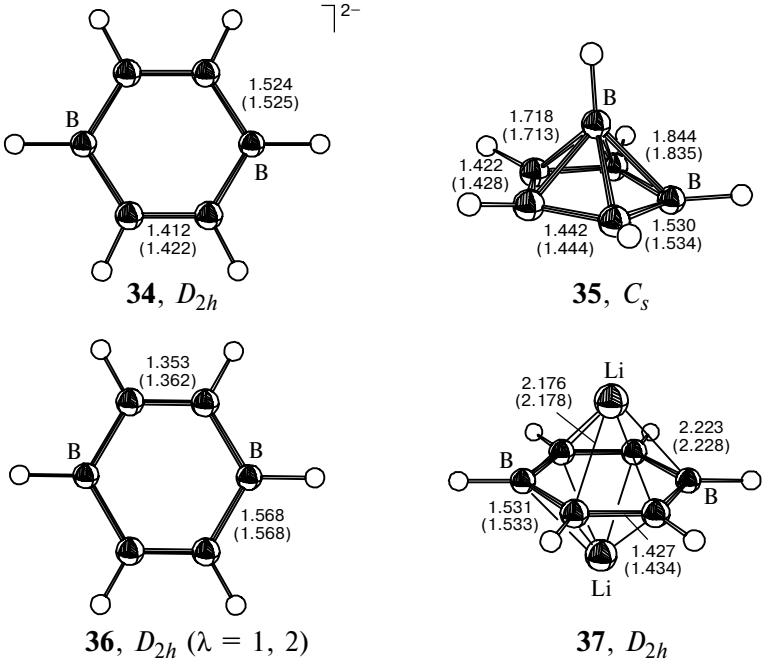


30, C_{2v} **31**, C_{2v}

32, C_s **33**, C_s ($\lambda = 1$)

Fig. 5. Geometric characteristics of structures **30—32** corresponding to minima and structure **33** corresponding to a saddle point on the PES calculated by the DFT (B3LYP/6-311+G**) and MP2(full)/6-311+G** (figures in parentheses) methods and the experimental data[58] (figures in brackets).

six π-electrons.[60,61] Indeed, molecule **31** has three filled π-orbitals and is characterized by equalization of all cyclic bonds. It should be noted that for borabenzene the orbital that matches the lone electron pair of the N atom in the pyridine molecule corresponds to the LUMO. Because of this, borabenzene is a strong Lewis acid and



34, D_{2h} **35**, C_s

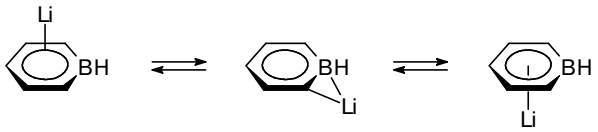
36, D_{2h} ($\lambda = 1, 2$) **37**, D_{2h}

Fig. 6. Geometric characteristics of structures **34—37** corresponding to minima on the PES calculated by the DFT (B3LYP/6-311+G**) and MP2(full)/6-311+G** (figures in parentheses) methods.

forms relatively stable donor-acceptor complexes even with such weak donors as CO and N_2.[61]

The formation of complex **32** between boratabenzene and lithium cation leads to a slight lengthening of all cyclic bonds in this complex as compared to anion **30**. By analogy (see above), this can be explained by large covalent contribution to the bonding between the Li atom and the ring in structure **32**. The Li atom can migrate from its position above the six-membered ring plane (structure **32a**) to the position under this plane (structure **32b**) *via* TS **33** (Scheme 5). We estimated the energy barrier to this migration at 19.7 (DFT) and 22.5 (MP2) kcal mol^{-1}.

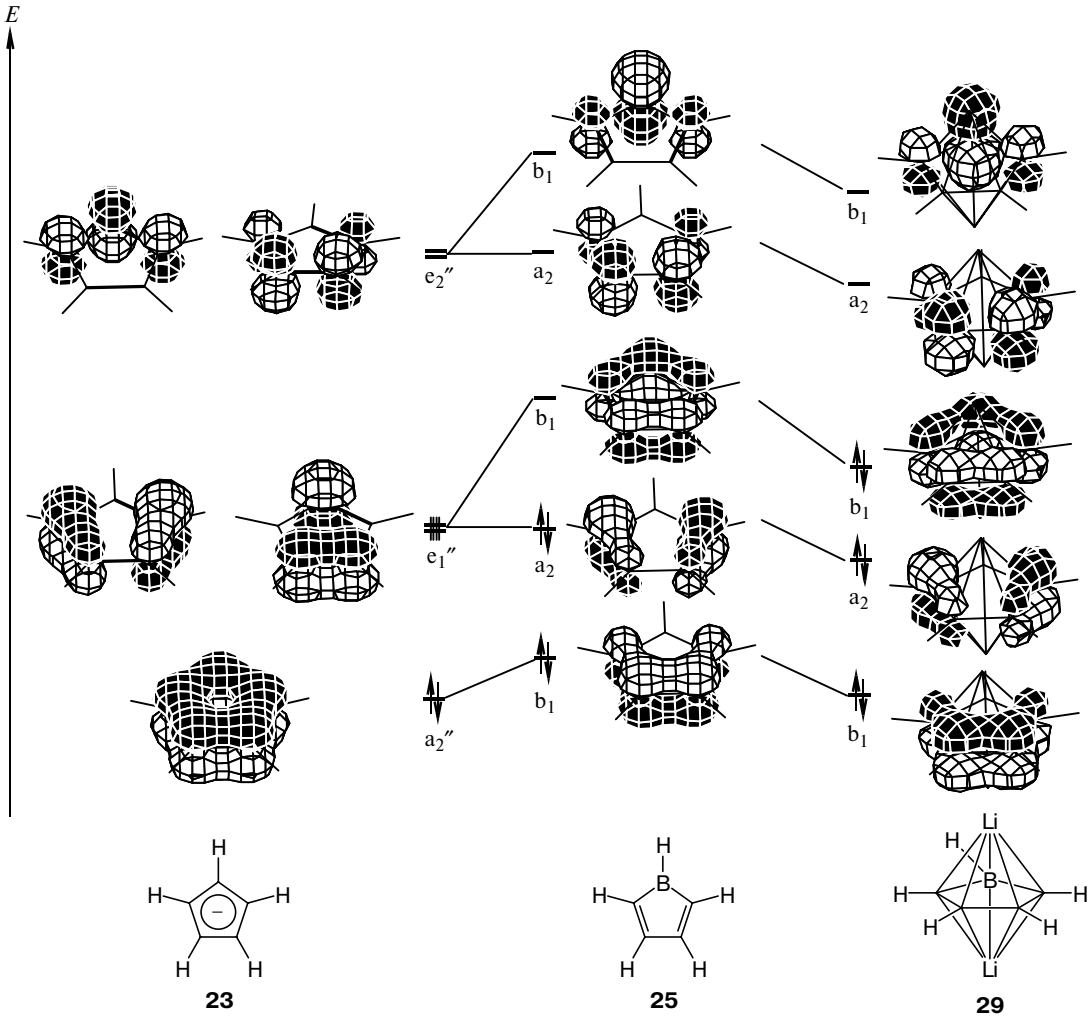
Scheme 5



32a **33** **32b**

1,4-Diboratabenzene dianion (34) and its dilithium complex. Only the nonclassical *nido*-structure **35** of carborane $B_2C_4H_6$ was reported.[62] Recent RHF/DZ calculations[63] showed that isomer **36** (with classical planar geometry), which also corresponds to a minimum on the PES, is energetically less favorable than structure **35**. In this work, we found (see Table 4 and Fig. 6) that *nido*-structure **35** is 19.1 (DFT) and 39.6 (MP2) kcal mol^{-1} energetically more favorable than planar structure **36** that does not correspond to a minimum on the PES of the system $B_2C_4H_6$ (this contradicts the conclusions drawn previously[63]).

Unlike neutral system $B_2C_4H_6$, planar aromatic structure **34** of the $B_2C_4H_6^{2-}$ dianion (no data are presented for this dianion) is much more stable than *nido*-structure **35**. Nevertheless, the latter structure also corresponds to a minimum on the PES of the system $B_2C_4H_6^{2-}$. Unstable planar structure **36** forms a stable bipyramidal complex **37** with two Li atoms. In this complex, the carbon—carbon and boron—carbon bonds are slightly lengthened (on the average, by 0.01 Å) as compared to those in dianion **34**. The interaction of system **35** with



23 **25** **29**

Fig. 7. Correlation diagram of π-MO energy levels of cyclopentadienyl anion **23**, borole **25**, and dilithiumborole **29**.

two Li atoms leads to cleavage of the boron—boron bond; however, the system does not undergo relaxation into bipyramidal structure **37**, though it remains energetically much less favorable (≥100 kcal mol^{-1}) than complex **37**.

Molecular orbital analysis and induced aromaticity effects. We performed a comparative analysis of the MOs of structurally identical systems with five-membered rings and different aromaticity characteristics, *viz.*, the cyclopentadienyl anion **23** (an aromatic system), the molecule of borole **25** (an antiaromatic system), and the dilithium complex of borole **29** (the system with induced aromaticity). As follows from the correlation diagram (Fig. 7), the cyclopentadienyl anion **23** is characterized by a stable aromatic system with six π-electrons and three filled bonding π-orbitals. In the borole molecule (a system with four π-electrons) one of the bonding π-levels is unfilled, which is responsible for the specific antiaromatic properties of this system.

Attachment of two Li atoms to the apical positions of the five-membered ring of the borole molecule leads, on the one hand, to substantial lowering of all π- and σ-orbital energy levels and, on the other hand, to filling of the π-LUMO (b_1) of the borole molecule and to a complete analogy with the aromatic system of the cyclopentadienyl anion **23** containing six π-electrons. The MO shapes of the bipyramidal dilithium complex **29** remain the same as those of isolated borole molecule. Thus, from the viewpoint of orbital effects the counteratoms play the role of electron donors to the π-system of the basal fragment. This is followed by substantial stabilization of all the orbital energy levels. An analogous mechanism of lithium-induced stabilization is characteristic of all the pyramidal and bipyramidal systems considered above.

The results of our calculations show that counterions play a crucial role in the stabilization of these types of systems, making their aromatic structures more stable, which is unstable in the absence of the counterions. Stabilization of these systems involves both charge transfer and covalent bonding with the aromatic system.

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