Asymmetry Associated with a Borate Salt

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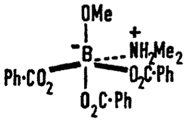
Summary A salt of the type $XB^{-}Y_3Z^{+}$ exhibits asymmetry that may be ascribed to stereospecific ion-pairing.

COMPOUNDS of the type $[Me_2ECHMePh]^{+}Br^{-}$ ($E = PhN$, PhP,S,Se) have very recently been shown to have magnetically nonequivalent methyl groups[1] and the possibility was raised that this was due, in part, to stereospecific ion-pair formation.

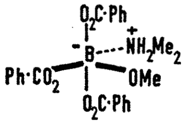
In the course of investigations on the mechanisms of various amide-forming reactions of boron derivatives,[2,3] a representative of a new series of boron derivative has been isolated and shown to exhibit isomerism probably due to stereospecific ion-pairing.

Reaction of the dimethylamine adduct of tribenzoyloxyborane, $(PhCO_2)_3B\text{-}NHMe_2$, with trimethoxyborane gave a high yield of the salt $(Me_2NH_2)^{+}[(PhCO_2)_3BOMe]^{-}$ (**1**). The assignment of structure is based on analysis, i.r. evidence, and comparison of properties with other boron derivatives.

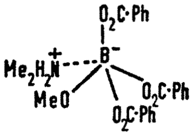
In the ^1H n.m.r. spectrum of an 8% (*w/v*) solution of (**1**) in $CDCl_3$ the resonances of the aromatic protons occur at τ 1·8 and 2·6 (15H), the $-NMe_2$ protons at τ 7·23 (6H), and the protons of the RNH_2^{+} group at τ0·0 (2H). However the resonances of methoxy protons appeared as two singlets (1 : 1 ratio; total integration 3H) at τ 6·44 and 6·50. Dilution to 3—4% caused the methoxy signals to coalesce to a singlet at τ 6·47, further dilution causing no alteration. On gentle warming (up to *ca.* 60°) the two methoxy signals of the 8% solution moved to become a singlet at τ 6·51. Rapid cooling did not cause the peak to split immediately, but there was slow reversion to the original positions at room temperature. Both cycles (dilution–concentration, warming–cooling) could be repeated and it would not seem that the changes were due to chemical reactions.



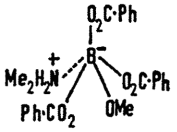
(**2**)



(**3**)



(**4**)



(**5**)

Stereoisomerism of the salts $XB^{-}Y_3Z^{+}$ becomes possible if stereospecific close ion-pairing can occur, the situation becoming similar to that around a five-co-ordinate metal.

As the original 1 : 1 mixture is regenerated on cooling the warm solution, it is obviously a mixture of the two thermodynamically most stable salts at room temperature, and ease of approach to the anion can give little clue to the structure of (**1**) in concentrated solution. Structural suggestions could involve the trigonal bipyramids (**2**) and (**3**) or the *cis*- and *trans*-square-pyramids (**4**) and (**5**) but there are very many other possibilities that could not be discounted without the isolation and structure determination of each isomer.

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[1] W. McFarlane and J. A. Nash, *Chem. Comm.*, 1969, 524.

[2] P. Nelson and A. Pelter, *J. Chem. Soc.*, 1965, 5142.

[3] T. E. Levitt and A. Pelter, *Nature*, 1966, **211**, 5046.