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The B–O bond lengths in orthorhombic metaboric acid.

By C. A. Coulson, *Mathematical Institute, Oxford University, England*

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In a recent paper Peters & Milberg (1964) have shown that the orthorhombic modification of metaboric acid is a trimer of formula $B_3O_3(OH)_3$, and that the B–O bond lengths in the central ring (Fig. 1) appear to be rather greater than those which project radially from the ring. They suggest that this difference may be genuine, and due to a difference in bond order. It is possible to show that their conjecture is correct, and that a difference of the observed order of magnitude (1·373 − 1·355 = 0·018 Å) is of the size to be expected on theoretical grounds.

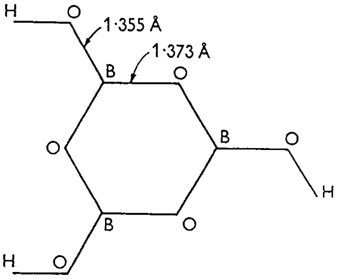

Fig. 1.

Since the molecule is planar we may suppose, in a first approximation, that the electrons are located in σ- and π-molecular orbitals. Since the σ-orbitals will form localized bonds, any differences in bond order will be due to the π-electrons. These π-bond orders may be calculated by standard Hückel-type analysis (see *e.g.* Coulson, 1961). We begin by supposing that all the B–O resonance integrals β are equal, and that there is a difference α between the Coulomb terms α_B and α_O of the boron and oxygen atoms. We thus treat all oxygen atoms as equivalent, and write $\alpha = \alpha_B - \alpha_O$. Numerically $\alpha > 0$, and is conveniently expressed as

$$\alpha = -k\beta, \quad (k > 0)$$

where k may be expected to be in the neighbourhood of 1 or 2. Later we shall relax some of these restrictions.

The calculation of the molecular orbitals is straightforward, and the π-bond orders are obtained after allotting the total of twelve π-electrons to the six lowest energy orbitals. Table 1 shows the results obtained for $k = 0, 1, 2$. It is clear from this that the external bonds do indeed have greater bond order than the ring (*i.e.* internal) bonds.

Table 1. *π-Bond orders for internal and external B–O bonds*

$k =$	0	1	2
p_{internal}	0·534	0·514	0·466
p_{external}	0·620	0·590	0·520

Unfortunately we do not know the shape of the order–length curve for B–O bonds. But if we assume that it is similar to that for C–C bonds, the differences in B–O length in the three cases calculated would be $\Delta l = 0{\cdot}016, 0{\cdot}014$ and 0·010 Å respectively. These are of the right order of magnitude.

There are two refinements, both of which would lead to an increase in the bond length difference Δl. First, instead of putting all β_{BO} equal, we should increase $|\beta|$ for short bonds and decrease it for long ones. This effect, which is well known for C–C bonds, always has the result of shortening short bonds and lengthening long ones. It would therefore increase Δl, perhaps by as much as 0·005 Å.

The second refinement allows for variations in α_O due to the fact that the hydroxyl oxygen atoms carry a different formal charge from the ring oxygen atoms. A rough calculation shows that there is a larger number of electrons on the hydroxyl oxygen atoms than on the ring ones. (The net charges are in the ratio of about 3:2.) Thus $|\alpha_O|$ would be smaller for the external oxygen atoms. This means that their effective electronegativity would be closer to that of the boron atoms, and hence the π-bonding would be more effective for the external B–O bonds than for the internal ones. This is because, for fixed β, the bond order of a diatomic molecule is greatest if the Coulomb terms of the two bonded atoms are equal; and it decreases as their difference increases. Thus this charge effect (as it may be called) will also increase Δl. However, this is only a second-order effect, and may perhaps increase the bond length difference by the order of 0·005 Å.

Our conclusion is that the difference in bond orders between the internal and external B–O bonds is quite real, and that it leads to a bond length difference of the order of 0·010 to 0·020 Å. In this way we provide some confirmation of the experimental difference 0·018 Å. In view of the rather large experimental uncertainty in Δl, this is about as far as it is worth pushing these calculations.

References

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