

Novel aromatic borafluorole, fluoraborabenzene and diborafluorabenzene heterocyclic systems: an *ab initio* study

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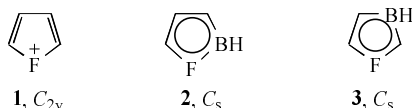
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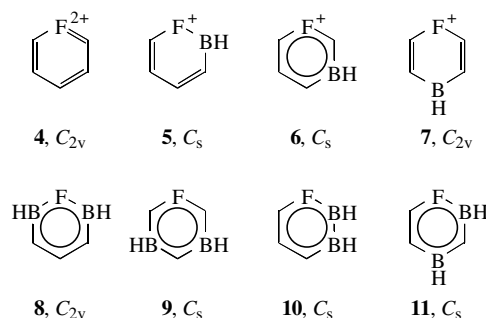
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The *ab initio* [MP2(fu)/6-311+G**] and DFT (B3LYP/6-311+G**) calculations predict aromatic stabilization of the planar structures of borafluorole, fluoraborabenzene and diborafluorabenzenes, boron-containing heterocycles with hypercoordinated fluorine centres.

Aromaticity is among the most important concepts of theoretical chemistry^{1,2} designed to predict and explain the stability and chemical properties of various, in particular, heterocyclic compounds. We have previously considered a simple method to design novel heteroaromatic systems by substituting CH units or CC bonds in the ring of the archetype aromatic system of benzene by equal numbers of isoelectronic (*e.g.*, BH⁺, N, O⁺ and F²⁺) or 2 π -electronic (NH, O and S) centres, respectively. The efficiency of the approach was demonstrated by the prediction of a significant stability of six-membered oxaboraheterocycles and oxa-1,8-diboranaphthalene.³ In a similar way, novel stable nonclassic molecular systems **1–3** can be produced starting from another aromatic system. Here, we report on the computational study of five-membered boron-containing heterocycles with hypercoordinated fluorine centres in the ring, which are derived from the aromatic cyclopentadienide anion. In addition,



calculations of a series of the six-membered fluorine- and boron-containing heterocyclic cations **4–7** and electrically neutral diborafluorabenzenes **8–11**, which are isoelectronic to benzene, have been performed to demonstrate the applicability of the method to the construction of nonclassic aromatic systems.



All calculations of compounds **1–11** and other possible positional isomers have been carried out with the help of *ab initio* [MP2(fu)/6-311+G**] and density function theory (B3LYP/6-311+G**) methods.⁴

The principal questions to be solved by calculations are: (i) whether the designed (4n + 2) π -electron systems remain stable to possible distortions of the planar structures and (ii) what is the magnitude of the additional stabilization of the cyclic systems, which is due to the π -electronic cyclic delocalization. To answer these questions, we have considered possible out-of-plane distortions of the planar structures of **1–11** and estimated the aromatic character of these compounds using the approach³ similar to that used for calculations of the Dewar resonance energies.^{1,2}

Table 1 The *ab initio* and DFT data for compounds **1–2**, **4–12**, **15**.^a

Structure, symmetry	Method	E_{tot}	ZPE	ΔE	ΔE_{ZPE}	ΔH	ΔG	ω_1
1 , C _{2v}	MP2(fu)/6-311+G**	–253.733629	0.066714	—	—	—	—	437.7
	B3LYP/6-311+G**	–254.326792	0.065893	—	—	—	—	423.8
2 , C _s	MP2(fu)/6-311+G**	–240.819808	0.062942	0	0	0	0	359.5
	B3LYP/6-311+G**	–241.402386	0.062162	0	0	0	0	276.4
12 , C _s	MP2(fu)/6-311+G**	–240.809152	0.061069	6.7	5.5	6.2	4.5	129.6
	B3LYP/6-311+G**	–241.396040	0.060910	4.0	3.2	3.8	2.4	152.1
4 , C _{2v}	MP2(fu)/6-311+G**	–291.846694	0.083322	—	—	—	—	239.0
	B3LYP/6-311+G**	–292.522902	0.082448	—	—	—	—	252.4
5 , C _s	MP2(fu)/6-311+G**	–279.203663	0.081574	0	0	0	0	217.8
	B3LYP/6-311+G**	–279.863714	0.081236	0	0	0	0	239.3
6 , C _s	MP2(fu)/6-311+G**	–279.080603	0.079992	77.2	76.2	76.3	76.2	185.7
	MP2(fu)/6-311+G**	–279.135828	0.079495	42.6	41.3	41.5	41.3	121.1
7 , C _{2v}	B3LYP/6-311+G**	–279.801776	0.078517	38.9	37.2	37.6	36.7	138.9
8 , C _{2v}	MP2(fu)/6-311+G**	–266.300209	0.078446	0	0	0	0	245.7
	B3LYP/6-311+G**	–266.949997	0.078003	0	0	0	0	271.8
9 , C _{2v}	MP2(fu)/6-311+G**	–266.094547	0.075042	129.1	126.9	127.2	126.7	188.7
	B3LYP/6-311+G**	–266.759355	0.073749	119.6	117.0	117.4	116.5	179.1
10 , C _s	MP2(fu)/6-311+G**	–266.176852	0.075937	77.4	75.8	76.2	74.9	123.6
	B3LYP/6-311+G**	–266.832591	0.075685	73.7	72.2	72.5	71.6	217.9
11 , C _s	MP2(fu)/6-311+G**	–266.229763	0.076241	44.2	42.8	43.2	42.0	164.5
	B3LYP/6-311+G**	–266.881886	0.075542	42.7	41.2	41.7	40.1	143.3
15 , C _s	MP2(fu)/6-311+G**	–266.277945	0.074911	14.0	11.7	12.8	9.7	77.3
	B3LYP/6-311+G**	–266.930541	0.074884	12.2	10.2	11.2	8.4	86.9

^a E_{tot} (a.u.) is the total energy (1 a.u. = 627.5095 kcal mol^{–1}); ZPE (a.u.) is the harmonic zero-point correction; ω_1 (cm^{–1}) is the smallest harmonic vibration frequency; ΔE (kcal mol^{–1}) is the relative energy; ΔE_{ZPE} (kcal mol^{–1}) is the relative energy including the harmonic zero-point correction; ΔH and ΔG (kcal mol^{–1}) are the relative enthalpy and relative Gibbs free energy at standard conditions ($P = 1$ atm and $T = 298.1$ K).

According to the calculations, the molecules of **1,2,4,5,7–11** possess planar structures and correspond to deep minima on the respective potential energy surfaces (PES). Their geometric and energy characteristics are listed in Table 1 and shown in Figures 1 and 2.

Other conceivable positional isomers are unstable in cyclic forms and do not correspond to minima on the PES.

As for furan, their isoelectronic analogues fluorole cation **1** and the most stable positional isomer of 1,2-borafluorole **2** have relatively low aromatic character displayed by the substantial alternation in the CC bond lengths (Figure 1), and the long BF distance (1.670 Å, MP2 and 1.683 Å, DFT) in **2** which is considerably longer than the standard length of an ordinary BF bond (~1.35 Å).^{7,8} This conclusion is consistent with previous calculations.^{1,5,6} To evaluate the thermodynamic stability of cyclic system **2** and the role of π -electronic cyclic delocalization, we compared it with isomeric polyene **12** as the reference structure. According to the calculations, the latter is 4.0 (DFT) and 6.7 (MP2) kcal mol⁻¹ less energy favourable than **2**.

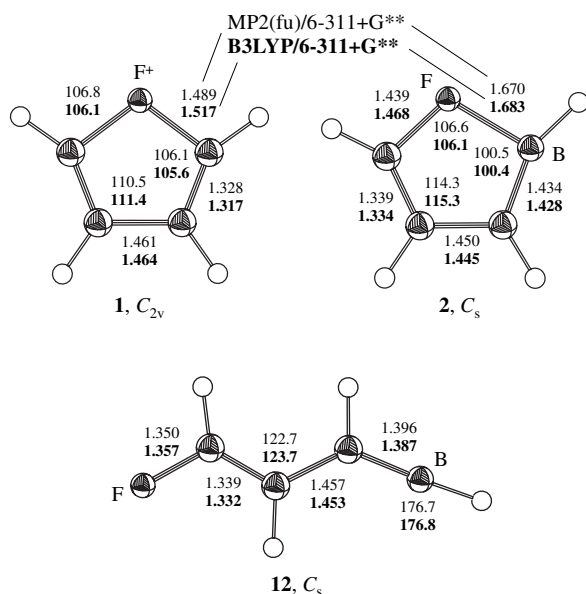


Figure 1 Geometry parameters of structures **1**, **2** and **12** calculated by *ab initio* and DFT methods. The bond lengths and angles are indicated in angstrom units and degrees, respectively.

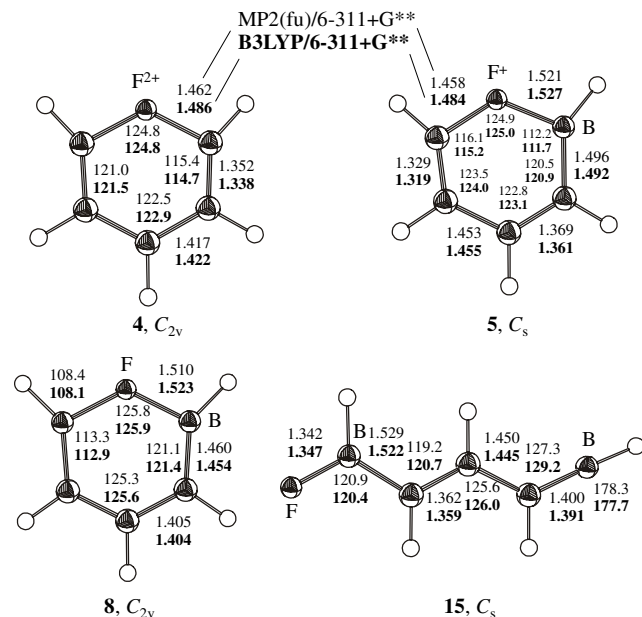
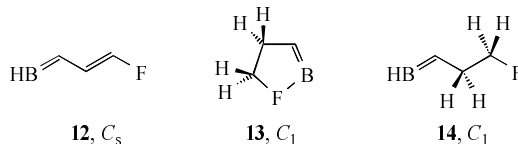


Figure 2 Geometry parameters of isomers **4**, **5**, **8** and **15** calculated by *ab initio* and DFT methods. The bond lengths and angles are indicated in angstrom units and degrees, respectively.



The length of the double BC bond in polyene **12** (1.387 Å, DFT and 1.396 Å, MP2) is close to that of a double BC bond in organoboron compounds.^{7,8} To evaluate the stabilization determined by π -electronic cyclic delocalization (ΔE_{arom}) in **2**, we used the equation

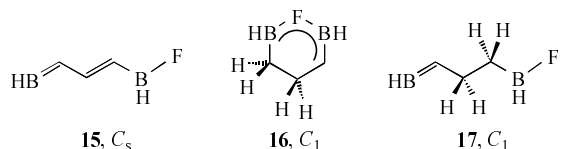
$$\Delta E_{\text{arom}}(\mathbf{2}) = \Delta E(\mathbf{2-12}) - \Delta E_{\text{BF}}, \quad (1)$$

where $\Delta E(\mathbf{2-12})$ is the difference between the total energies of **2** and **12**, ΔE_{BF} (1.8, DFT and 3.9 kcal mol⁻¹, MP2) corresponds to the energy of the BF bond in **2** calculated as the difference between the total energies of cyclic **13** and open chain **14** structures. The stereochemical surrounding of the BF bond in **13** is nearly the same as in **2**, the dihedral angle between the CF and CB bonds in **13** equals 17.3° (DFT) and 3.5° (MP2). However, in contrast to **2**, **13** does not embody a property of π -electronic cyclic delocalization. As can be seen in Table 1, the ΔE_{arom} values (2.2, DFT and 2.8 kcal mol⁻¹, MP2) for **2** are considerably lower than those (23–75 kcal mol⁻¹) for π -electronic cyclic delocalization of benzene as obtained by the use of various methods and different reference systems.²

Analogously, π -electronic cyclic delocalization energy in **8** is calculated according to the equation

$$\Delta E_{\text{arom}}(\mathbf{8}) = \Delta E(\mathbf{8-15}) - \Delta E_{\text{BF}}, \quad (2)$$

where $\Delta E(\mathbf{8-15})$ is the difference of the total energies of **8** and **15**, ΔE_{BF} is the BF bond energy in **8** estimated as the difference of the total energies of **16** and **17**. The values of $\Delta E_{\text{arom}}(\mathbf{8})$ obtained in such a way, 13.1 (DFT) and 13.6 (MP2) kcal mol⁻¹, are twice larger than the values of $\Delta E_{\text{arom}}(\mathbf{2})$, even though they remain lower than the cyclic π -electron delocalization energy of benzene.



In conclusion, the above calculations demonstrated the generality of an approach to the computational design of nonclassical aromatic systems based on replacing CH or CHCH units in parent aromatic hydrocarbons by hypercoordinated π -isoelectronic heteroatomic fragments. Hypothetical compounds **2**, **5** and **8**, containing hypercoordinated fluorine were found to have stable planar structures with weak aromatic stabilization.

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