Novel aromatic oxaborabenzene and 9-oxa-1,8-diboranaphthalene systems: an *ab initio* study

Ruslan M. Minyaev,* Vladimir I. Minkin, Tatyana N. Gribanova and Andrei G. Starikov

Institute of Physical and Organic Chemistry, Rostov State University, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 8632 28 5667; e-mail: minyaev@ipoc.rsu.ru

10.1070/MC2001v011n02ABEH001442

Ab initio **[MP2(fu)/6-31+G**, MP2(fu)/6-311+G**] and DFT [B3LYP/6-31+G**, B3LYP/6-311+G**] calculations predict the aromatic stabilization of planar 1,2-oxaborabenzene and 9-oxa-1,8-diboranaphthalene.**

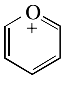
Aromaticity is an important theoretical concept of chemistry[1,2] designed to predict and explain the stability and chemical properties of various, in particular, heterocyclic, compounds. The simplest way to form a heteroaromatic compound starting from the archetype aromatic system of benzene is to replace CH units or CC bonds in a ring by equal numbers of isoelectronic (*e.g.*, N, O^+, BH^-) or 2π-electronic (NH, O, S) centres, respectively. With the use of a starting heteroaromatic system, a series of new heteroaromatics can be produced, some of which exhibit nonclassical structures that cannot be described in terms of Lewis structural formulae. An important question is whether $(4n+2)\pi$-electronic species thus formed remain persistent to possible distortions of the initial planar structure and display additional stability due to cyclic π-electron delocalization.

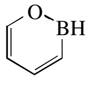
To solve this question, we performed *ab initio* calculations for pyrylium cation **1** and a series of six-membered oxaboraheterocycles **2**–**4** derived from **1**. One of these currently unknown heteroaromatic systems, namely, **3**, has a nonclassical structure. In addition, we studied another nonclassical oxadiboraheterocycle **5**, which can be considered as the result of insertion of a 3π-electron HB–O–BH unit into peri-positions of the naphthalene ring.

Table 1 *Ab initio* and DFT data for compounds **2**–**9**.[a]

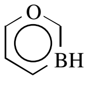
Structure, symmetry	Method	E_{tot}	ZPE	ω_1
2, C_s	MP2(fu)/6-31+G**	–254.793351	0.085455	318.9
	MP2(fu)/6-311+G**	–254.977024	0.084222	310.5
	B3LYP/6-31+G**	–255.555651	0.084650	332.4
	B3LYP/6-311+G**	–255.608372	0.084318	331.5
3, C_s	MP2(fu)/6-31+G**	–254.724767	0.084965	300.1
	MP2(fu)/6-311+G**	–254.909008	0.083897	294.9
	B3LYP/6-31+G**	–255.485647	0.083936	321.0
	B3LYP/6-311+G**	–255.538568	0.083656	319.5
4, C_{2v}	MP2(fu)/6-31+G**	–254.745222	0.085037	266.2
	MP2(fu)/6-311+G**	–254.929331	0.083996	263.3
	B3LYP/6-31+G**	–255.509674	0.084152	283.3
	B3LYP/6-311+G**	–255.562959	0.083847	283.7
5, C_{2v}	MP2(fu)/6-31+G**	–395.301912	0.138469	68.0
	B3LYP/6-31+G**	–396.515389	0.138170	114.8
	B3LYP/6-311+G**	–396.592365	0.137680	115.3
6, C_s	MP2(fu)/6-31+G**	–254.667375	0.079462	91.6
	MP2(fu)/6-311+G**	–254.853093	0.078284	89.0
	B3LYP/6-31+G**	–255.438712	0.078724	102.7
	B3LYP/6-311+G**	–255.494515	0.078439	100.5
7, C_s	MP2(fu)/6-31+G**	–395.127733	0.130082	32.0
	B3LYP/6-31+G**	–396.355221	0.129496	42.6
	B3LYP/6-311+G**	–396.436157	0.129024	40.9
8, C_s	MP2(fu)/6-31+G**	–255.900031	0.107317	231.6
	MP2(fu)/6-311+G**	–256.089025	0.106044	228.7
	B3LYP/6-31+G**	–256.686618	0.104885	231.8
	B3LYP/6-311+G**	–256.740321	0.104585	229.4
9, C_s	MP2(fu)/6-31+G**	–255.865396	0.103566	56.3
	MP2(fu)/6-311+G**	–256.054313	0.102047	56.8
	B3LYP/6-31+G**	–256.650205	0.101263	53.9
	B3LYP/6-311+G**	–256.706534	0.101017	56.7

[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; $\lambda = 0$, λ is the number of imaginary harmonic frequencies; ω_1 (cm^{-1}) is the smallest or imaginary harmonic vibration frequency.

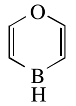

1, C_{2v}



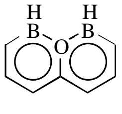
2, C_s



3, C_s



4, C_{2v}

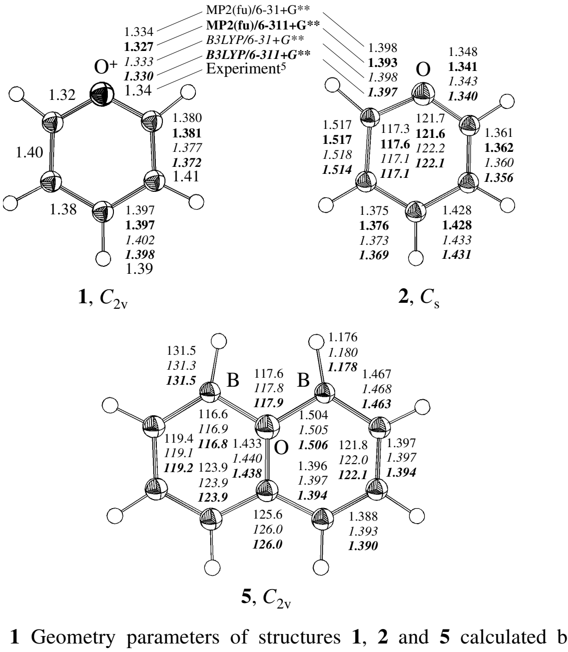


5, C_{2v}

Here, we report the results of *ab initio* [MP2(fu)/6-31+G**, MP2(fu)/6-311+G**] and density functional theory [B3LYP/6-31+G**, B3LYP/6-311+G**][3,4] calculations for compounds **1**–**4** and bicyclic oxadiboraheterocycle **5**, which is π-isoelectronic to naphthalene. The aromatic character of these compounds was estimated using an approach similar to that used for the calculations of Dewar resonance energies.[1]

According to the calculations, the molecules of all compounds **1**–**5** possess planar structures and correspond to minima on the respective potential energy surfaces (PESs). Their geometry and energy characteristics are listed in Tables 1 and 2 and shown in Figures 1 and 2.

1,2-Oxaborabenzene **2** was predicted to be the most stable isomer in the family of oxaborabenzenes **2**–**4**. The lengths of the BC bonds in cyclic systems **2**–**5** lie in the range 1.500–1.529 Å and are shorter than the standard BC bonds in aromatic compounds (~1.56 Å).[6] At the same time, these values are close to those for the BC bond lengths [1.514(2) Å] found by X-ray diffraction analysis in the lithium salts of boratabenzene[7] and boratastilbene.[8] The calculated BO bond lenghts (1.393–1.398 Å) are longer than the lengths of covalent bonds between tricoordinated boron and dicoordinated oxygen (~1.367 Å).[6] The CO bond lengths in **2**–**4** (1.337–1.358 Å) are close to those in pyrylium salts (~1.35 Å).[5] Note that all CC bonds in bicyclic



1, C_{2v}

2, C_s

5, C_{2v}

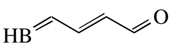
Figure 1 Geometry parameters of structures **1**, **2** and **5** calculated by *ab initio* and DFT methods. The bond lengths and angles are given in angström units and degrees, respectively.

Table 2 Relative energies calculated by *ab initio* and DFT methods for compounds **2**–**7**.[a]

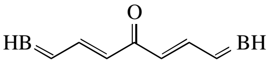
Structure, symmetry	Metod	ΔE	ΔE_{ZPE}	ΔH	ΔG
2, C_s	MP2(fu)/6-31+G**	57.3[b]	0	0	0
	MP2(fu)/6-311+G**	56.0[b]			
	B3LYP/6-31+G**	50.5[b]			
	B3LYP/6-311+G**	50.2[b]			
3, C_s	MP2(fu)/6-31+G**	43.0	42.7	42.7	42.7
	MP2(fu)/6-311+G**	42.7	42.5	42.5	42.5
	B3LYP/6-31+G**	43.9	43.5	43.5	43.5
	B3LYP/6-311+G**	43.8	43.4	43.4	43.4
4, C_{2v}	MP2(fu)/6-31+G**	30.2	29.9	30.0	29.9
	MP2(fu)/6-311+G**	29.9	29.8	29.8	29.7
	B3LYP/6-31+G**	28.8	28.5	28.6	28.9
	B3LYP/6-311+G**	28.5	28.2	28.3	28.6
5, C_{2v}	MP2(fu)/6-31+G**	65.9[b]	0	0	0
	B3LYP/6-31+G**	54.8[b]			
	B3LYP/6-311+G**	55.6[b]			
6, C_s	MP2(fu)/6-31+G**	79.0	75.3	76.6	73.7
	MP2(fu)/6-311+G**	77.8	74.0	75.3	72.4
	B3LYP/6-31+G**	73.4	69.7	70.9	68.2
	B3LYP/6-311+G**	71.4	67.8	69.0	66.3
7, C_{2v}	MP2(fu)/6-31+G**	109.3	103.9	105.0	102.2
	B3LYP/6-31+G**	100.5	95.1	97.2	91.9
	B3LYP/6-311+G**	98.0	92.6	94.7	89.4

[a] ΔE (kcal mol^{-1}) is the relative energy; ΔE_{ZPE} (kcal mol^{-1}) is the relative energy including harmonic zero-point correction; ΔH and ΔG (kcal mol^{-1}) are the relative enthalpy and the relative Gibbs free energy under standard conditions (P = 1 atm and T = 298.1 K). [b] ΔE_{arom}.

naphthalene-like system **5** are equalised, and they are similar to those in benzene (1.397 Å).[1]



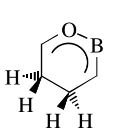
6, C_s



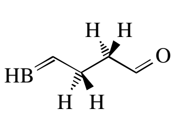
7, C_s

To evaluate the thermodynamic stability of the most stable cyclic (**2**) and bicyclic (**5**) systems, polyenes **6** and **7** were calculated. The symmetry of polyene **7** was predicted by MP2 calculations to be C_s with the dihedral angle OCCC about 2°, whereas DFT gives C_{2v} symmetry. The lengths of double BC bonds in polyenes **6** and **7** (~1.400 Å) are equal to the lengths of double BC bonds in organoboron compounds.[9,10] To evaluate the stabilization due to cyclic π-electron delocalization in **2** (ΔE_{arom}), we applied the equation (1), where ΔE is the difference in the total energies of cyclic isomer **2** and polyene **6**, and ΔE_{BO} is the energy of the BO bond in **2** calculated as the difference between the total energies of ring-closed and open structures, **8** and **9**, respectively.

$$\Delta E_{arom}(\mathbf{2}) = \Delta E(\mathbf{2}–\mathbf{6}) - \Delta E_{BO} \qquad (1)$$



8, C_1



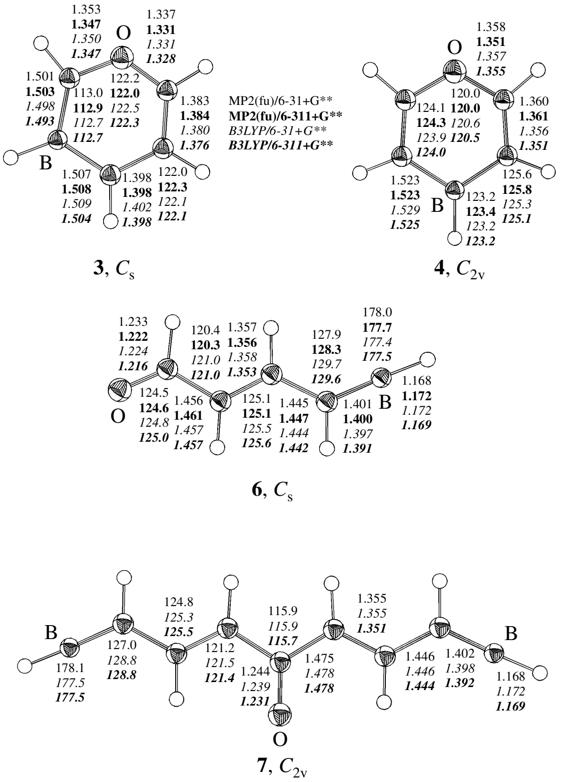
9, C_1

As is the case in **2**, the BO bond in **8** is a part of the conjugated system, slightly distorted in **8** (dihedral angle between CO and CB bonds is approximately equal to 13°). However, as distinct from **2**, no cyclic π-electron delocalization is inherent to **8**. As can be seen in Table 2, the ΔE_{arom} for **2** are about 50–56 kcal mol^{-1} depending on the computational level. These values are in the range (23–75 kcal mol^{-1}) typical of the effect of cyclic π-electron delocalization calculated for benzene using different methods and different reference systems.[2]

Similarly, the cyclic π-electron delocalization energy for **5** was calculated according to the equation

$$\Delta E_{arom}(\mathbf{5}) = \Delta E(\mathbf{5} - \mathbf{7}) - 2\Delta E_{BO}, \qquad (2)$$

where $\Delta E(\mathbf{5} - \mathbf{7})$ is the difference between the total energies of **5** and **7**, and ΔE_{BO} is the BO bond energy in **2**. The values of $\Delta E_{arom}(\mathbf{5})$ thus obtained lie in the range 55–66 kcal mol^{-1}, and they are even higher than those for monocyclic system **2**.



3, C_s **4**, C_{2v} **6**, C_s **7**, C_{2v}

Figure 2 Geometry parameters of isomers **3**, **4**, and **6**, **7** calculated by *ab initio* and DFT methods. The symmetry for **7** is predicted by MP2 and DFT calculations to be C_s and C_{2v}, respectively. The bond lengths and angles are given in angström units and degrees, respectively.

In conclusion, the results of the calculations of hypothetical compounds **2** and **5**, which are isoelectronic to benzene and naphthalene, respectively, demonstrate that they possess stable aromatic structures.

This work was supported by the Russian Foundation for Basic Research (grant nos. 00-15-97320 and 01-03-32546).

References

1 V. I. Minkin, M. N. Glukhovtsev and B. Ya. Simkin, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley, New York, 1994.

2 T. M. Krygowski, M. K. Cyranski, Z. Czarnocki, G. Hafelinger and A. R. Katritzky, *Tetrahedron*, 2000, **56**, 1783.

3 M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. AlLaham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian-94*, Revision B.3. Gaussian, Inc., Pittsburgh PA, USA, 1995.

4 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.

5 A. T. Balaban, A. Dinculescu, G. N. Dorofeenko, G. W. Fischer, A. V. Koblik and V. V. Mezheritskii, *Pyrylium Salts: Syntheses, Reactions, and Physical Properties*, Academic Press, New York, 1982.

6 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S. 1.

7 G. E. Herberich, B. Schmidt, U. Unglert and T. Wagner, *Organometallics*, 1993, **117**, 8480.

8 B. Y. Lee, S. Wang, M. Putzer, G. P. Bartholomew, X. Bu and G. C. Bazan, *J. Am. Chem. Soc.*, 2000, **122**, 3969.

9 P. P. Power, *Inorg. Chim. Acta*, 1992, **198–200**, 443.

10 W. J. Grigsby and P. P. Power, *Chem. Eur. J.*, 1997, **3**, 368.

Received: 19th February 2001; Com. 01/1768