

which are 0.022 and 0.018 Å respectively, is of the same sign as the difference in Nb displacements, and is in agreement with the proposed linear relation between relaxation extension and Nb displacement.

Further work is in progress using these ideas. Points of particular interest are the application of the theory to thermal expansion, about which qualitatively correct predictions can be made, and the possibility, by considering forces acting on the octahedron from the other cations, of explaining differences of length within the group of relaxed edges without altering predictions about their mean length. Applications to other structures than those quoted here must also be considered,

though there are not many that are known in very full detail. The effect is not confined to octahedra; off-centring of the same kind can be observed also in tetrahedra. These developments will be taken up in a later paper.

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The B–O Bond Lengths in Boron-Oxygen Compounds

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A simple molecular-orbital treatment of the π -electrons in a large variety of planar boron-oxygen compounds shows that variations in bond length are reasonably well explained in terms of a π -bond order. The ω -technique method is of no advantage here as compared with the simple Hückel method.

In most boron-oxygen compounds, the boron atom is bonded to three or four oxygen atoms. In the latter case, the four B–O bonds are arranged tetrahedrally around the boron atom. When only three bonds are formed, the boron atom is surrounded symmetrically by three oxygen atoms, all four atoms lying approximately in the same plane. The bond length of the trigonal B–O bond varies over the range 1.28 to 1.43 Å.

Since the boron-oxygen framework is planar, it is reasonable to assume that, as a first approximation, the wave function can be divided into σ - and π -molecular orbitals. Then, in analogy to carbon π -electron systems, any differences in bond length might be attributed to differences in π -bond order. Therefore, it should be possible to apply a standard Hückel type analysis to molecules containing trigonally bonded boron atoms.

Applications of π -bond theory to B–O bonds are rare. Coulson (1964) has used simple π -bond theory to explain the differences in bond length between the interior and exterior B–O bonds in metaboric acid. Mateson (1960) has used it to correlate reaction rates of reactions involving substituted ethyleneboronic acids. Armstrong & Perkins (1967) have used the more sophisticated Pariser-Parr-Pople (PPP) method to investigate some substituted phenylboronic acids. All

these calculations predict a migration of charge from the oxygen to the boron atom leading to a π -bond order in the range 0.3 to 0.5. This agrees with the general shortening of the BO bond observed in going from a tetrahedral to a trigonal state.

Zachariasen (1963) has used Pauling's valence neutralization concept to correlate the variations in B–O and H–O bond lengths in crystalline borate molecules. Basically, the theory tries to take into account the effect of nearby atoms on the lengths of bonds formed with a given atom. A parameter, the bond strength, v_{ij} , is defined for each bond in such a way that $\sum_j v_{ij} =$

valence of the i th atom. The bond length of a given type of bond is then correlated to its bond strength through an empirically determined bond-length-bond-strength curve. Using this method, Zachariasen is able to derive a bond-length-bond-strength curve which can predict bond lengths to within 0.04 Å.

The purpose of this paper is to report the application of simple π -electron theory to some boron-oxygen compounds in an attempt to correlate the observed differences in bond length with molecular structure. The π -bond orders of a number of boron-oxygen compounds were calculated by a standard Hückel-type analysis. Both the simple Hückel theory and ω -techniques were employed. The calculations were carried out on a KDF 9 computer at the University of Oxford, using a Self-Consistent Hückel Molecular Orbital pro-

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gram developed by M.D. Poole (see Coulson & Streitweiser, 1965).

In standard π -bond theory the coulomb integral of the r th atom, α_r , is given by the equation

$$\alpha_r = \alpha_0 + h_r \beta_0 + \omega(n_r - q_r) \beta_0,$$

where

- α_0 = coulomb term for a carbon atom in benzene
 h_r = parameter correcting for heteroatom
 n_r = no. of electrons donated to the π -electron system by the r th atom
 q_r = π -electron charge on the r th atom
 $\omega = 0$ for simple Hückel theory
 $\omega = 1.4$ for ω -technique
 β_0 = bond integral of C-C bond in benzene.

In any extension of π -bond theory to molecules containing heteroatoms, there is always some difficulty in choosing values for the heteroatom parameter, h_r . In this work the following values were chosen:

- 0.5 for the boron atom,
 +1.5 for a neutral oxygen atom,
 +0.5 and 1.0 for a negatively charged oxygen atom.

These values were chosen on the basis of Streitweiser's (1962) recommendations, calculations done on B-N compounds (*cf.* Kaufmann & Haman, 1964), and chemical intuition. They are somewhat arbitrary. However, calculations using other reasonable values were carried out and they gave results similar to those reported here. Variation of the parameter does not seem to affect the trends observed. This is in agreement with the conclusion reached by Kaufmann & Haman (1964).

A value of 0.9 β_0 was used for the bond integral of the B-OB and B-OH bonds and 1.0 β_0 for the B-O bonds. These values are also arbitrary, but if the bond integral is assumed to be roughly proportional to the overlap integral, (*cf.* Streitweiser), a value of 0.84 β_0

is obtained for the β of the B-O⁻ bond. This is not too far from the value used. Calculations done with different values for β_{BO} gave results comparable to those here.

Values for the borate chain were obtained from calculations of the bond order of bonds in the middle of the linear molecule $O(BO_2)_5^{7-}$. One test calculation on the molecule $O(BO_2)_8^{10-}$ gave identical results. Calculations on BO and BO_2 assumed two sets of orbitals at right angles. There was no significant difference between the results obtained when the two orbitals were treated separately or together in the ω -technique. The boron atom was assumed to be in an sp hybridized state; hence it contributed one electron to the π -system. This is consistent with the ground state of these molecules.

The bond orders obtained are given in Table 1. A plot of bond order (simple Hückel theory) *versus* bond length is given in Fig. 1 (taking $h_0 = 1.0$ for the O⁻ atom). The ω -technique gives a very similar curve. Both methods predict a general shortening of the B-O bond below the value (> 1.43 Å) observed in molecules where there is no π -bonding. Changing from a tetrahedral to a trigonal state could account for a small decrease but certainly not the one that is observed. The bond orders for the B-OH bonds lie in the range 0.45 to 0.50 close to the values of 0.39 calculated by Mateson (1960) using simple Hückel theory and 0.50 calculated by Armstrong & Perkins using the PPP method. This supports our choice of parameters.

Both methods semi-quantitatively predict the observed variations. However, there is no very close correlation between the bond order and bond length. A particularly bad deviation occurs with the metaborate ion $B_3O_3^{3-}$, marked with a cross in Fig. 1. Calculations done by either method and with a variety of parameters indicate that it should be very similar to the linear

Table 1. Calculated π -bond orders

	Formula	Bond	Bond length	Reference	Bond order			
					Simple theory $h_0 = 0.5$ 1.0		ω -Technique 0.5 1.0	
Cyclic metaborate ion	$B_3O_6^{3-}$	BO-B	1.433 Å	1	0.395	0.422	0.372	0.386
Linear metaborate ion	$(BO_2)_n^{n-}$	BO-B	1.394	2	0.392	0.417	0.370	0.383
Trimethylboroxine	$(CH_3)_3B_3O_3$	BO-B	1.39	3	0.534		0.470	
Pentaborate tetrahydrate	$B_5O_6(OH)_4^-$	BO-B	1.373	4	0.447		0.406	
	$H_2B_2O_3$	BO-B	1.38	5	0.515		0.457	
Metaboric acid	$B_3O_3(OH)_3$	BO-B	1.373	6	0.465		0.417	
	$H_2B_2O_3$	OO-B	1.365	5	0.620		0.543	
Orthoboric acid	$B(OH)_3$	HO-B	1.363	3	0.500		0.454	
Pentaborate tetrahydrate	$B_5O_6(OH)_4^-$	HO-B	1.355	4	0.512		0.464	
Metaboric acid	$B_3O_3(OH)_3$	HO-B	1.355	6	0.521		0.473	
Pentaborate tetrahydrate	$B_5O_6(OH)_4^-$	BO-B	1.349	4	0.512		0.464	
Orthoborate ion	BO_3^{3-}	B-O ⁻	1.35	3	0.555	0.530	0.503	0.479
Linear metaborate ion	$(BO_2)_n^{n-}$	B-O ⁻	1.328	2	0.715	0.625	0.601	0.543
Cyclic metaborate ion	$B_3O_6^{3-}$	B-O ⁻	1.280	1	0.712	0.622	0.599	0.542
Boron dioxide	BO_2	B-O	1.265	7		1.155		1.188
Boron oxide	BO	B-O	1.205	3		1.414		1.596

- References: (1) Marezio, Plettinger & Zachariasen (1963b)
 (2) Marezio, Plettinger & Zachariasen (1963a)
 (3) *Tables of Interatomic Distances* (1958)
 (4) Zachariasen & Plettinger (1963)

- (5) Brooks, Costain & Porter (1965)
 (6) Peters & Milberg (1964)
 (7) Johns (1961)

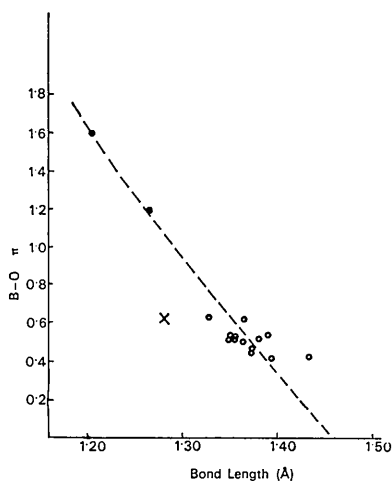


Fig. 1. B-O π -bond order *versus* bond length. The cross indicates the result for the metaborate ion.

chain. But the experimental values differ considerably. The deviations probably arise from the fact that the bond lengths used are not those in the isolated molecule. Most of the experimental data are obtained from X-ray studies of crystals. In the crystal the molecules are distorted to some extent by adjacent molecules and ions making our assumptions concerning planarity and symmetry only approximate. Symmetrically equivalent bonds in a single anion have different bond lengths and the same bond in a given anion has a different length when the anion is combined with a different cation. It should be possible to take crystal field effects into account by making the parameter h_r dependent upon the environment of the atom. Unfortunately this would probably make the simple π -bond theory too complicated to be of much use.

The curve in Fig. 1 is drawn to include points for the small molecules BO and BO₂, where the π -bonding is large. If it were permitted to disregard these points, a more slowly varying curve could be drawn through

the remaining points, and then B₃O₃³⁻ would be less anomalous.

Our conclusion is that the variations in the lengths of bonds involving oxygen and trigonal boron can be semi-quantitatively predicted by simple Hückel theory. In view of the rather large deviations in the bond-order-bond-length curve it is unnecessary to use the more complicated ω -technique. Our conclusion that a π -electron model can account for these B-O bond lengths does not rule out the possibility that other influences, such as the role of the cation in the valence balance, may also play a part. However, until the effect of the crystal field can be predicted easily this is about as far as these calculations can be taken.

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