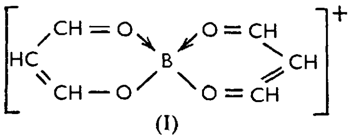
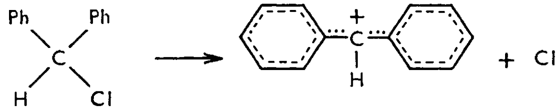
23. *The Existence of an Organic Cation containing Boron.*

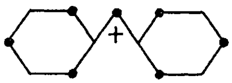
By J. M. Davidson and C. M. French.

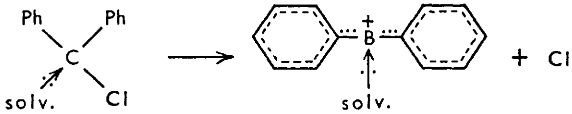
The ultraviolet absorption spectrum of a solution in ethyl methyl ketone of diphenylboron chloride containing 1 equiv. of aluminium trichloride has been compared with that of a solution in the same solvent of diphenylmethyl bromide and aluminium trichloride. The close agreement between the positions of the maxima of the two curves, and the agreement with the value predicted from molecular-orbital calculations for the diphenylboronium ion indicate the presence of this ion in the coloured ketone solution. Further evidence for this is adduced from conductivity measurements on solutions of diphenylboron chloride and aluminium trichloride separately and together in nitrobenzene, and from the ready reaction between the boron compound and silver perchlorate to precipitate silver chloride.

The only known cations which contain boron are the boronium salts obtained by Dilthey and Schumacher,[1] and these are chelate complexes of the type (I). In general the electronic structure of the boron atom precludes the existence of a positive centre of charge on it. The present work concerns the formation of boronium ions exactly analogous to the well-known carbonium ions. Cations of tervalent carbon invariably exist in a state which is stabilised by conjugation energy, or occasionally by release of steric hindrance. Thus aryl-substituted methyl chlorides ionise readily in polar solvents, to form a coloured cation. In solvents with readily available lone pairs of electrons, *e.g.*, ketones and nitrobenzene, compounds of the diarylboron chloride type will be solvated, and the boron atom will become isoelectronic with the central carbon atom of the arylmethyl chlorides [cf. (II) and (III)]. We have shown that in an ionising solvent diphenylboron chloride ionises to form the diphenylboronium ion.


(I)


(II)


(IV)


(III)

Diphenylboron chloride prepared by Abel, Dandegaonker, Gerrard, and Lappert's method [2] was dissolved in dry ethyl methyl ketone to form a colourless solution which had an equivalent conductance of $\Lambda = 3{\cdot}79 \times 10^{-2}$ ohm^{-1} cm.^{2} at a concentration of 0·0356M (all conductivity measurements were made at 15°). However, a solution in ethyl methyl ketone of equivalent amounts of the same halide and of aluminium trichloride, which was added to induce ionisation of the boron–chlorine linkage, was bright yellow and had $\Lambda = 36{\cdot}6$ ohm^{-1} cm.^{2} at 0·047M. Using a similar solution of concentration 0·022M, we recorded the ultraviolet absorption on " Unicam " spectrophotometer, and compared the spectrogram with that of a 0·006M solution of diphenylmethyl bromide similarly mixed with 1 equiv. of aluminium trichloride in ethyl methyl ketone (Fig. 1). In view of the concentrated solutions used, the actual intensity of absorption in 1 cm. cells represents too low a degree of ionisation to permit calculation of the extinction coefficients.

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[1] Dilthey and Schumacher, *Annalen*, 1906, **344**, 300, 326.

[2] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

The maxima at 337 mμ for the diphenylboronium ion, and 327 mμ for the diphenylmethyl cation, qualitatively agree well from the point of view of the identity of the former system. The colour of both these cations may be considered as due to the isoelectronic π-electron systems in the odd-alternant cations (IV).

The boron compound system comprises twelve carbon 2*p* orbitals and one boron 2*p* orbital, and the conjugated system will have six filled bonding molecular orbitals, six antibonding ones, and one non-bonding one, all of which will be unfilled. Let Υ be the wave function of one of the bonding molecular orbitals of energy E. The first absorption band will be due to the transition between this orbital and the non-bonding orbital which will have the same energy as a carbon 2*p* orbital, and may be taken as an arbitrary zero,[3]

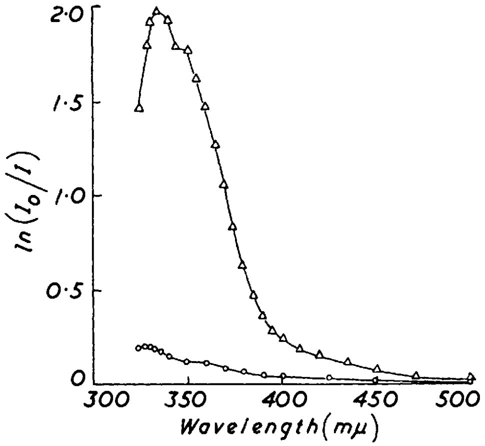
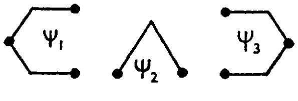


FIG. 1.
△ Ph_2BCl–$AlCl_3$.
○ Ph_2CHBr–$AlCl_3$.

$$H\Upsilon = E\Upsilon$$

where H is the Hamiltonian operator for the system. Now the above alternant system can be divided into three odd-alternant systems so that it becomes a linear combination of these three:



$$\Upsilon_k = C_1\psi_1 + C_2\psi_2 + C_3\psi_3$$

The secular equation derived from the perturbation treatment can be written down at once:

$$\begin{vmatrix} (\int\psi_1 H\psi_1 d\tau - & \int\psi_1 H\psi_2 d\tau & \int\psi_1 H\psi_3 d\tau \\ \int\psi_2 H\psi_1 d\tau & (\int\psi_2 H\psi_2 d\tau - E) & \int\psi_2 H\psi_3 d\tau \\ \int\psi_3 H\psi_1 d\tau & \int\psi_3 H\psi_2 d\tau & (\int\psi_3 H\psi_3 d\tau - E) \end{vmatrix} = 0$$

However, the three molecular orbitals can now be further expanded as a linear combination

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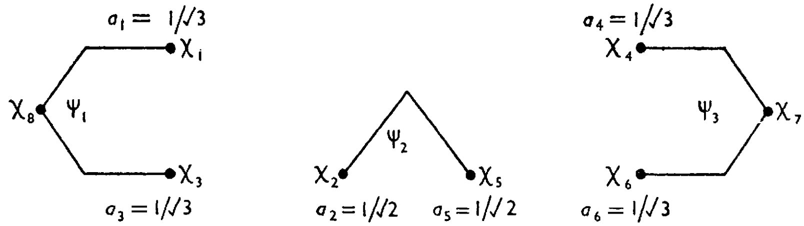
[3] Dewar, *J.*, 1952, 3532.

of atomic orbitals in which the distribution coefficients can be written down at sight, for:[4]

$$\Sigma(a_{oi})^2 = 1$$



The molecular orbitals of the alternant systems are a linear combination of these atomic orbitals, *i.e.*,

$$\psi_1 = a_1\chi_1 + a_3\chi_3 + a_8\chi_8$$
$$\psi_2 = a_2\chi_2 + a_5\chi_5$$
$$\psi_3 = a_4\chi_4 + a_6\chi_6 + a_7\chi_7$$
$$\therefore \int\psi_1 H\psi_2 d\tau = a_1a_2\int\chi_1 H\chi_2 d\tau + a_3a_2\int\chi_3 H\chi_2 d\tau \ . \ . \ . \ \text{etc.}$$

This expansion omits all integrals in which the χ's do not overlap. However, the χ wave functions are merely carbon $2p$ orbitals, and so $\int\chi_1 H\chi_2 d\tau = \beta$ where β is the resonance integral. Similarly $\int\chi_1 H\chi_1 d\tau = \alpha$ where α is the Coulomb integral. Now $(\alpha - E) = x$

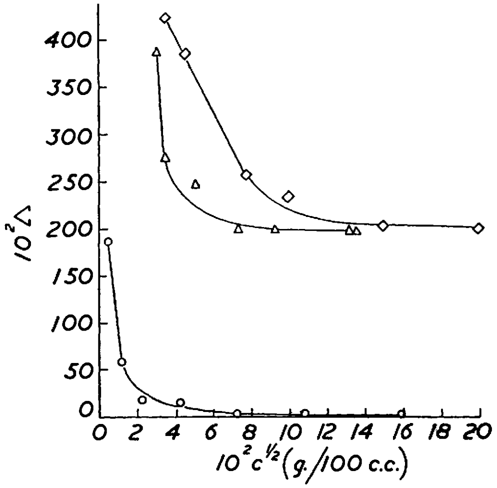


FIG. 2.

○ Ph_2BCl.
◇ $AlCl_3$.
△ Ph_2BCl–$AlCl_3$.

where x represents the energy interval between the conjugated system and the non-bonding molecular oblital, which is the energy associated with the first absorption band. Hence

$$\begin{vmatrix} x & \left(\frac{1}{\sqrt{3}\sqrt{2}} + \frac{1}{\sqrt{3}\sqrt{2}}\right)\beta & 0 \\ \left(\frac{1}{\sqrt{3}\sqrt{2}} + \frac{1}{\sqrt{3}\sqrt{2}}\right)\beta & x & \left(\frac{1}{\sqrt{3}\sqrt{2}} + \frac{1}{\sqrt{3}\sqrt{2}}\right)\beta \\ 0 & \left(\frac{1}{\sqrt{3}\sqrt{2}} + \frac{1}{\sqrt{3}\sqrt{2}}\right)\beta & x \end{vmatrix} = \begin{vmatrix} x & \beta\sqrt{\tfrac{2}{3}} & 0 \\ \beta\sqrt{\tfrac{2}{3}} & x & \beta\sqrt{\tfrac{2}{3}} \\ 0 & \beta\sqrt{\tfrac{2}{3}} & x \end{vmatrix}$$

Therefore $x = 2\beta/\sqrt{3}$.

But $x = h\nu$, and therefore $hc/\lambda = 2\beta/\sqrt{3}$.

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[4] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341 *et seq.*

The wavelength λ of the first absorption band for benzene is 208 mμ for a transition of energy 2β. Hence

$$hc/208 = 2\beta;\ hc/\beta = 416;\ \lambda = 416 \times 3^{\frac{1}{2}}/2 = 360 \text{ m}\mu$$

This value of 360 mμ is in very fair agreement with the observed values.

Attempts to study the electrochemistry of the diphenylboronium ion in ethyl methyl ketone solution have not been successful, as the solvent cannot be adequately dried for a conductance run involving low concentrations. The reason for this is that even very small traces of water in the solvent result in the diphenylboron chloride's becoming more hydrolysed as solvent is added in successive dilutions, and the resulting hydrogen chloride interferes. Conductance measurements in dry nitrobenzene were more successful, and the conductance of diphenylboron chloride in this solvent is shown in Fig. 2. An accurate estimate of Λ_0 has not been obtained, but assuming $\Lambda_0 = 25{\cdot}0$ to be a typical value for weak electrolytes in this solvent, and taking Λ/Λ_0 as an approximate measure of the degree of ionisation, we find that the latter is much less than 1% at the higher concentrations used here.

A solution of equivalent amounts of diphenylboron chloride and aluminium trichloride is darker in colour than the pure solvent, and a comparison of the conductivity curve for this system with that of aluminium trichloride alone in nitrobenzene shows the interaction of the two halides. Although aluminium trichloride itself is a weak electrolyte, in dilute solution, at least, the conductivity of a system containing solvated diphenylboronium ions and $AlCl_4^-$ ions should be lower, as these large ions should have lower mobilities, and thus lower equivalent conductivities. At higher concentrations however, the degree of ionisation of the salt having the larger ions should be greater than that of aluminium trichloride, and hence the two curves should at least approach each other, as is the case.

Despite the very low apparent degree of dissociation of diphenylboron chloride in nitrobenzene, metathesis takes place with silver perchlorate, and silver chloride is precipitated at once. After filtration the solution contains diphenylboron perchlorate (Ph_2BClO_4), and such a solution made up to 0·03M had an equivalent conductance of $\Lambda = 3{\cdot}4$ ohm^{-1} cm.^{2}, which is very similar to the value for $(Ph_2B^+)(AlCl_4^-)$ and is evidence for the existence of the same cation in both solutions.

We could not precipitate a solid perchlorate by addition of other organic solvents such as dry ether, carbon tetrachloride, etc., to the nitrobenzene solution.

EXPERIMENTAL

Nitrobenzene was fractionated over phosphoric oxide; the middle fraction was kept over baked-out activated alumina for three days with intermittent shaking, then filtered off in a dry box (b. p. 54°/0·13 mm.; n_D^{20} 1·5519; d_4^{15} 1·2082; specific conductivity at 15°, 9×10^{-9} ohm^{-1} cm.$^{-1}$).

"AnalaR" ethyl methyl ketone was fractionated, and after the fore-run had been neglected, the fraction of b. p. 79·2°/760 mm. was collected and further dried by refluxing over baked-out activated alumina (n_D^{20} 1·3760; d_4^{15} 0·8100).

Aluminium trichloride was repeatedly sublimed first at atmospheric pressure and then *in vacuo*, with a sublimator that was loaded and unloaded in an atmosphere of nitrogen in a dry-box.

All solutions were made up in the dry-box.

Conductivity measurements were made by using the a.c. bridge technique and apparatus.[5]

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[5] French and Glover, *Trans. Faraday Soc.*, 1955, **51**, 1418.