Mendeleev Commun., 2004, 14(5), 181–191

Intramolecular polarization of the dative B–O bond in the donor–acceptor complexes of 1-boraadamantanes with tetrahydrofuran

Konstantin A. Lyssenko,*[a] Vladimir A. Ponomarev,[b] Mikhail E. Gurskii,[b] Yurii N. Bubnov[a] and Mikhail Yu. Antipin[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: kostya@xrlab.ineos.ac.ru*

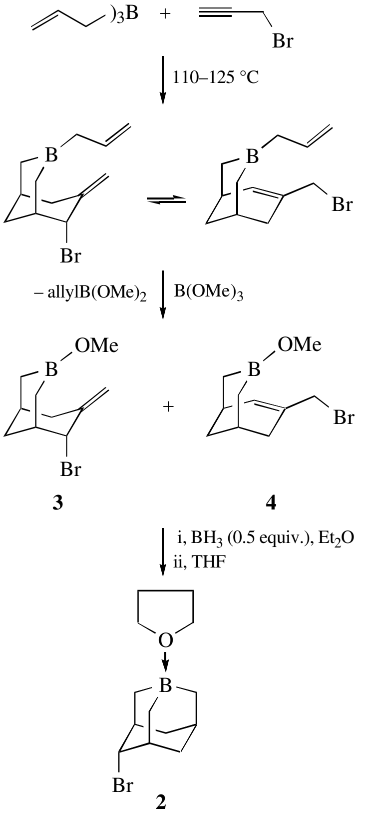
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5328; e-mail: bor@ioc.ac.ru*

DOI: 10.1070/MC2004v014n05ABEH001920

The X-ray diffraction studies and B3LYP/6-311G* calculations of the complexes of 1-boraadamantane and 4-bromo-1-bora-adamantane with THF have revealed that the introduction of a halogen atom results in a shortening of the B–O bond due to intramolecular polarization.

The donor–acceptor complexes of boron are of great interest due to the fact that the B-donor (electron lone pair) distance (B–D$_{LP}$) is extremely sensitive to the aggregation state with its pronounced elongation in the gas phase.[1–5] For example, in the MeCN–BF$_3$ complex, the B–N distance is equal to 2.011(7) Å in a gas phase or 1.630(4) Å in a crystal.[5] Elongation of the B–N bond on change of the media is not a unique feature of the latter complex; depending on the Lewis acidity and basicity of the donor and acceptor fragments, the difference in the bond lengths in the gas and solid states varies from 0.04 Å in the Me$_3$N–BCl$_3$ complex up to 1.24 Å in the case of the MeCN–BCl$_3$ complex.[1,2,4] Due to such an unusual behaviour of the B–D$_{LP}$ bond length, such complexes were called ‘partially bonded molecules’.[4]

The quantum-chemical calculations of isolated donor–acceptor boron complexes reproduce experimental values in the gas phase. On the other hand, calculations taking into account the non-specific solvation of the complexes within the self-consistent reaction field model result in the B–D$_{LP}$ distances, which are observed in the solid state.[6,7] Thus, X-ray diffraction analysis of donor–acceptor boron complexes is of great interest because the geometry of a molecule in solution is closer to that in the crystal than in the gas phase according to *ab initio* calculations.



Scheme 1

In contrast to the macroscopic effects on the B–D$_{LP}$ interaction, the intramolecular polarization of this bond was not analysed previously. This is partially due to the fact that it is difficult to introduce a polar group into a molecule without distortion of the boron centre. Thus, from this point of view, 1-boraadamantane (1-BAD), as a rigid polyhedron, is an ideal acceptor fragment for analysis of both steric (2-substituted 1-BAD) and intramolecular polarization effects (4-substituted 1-BAD) on the B–D$_{LP}$ bond.

Using this idea we synthesised THF complexes of 1-bora-adamantane **1**[8] and 4-bromo-1-boraadamantane **2**.[†] Compound **2** was obtained in three steps by a modified method[9] (Scheme 1). The first step is condensation of triallylborane and propargyl bromide at 110–125 °C followed by treatment with trimethyl borate leading to a 1:1 mixture of compounds **3** and **4**. The use of trimethyl borate for the replacement of an allylic group by a methoxy group allowed us to carry out this procedure under mild and neutral conditions.[†] The second step is the hydroboration of a mixture of **3** + **4** with tetrapropyldiborane (0.5 equiv.) in THF.[10]

In order to reveal the role of intramolecular polarization on the B–O bond length, we carried out X-ray diffraction analysis[‡]

[†] All manipulations with organoboron compounds were carried out in a dry argon atmosphere.

General method for **2**.

(1) A mixture of **3** + **4** was obtained by a modified method[9] and involved the addition of propargyl bromide (15.8 ml, 0.177 mol) to a suspension of phenothiazine (0.2 g) in triallylborane (23.87 g, 0.178 mol) at 50 °C followed by heating the reaction mixture up to 125 °C. The mixture was kept at 125 °C for 2 h; then, it was allowed to chill to room temperature. It was treated with trimethyl borate (1.0 equiv.), and the resulting solution was stirred at room temperature for 5 h. Distillation *in vacuo* yielded 21.98 g (51%) of **1** and **2** as a 1:1 mixture (according to ^{1}H NMR). Characteristic data of **3** and **4**: bp 110–113 °C (1 Torr). ^{1}H NMR (200 MHz, CDCl$_3$) δ: 0.8–2.6 (m, 20H, intricate multiplet of aliphatic protons), 3.59 and 3.63 (s, 6H, B–OMe of **3** and **4**), 3.89 (s, 2H, CH$_2$–Br), 4.90 and 5.09 (s, 2H, C=CH$_2$), 5.88 (d, 1H, C=C*H*–CH, ^3J 5 Hz). ^{11}B NMR (64.21 MHz, CDCl$_3$) δ: 53.3. Found (%): C, 48.52; H, 6.56; B, 4.15; Br, 32.87. Calc. for C$_{10}$H$_{16}$BBrO (%): C, 49.44; H, 6.64; B, 4.45; Br, 32.89.

(2) To a solution of a mixture of **3**, **4** (30.46 g, 0.125 mol) in THF (10 ml) tetrapropyl diborane (0.081 mol) in THF (15 ml) was added. The mixture was kept at room temperature for 30 h with stirring. Then, volatile substances were distilled off in a vacuum (1 Torr), and 30 ml of *n*-pentane was added to the residue. The mixture was cooled to –78 °C; the precipitate formed was washed with *n*-pentane (2×5 ml) and dried *in vacuo*. Characteristic data for **2**: yield 33% (based on isomer **3**, 66%); mp 76–78 °C. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 0.6–2.5 (m, 17H, intricate multiplet with the evaluated multiplet of the CH$_2$–CH$_2$ fragment of THF), 3.92 (m, 4H, O–CH$_2$ of THF), 4.62 (m, 1H, CH–Br). ^{11}B NMR (64.21 MHz, CDCl$_3$) δ: 9.5. ^{13}C NMR (50.32 MHz, CDCl$_3$) δ: 24.6 [C(3)–C(4) of THF], 29.0 (C-2, C-8, C-9), 32.8 (C-7), 33.6 (C-6, C-10), 41.3 (C-3, C-5), 69.2 (CH$_2$OCH$_2$ THF), 69.8 (C-4).

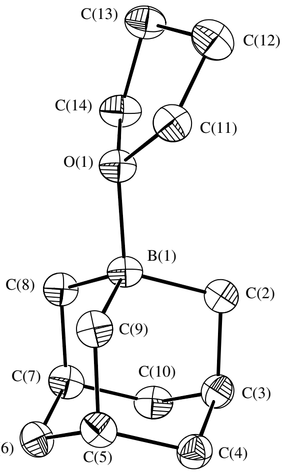


Figure 1 General view of the complex of **1**. Principal bond lengths (Å, the average values for two independent molecules according to XRD): B(1)–O(1) 1.647(2), B(1)–C(2) 1.618(3), B(1)–C(8) 1.615(3), B(1)–C(9) 1.610(3); bond angles (°): C(9)–B(1)–C(2) 110.9(2), C(9)–B(1)–C(8) 109.9(2), C(2)–B(1)–C(8) 110.6(2), C(14)–O(1)–C(11) 109.3(1), C(14)–O(1)–B(1) 117.5(1), C(11)–O(1)–B(1) 119.2(1), C(9)–B(1)–O(1) 107.2(1), C(2)–B(1)–O(1) 110.7(1), C(8)–B(1)–O(1) 107.33(15).

of **1** and **2**. In addition, we have performed the DFT calculation (B3LYP functional) of complexes **1** and **2** and the model THF complex of 4-fluoro-1-boraadamantane **5** using the 6-311G* basis set.§

X-Ray diffraction analysis of **1** at 153 K was reported recently.[11] Taking into account that the molecular geometry is sensitive to temperature, we redetermined this structure at 120 K to minimise systematic errors related to a libration correction for **1** and **2** within the LTS model.[12] General features of the molecular geometry in both structures are close to each other (Figures 1 and 2). The only difference in the geometry of two independent molecules of **1** is the degree of distortion of the twist conformation of the THF ring.

In both crystals, the boron atom is characterised by a slightly distorted tetrahedral configuration. The distortions are reflected in an increase in the C(2)B(1)O(1) bond angles up to 110.3(2)–110.9(1)° in comparison to the other values 107.0(1)–108.0(2)°. In both of the structures, the electron lone pair (LP_O) of the O(1) atom is in the antiperiplanar orientation to the B(1)–C(2) bond with the pseudotorsion angle LP_OO(1)B(1)C(2) equal to 175 or 178° in **1** or **2**, respectively. We propose, therefore, that the widening of the C(2)B(1)O(1) angle as well as the trend to elongation of the B(1)–C(2) distance in comparison to B(1)–C(8) and B(1)–C(9) ones, may be in part the manifestation of the $LP_O \rightarrow \sigma^*$[B(1)–C(2)] charge transfer.

Despite of similar molecular geometries of **1** and **2**, a comparison of B(1)–O(1) distances reveals surprisingly that the introduction of the bromine atom at the axial position causes the shortening of the B(1)–O(1) bond from 1.647(2) Å in **1** to 1.621(3) Å in **2**. In contrast, the deviation of the boron atom from the C(2)C(8)C(9) plane (δ) in **1** and **2** is less sensitive to the introduction of the substituent, and it is equal to 0.512 and 0.517 Å, respectively. Note that, although the B–O bond lengths in **1** and **2** are similar to the B–N distance in the complex of 2-methyl-1-boraadamantane with (*S*)-(–)-phenylethylamine (1.641 Å),[13] the degree of pyramidalization of the boron atom in the later compound is more pronounced (δ = 0.537 Å). Thus, the δ value is more characteristic of the description of B–D_{LP} bonds for different donor systems.

The observed variation of the B(1)–O(1) bond lengths in **1** and **2** may result from either intramolecular polarization of this bond by the dipole of the C–Br bond [the angle between the B(1)–O(1) and C(4)–Br(1) lines is 9°] or polarization by polar crystal media. Taking into consideration that molecules are assembled into ‘tail-to-tail’ dimers by the Br(1)···Br(1A) ($-x + 1$, $-y + 1$, $-z + 1$) intermolecular contacts [Br(1)···Br(1A) 3.743(1) Å, C(4)Br(3)Br(3A) 163.8(1)°] in the crystal of **2**, we cannot exclude that the reason of the observed shortening of the B(1)–O(1) bond in **2** is the influence of a crystal field or a specific shortened contact. However, B3LYP/6-311G* calculations§ have revealed that the observed variation of the B–O bond lengths in **1** and **2** remained the same in the case of isolated molecules.

It was mentioned above that quantum-chemical calculations of the isolated molecule lead to an increase of donor–acceptor

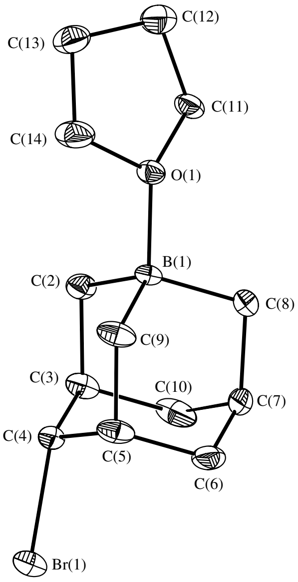


Figure 2 General view of the complex of **2**. Principal bond lengths (Å) according to XRD: B(1)–O(1) 1.621(3), B(1)–C(2) 1.614(4), B(1)–C(8) 1.601(4), B(1)–C(9) 1.609(4); bond angles (°): C(8)–B(1)–C(9) 110.2(3), C(8)–B(1)–C(2) 110.1(3), C(9)–B(1)–C(2) 109.9(2), C(8)–B(1)–O(1) 108.3(2), C(9)–B(1)–O(1) 108.0(2), C(2)–B(1)–O(1) 110.3(2), C(14)–O(1)–C(11) 109.8(2), C(14)–O(1)–B(1) 119.7(2), C(11)–O(1)–B(1) 118.5(2).

---

‡ *Crystallographic data*. Crystals of **1** ($C_{13}H_{23}BO$, $M = 206.12$) are monoclinic, space group $P2_1/c$, at 120 K: $a = 13.413(6)$, $b = 19.160(9)$ and $c = 9.574(5)$ Å, $\beta = 102.61(1)°$, $V = 2401(2)$ Å^3, $Z = 8$ ($Z' = 2$), $d_{calc} = 1.140$ g cm^{-3}, μ(MoKα) = 0.68 cm^{-1}, $F(000) = 912$. Crystals of **2** ($C_{13}H_{22}BOBr$, $M = 220.30$) are triclinic, space group $P\bar{1}$, at 110 K: $a = 6.534(2)$, $b = 9.753(3)$ and $c = 11.073(3)$ Å, $\alpha = 110.390(9)°$, $\beta = 99.353(11)°$, $\gamma = 98.835(9)°$, $V = 635.6(3)$ Å^3, $Z = 2$ ($Z' = 1$), $d_{calc} = 1.489$ g cm^{-3}, μ(MoKα) = 32.10 cm^{-1}, $F(000) = 296$.

The intensities of 16910 (**1**) and 7041 (**2**) reflections were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω and 15 s per frame exposure, $2\theta < 56°$ (**1**) and 58° (**2**)]; 5748 (**1**) and 3342 (**2**) independent reflections [$R_{int} = 0.0596$ (**1**), 0.0342 (**2**)] were used in a further refinement. The absorption correction was applied semiempirically from equivalents. The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. For **1**, the refinement converged to $wR_2 = 0.1454$ and GOF = 1.074 for all independent reflections [$R_1 = 0.0623$ was calculated against F for 3476 observed reflections with $I > 2\sigma(I)$], and for **2** to $wR_2 = 0.1014$ and GOF = 1.060 for all independent reflections [$R_1 = 0.0412$ was calculated against F for 2810 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 250912 and 250913. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2004.

§ All calculations were carried out with the Gaussian 98 program package,[14] in which fine grid (75302) is the default for evaluating integrals numerically and the 10^{-8} hartree disignation is the default for the SCF convergence. As convergence criteria threshold limits 1.5×10^{-5} and 6×10^{-5} a.u. were used for maximum force and displacement, respectively.

bond lengths. In particular, in the case of **1**, **2** and **5**, the B–O bond lengths become as long as 1.717, 1.699 and 1.702 Å, respectively. General features of molecular geometry in **1** and **2** in isolated molecules are close to those found in the solid. In particular, the antiperiplanar orientation of the LP of O(1) towards the B(1)–C(2) bond and distortion of the boron centre remain the same. Despite an elongation with respect to that in the crystal, the relative difference between B–O bond lengths in **1** and **2** is also observed in the isolated molecules, and it is equal to 0.018 Å. As regards the small increase of the B(1)–O(1) distance in fluorine-substituted compound **5**, it is in line with the decrease of the dipole moment of the C–F bond in comparison to C–Br. Note that, although the B–O distance in a gas phase becomes significantly longer, the δ value is less sensitive to polarization, and it is equal to 0.495, 0.502 and 0.501 Å for **1**, **2** and **5**, respectively. Thus, we can conclude that this value, at least in the case of 1-boraadamantane, is not characteristic of the description of the B–D$_{\mathrm{LP}}$ bond in different media.

A topological analysis of the electron density function $\rho(r)$ demonstrated that, according to published data,[2,6,7] the B–O bond in complexes **1**, **2** and **5** corresponds to an intermediate type of atomic interactions. The values of $\rho(r)$ at the critical point (3, –1) of the B–O bond correlate with its lengths and attain a maximum value (0.502 eÅ^{-3}) in the case of complex **2**. Despite the elongation of B–O bonds, the distance from the critical point (3, –1) to the boron atom remains the same. Thus, intramolecular polarization mainly influences the donor fragment.

In summary, we can conclude, based on an X-ray diffraction study and DFT calculations of the THF complexes of 1-boraadamantane and 4-bromo-1-boraadamantane, that a decrease of the B(1)–O(1) bond length in the 4-bromo analogue is an intrinsic feature of this system, and it is mainly governed by the intramolecular polarization of the B–O bond by the dipole moment of a C–halogen dipole.

This work was supported by the Russian Foundation for Basic Research (grant no. 03-03-32214), the Support of Leading Scientific Schools of the President of the Russian Federation (grant nos. 1060.2003.3, 1917.2003.3 and YC-1209.2003.03) and the Division of Chemistry and Materials Science (Programme no. 1).

References

1 A. Haaland, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 992.
2 V. Jonas, G. Freking and M. Reetz, *J. Am. Chem. Soc.*, 1994, **116**, 8741.
3 R. Boese, N. Niederprüm and D. Bläser in *Molecules in Natural Science and Medicine: an Encomium for Linus Pauling*, ed. Z. Maksić and M. Eckert-Maksić, Ellis Horwood Limited, England, 1991, pp. 103–141.
4 K. R. Leopold, M. Canagaratna and J. A. Philips, *Acc. Chem. Res.*, 1997, **30**, 57.
5 D. J. Giesen and J. A. Phillips, *J. Phys. Chem.*, 2003, **A107**, 4009.
6 G. Merinio, V. I. Bakhmutov and A. Vela, *J. Phys. Chem.*, 2002, **A106**, 8491.
7 A. A. Korlyukov, K. A. Lyssenko, M. Yu. Antipin, V. N. Kirin, E. A. Chernyshev and S. P. Knyazev, *Inorg. Chem.*, 2002, **41**, 5043.
8 B. M. Mikhailov, T. K. Baryshnikova, V. G. Kiselev and A. S. Shashkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2544 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28**, 2361).
9 B. M. Mikhailov, T. K. Kozminskaya and B. I. Bryantsev, *Zh. Obshch. Khim.*, 1976, **46**, 87.
10 B. M. Mikhailov and K. L. Cherkasova, *J. Organomet. Chem.*, 1983, **246**, 9.
11 C. E. Wagner, J.-S. Kim and K. J. Shea, *J. Am. Chem. Soc.*, 2003, **40**, 12179.
12 V. Schomaker and K. N. Trueblood, *Acta Crystallogr.*, 1968, **B24**, 63.
13 M. E. Gurskii, V. A. Ponomarev, K. A. Lyssenko, M. Yu. Antipin, P. Renaud and Yu. N. Bubnov, *Mendeleev Commun.*, 2003, 121.
14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh PA, 1998.

Received: 29th March 2004; Com. 04/2246