The Self-association of Dibenzyl Phenylboronate

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A NUCLEAR magnetic resonance study of dibenzyl phenylboronate [(I) $PhB(OR)_2$, $R = PhCH_2$] has revealed the first instance of intermolecular self-association in acyclic boron compounds. The observation of two distinct benzylic methylene proton signals in bis(benzylamino)phenylboron [(II) $PhB(NHR)_2$, $R = PhCH_2$] was expected on the basis of restricted rotation about the B–N bond. This stereochemical feature of tervalent boron–nitrogen compounds, arising from the double-bond character involving p_π–p_π overlap between the two atoms, has been well established both from n.m.r.[1] and i.r. studies.[2] In this latter work[2] it was concluded that, while there is substantial B–N double-bond character in (II), the corresponding boronates (I) do not exhibit B–O double-bond character to the same extent.

In view of this latter conclusion, the observation of two separate benzylic methylene resonance signals in (I; $R = PhCH_2$), similar to those found in

(II; R=PhCH$_2$) (Table), was most unexpected. The steric size of the benzyl group cannot account for the two resonance signals, since in the cases of (I and II; R=Bu^t) infrared evidence suggested the presence of a single isomer; this was confirmed by the observation of a single t-butyl resonance signal. The methylene resonance signal of (I; R=PhCH$_2$) has been investigated in a variety of solvents, and the spectrum obtained was found to be both solvent and concentration dependent. In carbon tetrachloride solution, the low-field signal gradually decreased in intensity as the concentration of the solvent was increased, finally resulting in a singlet at concentrations of ester below 20% w/v. Similar solvent behaviour was observed in benzene, carbon disulphide, and deuterochloroform. With acetone and pyridine, complete collapse of the methylene resonance doublet to a singlet occurred as soon as the first drops of solvent were added to the neat boronate ester. The methylene resonance of the neat ester was also shown to be temperature dependent. Collapse of the signal, to a broad singlet, occurred at 180°, but the increased viscosity of the ester at low temperature prevented any reliable deductions being made below 0°, at which temperature the methylene resonance signal was considerably broadened.

TABLE

^{1}H *Chemical shifts of dibenzyl derivatives of* (I) *and* (II) (*in* τ-*units*) *for the neat liquids*

	(I)	(II)
CH$_2$	4·84 5·04	5·84 6·03
Aryl ..	2·6—2·8	2·6—3·1

The concentration dependence of the methylene resonance is due to the intermolecular association of the boronate molecules. This has previously been shown to occur in cyclic boron compounds,[3] in which association results in relief of the ring strain present in the monomeric five-membered cyclic molecules. In the case of the boronate (I; R=PhCH$_2$) two different methylene resonance signals arise from the nonequivalence of the two CH$_2$ groups. The association probably gives rise to a stacking arrangement of the molecules, and the spatially different methylene groups give rise to separate signals due to the unequal shielding arising from the ring-current effects of the aromatic substituents. This behaviour is in contrast to that found in the dibenzyl phenylphosphinate [(III) PhP(OR)$_2$, R=PhCH$_2$] where, because of the pyramidal structure, the shielding by the phenyl group causes the two hydrogens of each methylene group to be nonequivalent and thus give an AB spectrum.[4]

Further evidence for the association, through boron–oxygen bridging, accompanied by change in hybridisation at the boron atom ($sp^2 \rightarrow sp^3$), is afforded by the variation of the boron-11 chemical shift* with varying concentration in carbon tetrachloride solution (Figure). From our studies of the boron-11 shifts in donor–acceptor systems,[5] it is clear that in the neat state, the boron atom of the ester is approaching the tetrahedral co-ordinate state, while at concentrations of 10% or less the ester is monomeric with the boron atom in the tercovalent planar environment. This conclusion is supported by the observation that the shift of the ester in 50% pyridine solution is 14·5 p.p.m. to high field of Me$_2$O,BF$_3$. In this latter solvent there is co-ordination of the base to the ester, thus breaking down the intermolecular association. The co-ordination of pyridine and acetone to the ester explains the immediate collapse of the methylene doublet on the addition of the solvent. There is qualitative agreement between the ^{1}H and ^{11}B resonance observations both of which indicate that at concentrations of about 10% or less the ester is unassociated. This

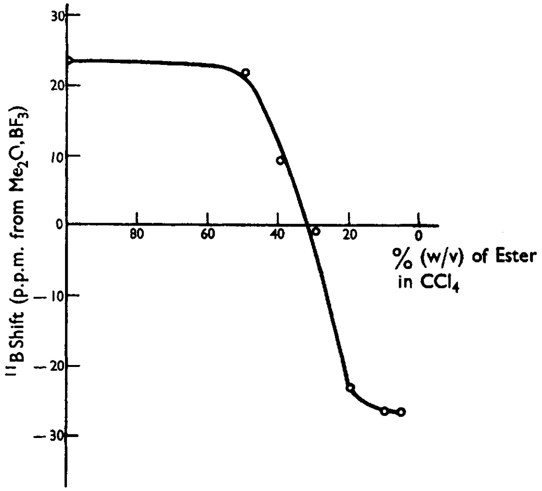

FIGURE. *Variation of the* ^{11}B *shift of dibenzyl phenylboronate in carbon tetrachloride solution.*

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* The ^{1}H and ^{11}B spectra were measured on Perkin-Elmer spectrometers at 60·0 and 12·83 Mc./sec. respectively. The ^{11}B measurements were made using the Northern Scientific 544 C.A.T. attachment.

explains why our original infrared investigation[2] failed to reveal this boron–oxygen bridging, for the spectra were recorded in dilute solution; in systems where there is stable B–O bridging, *e.g.*, in the alkyl difluoroborinates [$(ROBF_2)_3$], there is a substantial reduction in the frequency of the ν_{B-O} mode.[6]

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