Dynamic parameters of the hypervalent $O_3B...O$ bond

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The results of investigations of the common and distinctive features of various chemical bonds, including intermolecular bonds, were considered. The geometries, atom charges, and force constants of the bonds in a dependent system of coordinates were calculated for five boroxide molecular species using the MINDO/3 method. The correlations found between the force constants and the bond energies in the $O_3B...O$ bridge were compared with the analogous relations for the OH...O bridge.

Key words: hydrogen bond, intermolecular interactions, bond strength, force constant of an intermolecular bond.

This work continues the studies dealing with common and distinctive features of various chemical bonds, including hydrogen bonds. This task was set because of the duality of opinions on this topic. Indeed, since the end of the previous century, it has been widely believed[1–5] that an H-bond possesses unique properties due to specific features of the electronic structure of the H atom. Therefore, it comes as no surprise that, after directional interaction between a valence-saturated Li atom of one molecule and the lone electron pair of another molecule had been discovered (resorting to vibrational spectra), it was concluded that the lithium bond can also exist, in addition to the hydrogen bond.[6–10] Later, some researchers have expressed the idea that H-bonds themselves are not always identical but possess certain specific properties depending on the structure of the fragment in which they have formed. Both bifurcate bonds[2,5] and those involving transition metal d electrons[11] are often regarded as H-bonds having specific properties.

In recent years, similarity of purely chemical and some intermolecular bonds has been noted in some publications. Thus it has been convincingly demonstrated[12–14] that all the main spectral manifestations of the H-bond, *e.g.*, the decrease in the ν(XH) vibration frequency, the increase in its intensity, the increase in the half-width of the corresponding band, and the change in the shape of its contour, are also observed in the case of typical van der Waals complexes. At about the same time, it was found[15,16] that the relationships between the elongation of the covalent bond and shortening of the intermolecular bond with respect to the sum of the (Pauling) van der Waals radii of the atoms following the formation of RO(N,S)...HO(N,Hal) H-complexes and halogen nσ-complexes RO(N,S,Se)...Hal—Hal (Hal = Cl, Br, I) are approximated by the same curve. The ratio of the terms of the polynomial series describing the cross section of the potential energy surface of the molecule along the coordinate of the bond being stretched proved to be the same for hydrogen, covalent, and multiple bonds.[17] No qualitative differences in the profiles of force densities[18] ensuring the formation of these bonds have been found.

When considering the latest results obtained by vibrational spectroscopy and quantum chemistry, it is pertinent to mention the views of M. A. Il'insky that had been formulated 40 years before these methods appeared. While studying tautomerism in nitrosonaphthols,[19,20] he concluded that bond multiplicity is not necessarily an integer but can also be fractional and smaller than unity. In M. A. Il'insky's opinion, hypervalent bonds arise at the expense of weakening of the initial covalent bonds. He believed that, with a particular mutual arrangement of the atoms, a hypervalent bond can be formed not only by an H atom, as in nitrosonaphthols, but also by any other atom. Unfortunately, even after these statements of the theory of valence, which were novel for that time, had been published,[21] they remained unnoticed.[22]

By the term "hypervalent bond," M. A. Il'insky meant a bond formed by an atom beyond its valence. Naturally, this notion did not include the modern views on valence atomic orbitals (AO) and the possibility of their hybridization with virtual AO under the influence of surrounding atoms, which now forms the basis of coordination chemistry.[23]

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Investigation object

To verify the idea of similarity of the properties of various hypervalent bonds, it is better to consider at the first stage the valence fragmentation for a polyvalent rather than a monovalent atom (H, Li). Boron-and-oxygen compounds appear to be the most convenient objects whose properties can be compared with those of the O—H...O hydrogen bridge. The ability of the B atom to form four virtually identical B—O bonds has long been known in crystallography.[24–27] When these bonds are equivalent, the bond length in a planar symmetrical BO_3 fragment is 1.37 Å and that in a tetrahedron is 1.48 Å. Comparison of the IR spectra of diversified minerals showed that the vibration frequencies of this BO_3 fragment (1300—1200, 950—850, and 760—700 cm^{-1}) are much higher than those of the BO_4 tetrahedron (1100—850, 800—700, and ~500 cm^{-1}).[28,29] This effect is so sharp that it even has been used as an analytical indication of the coordination number of a B atom in crystals with unknown structures.

Comparison of the structures of 75 natural and synthetic boron oxides[30] showed that, when the fourth O atom is located on the threefold axis of the planar BO_3 system, the B atom deviates from the plane toward this atom. Within the framework of a standard deviation equal to 0.005 Å, the O—O distances in the triangle virtually do not change, the B—O valence bonds become longer, and the length of the fourth, hypervalent, B...O bond for small heights *h* of the symmetrical BO_3 pyramid can be found from the equation

$$R(B...O) = 2.90\ Å - 10h(BO_3). \qquad (1)$$

Analysis of the structure of calcium hydroborate $Ca[B_3O_4(OH)_3]$, which was solved later and more rigorously (by the direct method in the anisotropic approximation with localization of the H atoms and a discrepancy factor of 96.5%), confirmed[31] that this relation holds if $0 < h(BO_3) < 0.1$ Å.

Thus, the relationship between the B...O and B—O bond lengths has been partly known, unlike the energy characteristics of these bonds. This is due to the fact that calculation of the vibrations of a three-dimensional periodic lattice, whose unit cell contains more than twenty atoms, still faces substantial calculation difficulties. Therefore, it is yet impossible not only to determine bond elasticities for most real crystals but even to interpret all of the bands observed in their spectra.

It followed from published data[28,29] that only in the case where a boron atom is symmetrically surrounded by oxygens, does increase in the boron coordination num-

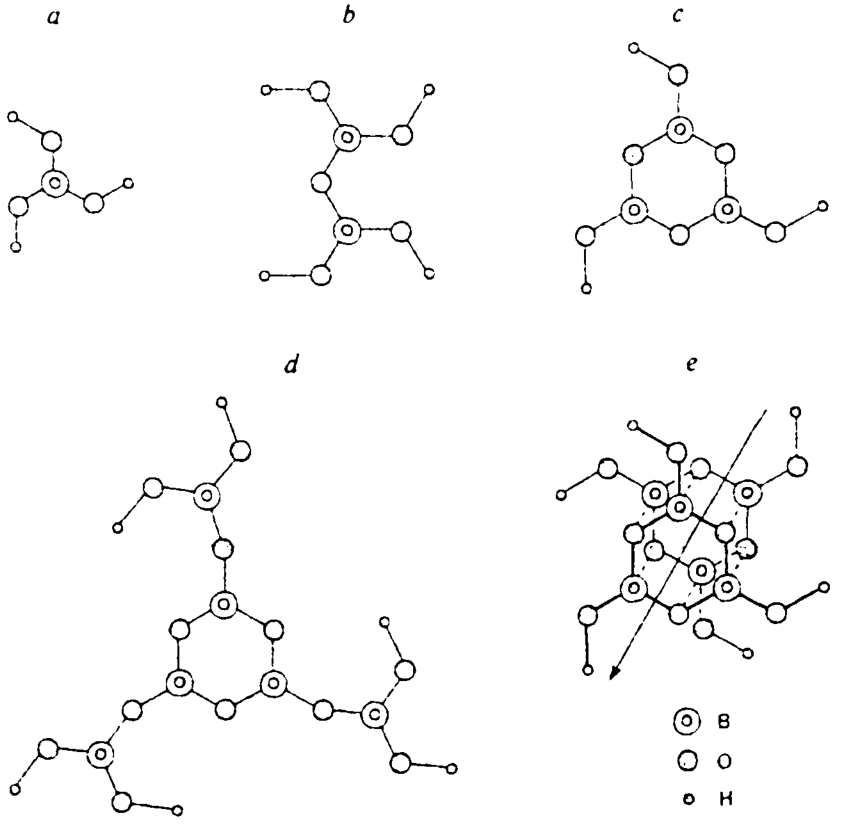

Fig. 1. Structures of the molecular systems studied: planar peroxides $B(OH)_3$ (*a*), $(HO)_2BOB(OH)_2$ (*b*), $B_3O_3(OH)_3$ (*c*), and $B_6O_6(OH)_6$ (*d*) and the three-dimensional complex $B_6O_6(OH)_6$ (*e*).

ber from three to four decreases the force constant of the B—O bond approximately twofold. The first estimates of the force constants of the B—O bonds in asymmetrical boron oxide fragments showed[32,33] that the formation of a hypervalent B...O bond is accompanied by weakening of the initial covalent B—O bonds (decreases their force constants).

In this work, we carried out a more detailed comparison of the dynamic parameters of the valence and hypervalent B—O bonds. To this end, we carried out semiempirical MINDO/3 calculations for four planar hydroxides ($B(OH)_3$, $(HO)_2BOB(OH)_2$, $B_3O_3(OH)_3$, and $B_6O_6(OH)_6$), in which the BO_3 moieties are linked to one another in different ways but the B atoms are tricoordinated in all cases (Fig. 1, *a—d*). In addition, we studied the three-dimensional $B_6O_6(OH)_6$ complex, in which all B atoms are coordinated by four O atoms (see Fig. 1, *e*). Despite the presence of natural related coordinates in all of these structures, the use of the method and algorithm reported previously[34—37] allowed us to determine the force constants and electrooptical parameters for each natural coordinate.

Results and Discussion

The results of our calculations demonstrate that in all the cases considered, irrespective of the molecular structure, the lengths of the B—O bonds in the ring, in the bridge, and near the OH groups do not change significantly as long as the B atom remains in the three-coordinate state. The average B—O bond lengths differ by less than 0.01 Å (Table 1). The charges on the atoms in these molecules remain equally invariable (the relative scatter is less than 1%).

Before comparing the force constants of the same bonds in different molecules, it is necessary to stress that the incorrectness of this comparison is mainly due to the fact that all these molecules cannot, in principle, be described by identical sets of natural coordinates rather than to the error of determination of their potential energy surfaces. Therefore, the resulting force constants should be considered only as rough estimates even after the systematic errors of their calculation have been taken into account. With allowance for these circumstances, the diagonal force constants of the bonds and their dipole moments for the four planar molecules should be regarded as invariable (Table 2) (the off-diagonal constants are not given because their correlation with the strength of hypervalent bonds of interest is yet unknown).

In the calculations of the three-dimensional species $B_6O_6(OH)_6$, the structure of the $[B_3O_3(OH)_3]_2$ dimer with C_3 symmetry was optimized. This configuration proved to be stable and energetically more favorable than both the two $B_3O_3(OH)_3$ molecules (by 4.07 eV) and its planar isomer $B_6O_6(OH)_6$ (by 3.30 eV). The geometry of each $B_3O_3(OH)_3$ unit in this "dimer" has substantially changed: the boroxide ring is no longer planar (the B—O—B angle is 122.5° and the OBO angle is 111.5°) and one molecule is rotated relative to the other molecule through 60° around the common C_3 axis. The planes through the B atoms of each molecule are spaced by a distance of 1.292 Å. The planes of the O atoms of the OH groups and the boroxide rings are shifted outwards in relation to the boron planes by 0.040 and 0.323 Å, respectively (Fig. 2). Consequently, the initially planar BO_3 unit is converted into an ~0.21 Å-high pyramid.

The distance from the dimer axis to the B atoms is 0.050 Å greater than the distance to the O atoms of the same boroxide ring. Therefore, the hypervalent B...O bond, whose length is 1.616 Å, is not parallel to the molecule axis but is arranged at an angle of 2°. The B—O and O—H bond lengths in the BOH fragments of the three-dimensional species are equal to those found for the planar molecules. The B—O bond lengths of the boroxide ring and the charges on its atoms are somewhat greater.

Table 1. Total energies (*E*/eV), bond lengths (*R*/Å), and charges on atoms (*Q*/au) of the boroxide molecular species

Species	$-E$	R_{OH}	R_{BO}					Q		
			terminal	bridging	ring	B...O	average	H	B	O
$B(OH)_3$	1051.202	0.947	1.370				1.370	0.27	1.00	−0.60
$(HO)_2BOB(OH)_2$	1761.384	0.941, 0.953	1.352, 1.381	1.361			1.365	0.27	0.99	−0.57—−0.64
$B_3O_3(OH)_3$	2130.337	0.930	1.324		1.355, 1.396		1.358	0.27	0.98	−0.59—−0.66
$B_6O_6(OH)_6$ (planar structure)	4261.442	0.930, 0.928	1.330, 1.364	1.340, 1.350	1.357, 1.370		1.352	0.27	0.96—1.00	−0.59—−0.6
$B_6O_6(OH)_6$ (three-dimensional structure)	4264.742	0.935	1.356		1.422, 1.443	1.626	1.462	0.28	1.14	−0.65—−0.76

Table 2. Force constants ($K \cdot 10^{-6}$/cm^{-2}) and dipole moments (μ/D) for the bonds in boroxide molecular species

Bond	Type of bond	$B(OH)_3$		$(HO)_2BOB(OH)_2$		$B_3O_3(OH)_3$		$B_6O_6(OH)_6$			
		K	μ	K	μ	K	μ	planar structure		three-dimensional structure	
								K	μ	K	μ
OH		15.49	1.20	14.86 and 15.77	1.17 and 1.20	15.15	1.20	15.03	1.20 and 1.18	15.15	1.28
BO	Terminal	8.68	2.2	7.88, 9.32	2.0, 2.5	10.41	2.1	9.12	2.15, 2.14	9.07	2.41
	Bridging	—	—	8.49	2.0			8.9, 10.4	1.9, 2.0	—	—
	Ring	—	—	—	—	6.91, 8.83	2.20, 2.14	7.4, 9.1	2.14, 2.12	5.47	1.56, 1.57
	Hypervalent	—	—	—	—					0.92	2.52
	Average	8.68	2.2	8.50	2.17	8.72	2.15	9.01	2.07	—	2.01

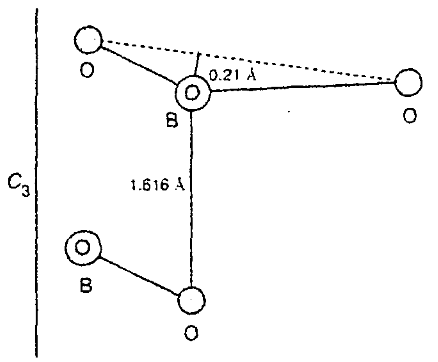

Fig. 2. Mutual arrangement of the B and O atoms in the three-dimensional molecular system $B_6O_6(OH)_6$. The cross section is drawn through the C_3 symmetry axis and the terminal O atom; the pairs of O and B atoms are located symmetrically on both sides of the cross-sectional plane at a distance of ~1.19 Å.

The lengths found for the hypervalent B...O bonds and the heights of the BO_3 pyramid could be related by an equation of type (1) if the factor at $h(BO_3)$ in this equation is diminished from 10 to 6.1. It has been noted above that a factor of 10 was proposed[30] for $h(BO_3) < 0.1$ Å. Meanwhile, earlier publications[28,29] indicate that for $h(BO_3) = 0.49$ Å, this factor should diminish to 3. Therefore, a value of ~6 for the factor at $h(BO_3)$ with $h(BO_3) = 0.21$ Å appears quite reasonable. This agreement of the results of our calculation with the data obtained by other researchers lends credibility to the K(BO) and K(B...O) force constants found, which characterize the elasticities of the valence (BO) and hypervalent (B...O) bonds, respectively. The elasticity constants calculated for the terminal B—OH groups, the boroxide rings, and bonds between the rings in the $[B_3O_3(OH)_3]_2$ dimer are $9.07 \cdot 10^6$, $5.47 \cdot 10^6$, and $0.92 \cdot 10^6$ cm^{-2}, respectively. This implies that dimerization, which gives six new hypervalent bonds, is accompanied by a decrease in the elasticity of eighteen B—O valence bonds. The overall decrease in the force constants ($\Sigma\Delta K$(BO)) is $36.9 \cdot 10^6$ cm^{-2}, which is almost 7 times as great as the overall rigidity developed (ΣK(B...O)). With allowance for the accuracy of the calculations performed (see above), it should be admitted that the $\Sigma\Delta K(BO)/\Sigma K(B...O) = 6.7$ ratio is in good agreement with the value known for a hydrogen bridge ($\Delta K(OH)/K(H...O) = 8.63$).[33,38]

It follows from the presented data that the formation of a directional intermolecular bond does not change the general pattern of the dynamic properties of the O—H...O and O—B...O bridges. In fact, in both cases, the formation of this bond weakens the adjacent O—B and O—H covalent bonds, the decrease in the force constant of the covalent bond substantially exceeds the force constant of the intermolecular bond formed, and the corresponding ratios are very close: $\Delta K(OH)/K(H...O) \approx 8.6$, $\Sigma\Delta K(O_3B)/\Sigma K(B...O) \approx 7$. In addition, the ratios of the enthalpies of formation of complexes to the force constants of the intermolecular bonds thus formed also differ insignificantly with allowance for the error of calculations. Whereas this ratio for complexes with OH...O bridges is, on the average, 20±2 kcal cm^2/(10^6 bond mol),[38] in the case of the OB...O bridge (for the bond enthalpy estimated from the difference of the total energies and for the calculation error estimated based on the published data[39]), this value is $94/(6 \cdot 0.92) \approx 17 \pm 3$ kcal cm^2/(10^6 bond mol).

The data obtained demonstrate that the dynamic properties of hypervalent bonds formed by B and H atoms are very similar. To find out whether analogous hypervalent bonds can actually be formed by any other atoms,[21] a broader range of systems should be studied.

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