π-Bonding in the Boron–Oxygen Bond

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VARIABLE temperature n.m.r. studies of dimethylboric anhydride showed that the single boron-methyl resonance at τ 9·57 exhibited by this compound broadened as the temperature was lowered and split into two separate resonances below −68°. The activation energy for this phenomenon, calculated according to Gutowsky and Holm,[1] is 8·6 ± 0·5 kcal. The spectrum of the carbon analogue, di-isopropyl ether, remained unaffected as low as −100°.

To account for this unexpected splitting, we suggest that the dimethylboron groups are so aligned as to maximize their individual overlaps with the two sp^3-hybridized lone pairs of oxygen. In this conformation (see Figure) there are two distinct environments which might be termed "inner" (Me-2 and Me-3) and "outer" (Me-1 and Me-4).

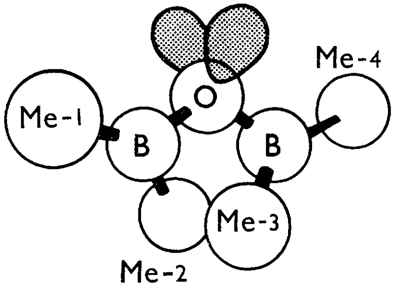

FIGURE. *Conformation of dimethylboric anhydride permitting maximum overlap of oxygen lone pairs (shaded) with vacant boron orbitals.*

There has been speculation concerning B–O π-bonding,[2] and in the light of n.m.r. studies of B–N systems,[3] the n.m.r. spectrum of dimethylmethoxyboron was examined in the temperature range 30 to −90°. Above −40°, the compound exhibited resonances at τ 6·35 and 9·66, in a ratio of 1 : 2, which were assigned to oxygen–methyl and boron–methyl respectively. As the temperature was lowered, the boron–methyl resonance broadened and at −44° separated into two distinct signals. The activation energy for this process was 8·5 ± 0·3 kcal. We have interpreted this as the barrier to rotation about the B—O bond due to overlap of an sp^3-hybridized lone pair of oxygen with the vacant p-orbital of boron. This is consistent with the interpretation of the results for dimethylboric anhydride.

Addition of one equivalent of trimethylamine to dimethylmethoxyboron causes the low-temperature boron–methyl resonances to coalesce. The boron atom, when co-ordinated by amine, has no vacant orbital for π-bonding to oxygen. Samples containing 0·5 and 2·0 equivalents of trimethylamine failed to exhibit separate resonances for free and adducted molecules, indicating rapid exchange as low as −100°. Furthermore, tensiometric measurements indicated complete dissociation of the adduct in the gas phase. However, using the chemical shifts of unadducted and adducted boron methyl groups, the latter obtained by a small extrapolation as the limiting shift at low temperatures, the enthalpy of dissociation of $Me_2BOMe \cdot NMe_3$ was found to be 7·8 ± 0·2 kcal.

An investigation of the base strength of oxygen in these compounds, using the infinite dilution chemical shift of chloroform,[4,5] is consistent with the above interpretation. The shift for Me_2BOBMe_2 is 7·9 c./sec., indicating a marked lowering of the availability of the oxygen lone-pairs relative to the carbon analogue, di-isopropyl ether, for which the shift is 46·3 c./sec.[5] The view that both lone pairs in dimethylboric anhydride are involved in π-bonding to the two boron atoms is upheld by the intermediate value of the shift (22·0 c./sec. in Me_2BOMe.

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