Short Communication

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Acta Cryst. (1969). B**25**, 807

A note on cyclic $H_2B_2O_3$.

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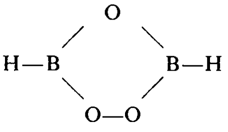
(*Received* 2 *January* 1969)

A molecular-orbital treatment shows that the experimental bond lengths are well explained by the π-bond orders.

Recent microwave studies of $H_2B_2O_3$ by Brooks, Costain & Porter (1967) have shown the molecule to be planar, with the C_{2v} structure (I). This molecule is interesting because it is one of the very few gaseous molecules containing only H, B and O atoms. Moreover, being neutral, its B–O and O–O bond lengths are not subject to the influence of adjacent ± charges, as is so often the case with crystals. It thus provides a good example on which to test the theory of π-electron bonding in these trigonally coordinated boron compounds, developed by Coulson (1964) and by Coulson & Dingle (1968).



(I)

The O_{apex} angle is normal, at 104°0′; and so is the B–O–O angle at the base, which is 104°57′. But there are two features of this molecule that are not so much expected, and which may be studied theoretically. The first is the difference in the B–O bond lengths (B–O_{apex} is $1{\cdot}380 \pm 0{\cdot}003$ Å, B–O_{base} is $1{\cdot}365 \pm 0{\cdot}004$ Å). The second is the O–O bond length ($1{\cdot}470 \pm 0{\cdot}002$ Å). Since this is only a little shorter than a normal peroxide bond length (1·48Å in H_2O_2) it looks at first as if the π-electron delocalization postulated by Coulson & Dingle is not very evident. The purpose of the present note is to show that in fact both of these features fit well with theoretical calculations.

First let us consider the B–O bonds. Using precisely the same values of the fundamental parameters chosen by Coulson & Dingle (1968) and the ω-technique of Streitwieser (1962) the π-bond orders are found to be 0·457 for B–O_{apex} and 0·543 for B–O_{base}. This corresponds to a bond length difference of 0·017 Å, in complete agreement in magnitude and direction with the experimental difference $0{\cdot}015 \pm 0{\cdot}005$ Å. If we had not bothered with the ω-method, and had used instead the simple Hückel method, the π-bond orders would have been 0·515 and 0·620, leading to a calculated bond length difference of 0·021 Å. This is just a little too big, indicating a small improvement with the partial self-consistence of the ω-technique approximation.

The situation is more striking with the O–O bond. With the same parameters as before, and using the ω-technique, the π-bond order of the O–O bond turns out to be as small as 0·079. We should therefore expect very little shortening with respect to a normal peroxide bond. (Even this would be offset by an increase of the same order of magnitude, 0·01 Å, as a result of electrostatic repulsion between the net charges on the O atoms.) It is rather remarkable that in the five-membered ring the other bond orders all lie between 0·45 and 0·55, while this one is so much smaller. It may be added that if we had adopted the simpler Hückel approximation, this order would still have been quite small (0·136), but sufficiently large to have indicated a measurable shortening of the O–O bond.

A final check on the model may be obtained from the dipole moment, measured by Brooks *et al.* (1968) to be $\mu = 0{\cdot}95 \pm 0{\cdot}01$ D. The calculated net π-charges are $+0{\cdot}254$ $(O)_{apex}$, $+0{\cdot}182$ (O_{base}), $-0{\cdot}309$ (B), leading to a π-moment 1·28 D. This would be slightly increased by the B–O σ-bond moments, which do not quite cancel, leading us (as usual with this model) to a calculated μ which is 1·5–2 times the experimental μ. The negative end of the dipole is indicated to be at the apex of the ring (I) and the positive end at the base.

In conclusion it should be added that several alternative sets of values for the fundamental parameters have also been tried; and always with substantially the same results. Only the ones corresponding to the preferred values have therefore been reported.

Grateful acknowledgement is made to Dr T. W. Dingle of the University of Victoria, British Columbia, for his kindness in making available the numerical results of his earlier calculations on this molecule.

References

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