Thermochemistry of Organo-boron Compounds. Part IV. Dimethylaminochloroborines.*

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Values are reported for the heat of hydrolysis of dimethylaminodichloroborine, and for the heat of hydrolysis in hydrochloric acid of bisdimethylaminochloroborine. From these data, the heats of formation of the compounds in the liquid state are derived, *viz.* :

$$\Delta Hf^\circ[\mathrm{B(NMe_2)Cl_2,liq.}] = -108{\cdot}0 \pm 1{\cdot}5 \text{ kcal./mole}$$

and

$$\Delta Hf^\circ[\mathrm{B(NMe_2)_2Cl,liq.}] = -95{\cdot}2_5 \pm 1{\cdot}5 \text{ kcal./mole}$$

In the group of compounds $B(NMe_2)_nCl_{3-n}$ ($n = 0, 1, 2, 3$), for which thermal data are now complete, the bond energy term values $\bar{D}$(B–Cl) and $\bar{D}$(B–NMe_2) are not constant throughout the group. It is shown that the $B(NMe_2)Cl_2$ molecule is more stable by 12·1 kcal./mole, and the $B(NMe_2)_2Cl$ molecule more stable by 8·9 kcal./mole, than would be the case if the B–Cl and B–NMe_2 bonds in these molecules had the same energy as in BCl_3 and $B(NMe_2)_3$.

An explanation of the enhanced bond-energy term values in the mixed molecules is given by a molecular-orbital treatment of back-co-ordination in this group of molecules. Agreement with the experimental results is obtained if it is assumed that back-co-ordination is more powerful from nitrogen to boron than it is from chlorine to boron. The nitrogen atom would seem to be of the order of three times as effective as the chlorine atom in this respect.

Wiberg and Schuster (*Z. anorg. Chem.*, 1933, **213**, 94) have described the properties of the compounds $B(NMe_2)_nCl_{3-n}$ ($n = 1, 2, 3$), obtained from the reaction under controlled conditions of dimethylamine with boron trichloride. In Part III * we reported on the heat of hydrolysis in hydrochloric acid of one of these compounds, trisdimethylaminoborine, $B(NMe_2)_3$. We have also (Skinner and Smith, *Trans. Faraday Soc.*, 1953, **49**, 601) re-measured

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* Part III, Skinner and Smith, *J.*, 1953, 4025.

the heat of hydrolysis of boron trichloride. The present paper deals with the heats of hydrolysis of the two intervening compounds in the series, bisdimethylaminochloroborine, $B(NMe_2)_2Cl$, and dimethylaminodichloroborine, $B(NMe_2)Cl_2$. Series of this type are of interest in that they provide group data, which can be examined in terms of simple additivity postulates; in the present case we find that the bond-energy terms of the B–Cl and $B–NMe_2$ linkages are not additive in the group $B(NMe_2)_nCl_{3-n}$ ($n = 0, 1, 2$ 3) and that the deviations from additivity are appreciable.

EXPERIMENTAL

Preparation of Compounds.—Dimethylaminodichloroborine was prepared by Brown's method (*J. Amer. Chem. Soc.*, 1952, **74**, 1219), interaction of equivalent quantities of boron trichloride and dimethylamine in dry benzene, followed by addition of triethylamine (which is precipitated as the base hydrochloride, NEt_3,HCl, on standing). After filtration from the solid products, the benzene was separated by distillation through a Fenske column. The high-boiling residue was transferred to a smaller distillation unit and fractionated in nitrogen at reduced pressure through a 6" steel-gauze packed column; the fraction, b. p. 52—54°/92 mm., was retained. This was further distilled in a high vacuum, and the purified sample stored at −80°. Brown and Osthoff (*ibid.*, p. 2340) have reported that the dimerisation of dimethylaminodichloroborine, which occurs easily at room temperature, is considerably suppressed if the monomer is stored *in vacuo* at low temperatures.

Bisdimethylaminochloroborine was prepared by an extension of Brown's method (*loc. cit.*). A solution of dimethylaminodichloroborine in benzene was prepared, as described above, and this was then treated with a second equivalent of dimethylamine, followed by a further addition of triethylamine. After standing, solid products were filtered off, and the clear solution was distilled through a Fenske column at atmospheric pressure. The fraction, b. p. 145—148°, was collected and redistilled under reduced pressure in the small distillation unit; the sample, b. p. 50—52°/21 mm., was retained. This was further distilled *in vacuo*, and small samples were collected and sealed in thin, weighed, glass ampoules.

Calorimeter.—The calorimeter was described by Skinner and Smith (*loc. cit.*). The hydrolysis studies were carried out by breaking ampoules of the reactants under the surface either of 500 ml. of water or of 500 ml. of N-hydrochloric acid contained in the Dewar vessel, and following the ensuing temperature changes through the resistance changes of a shielded thermistor element immersed in the solution. The experiments were done at 25°.

Units.—The calorimeter was calibrated electrically. Heat quantities are given in thermochemical calories, 1 cal. = 4·1840 abs. joules.

Results.—(1) *Dimethylaminodichloroborine.* This substance is hydrolysed extremely rapidly at 25°, and the reaction may take place with explosive violence. Capillary side-arm ampoules—such as we have used successfully to moderate the violence of the hydrolysis of boron trichloride—were not always satisfactory in the present case, and several Dewar reaction vessels were shattered as a result. Ultimately, the method adopted was to dilute the dimethylaminodichloroborine; the ampoules were part-filled with reactant, to which approximately twice as much carbon tetrachloride (by volume) was then added as diluent. When these ampoules were broken, hydrolysis occurred rapidly, but non-explosively.

The observed heats of hydrolysis, $\Delta H_{\text{obs.}}$, refer to the reaction system

$$B(NMe_2)Cl_2(\text{liq.}/CCl_4) + (n + 3)H_2O(\text{liq.}) \longrightarrow (H_3BO_3 + NH_2Me_2Cl + HCl),nH_2O \quad . \quad (1)$$

and are related to the heat of formation of liquid dimethylaminodichloroborine by the thermochemical equation

$$\Delta Hf^\circ[B(NMe_2)Cl_2,\text{liq.}] = \Delta Hf^\circ(H_3BO_3 + NH_2Me_2Cl + HCl),nH_2O - 3\Delta Hf^\circ(H_2O,\text{liq.}) - \Delta H_{\text{obs.}} \quad . \quad . \quad (2)$$

In using * eqn. (2), thermal data from the following sources were assumed: $\Delta Hf^\circ(HCl,nH_2O)$ and $\Delta Hf^\circ(NH_2Me_2Cl,nH_2O)$ from " Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., Washington, Circular No. 500; $\Delta Hf^\circ(H_2O,\text{liq.}) = -68{\cdot}317$ kcal./mole (N.B.S. tables); $\Delta Hf^\circ(H_3BO_3,nH_2O)$ from Prosen, Johnson, and Pergiel (Nat. Bur. Stand., Report No. 1552, 1953).

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* The heat of mixing of $B(NMe_2)Cl_2$(liq.) with CCl_4(liq.) was measured independently, and found to be negligible. The heat of mixing of the products was also found to be negligible.

A selected group of the results obtained is given in Table 1.

TABLE 1. *Heat of hydrolysis of* $B(NMe_2)Cl_2$.

Expt.	$B(NMe_2)Cl_2$ (moles)	n	$-\Delta H_{obs.}$ (kcal.)	$\Delta Hf^\circ[B(NMe_2)Cl_2]$ (kcal./mole)	Mean values (kcal./mole)
1	0·00670	4146	54·9	−108·2	
2	0·00622	4466	55·0	−108·1	$-\Delta H_{obs.} = 55\cdot1$
3	0·00781	3556	55·7	−107·4	$\Delta Hf^\circ = -108\cdot0$
4	0·00702	3957	54·8	−108·5	
5	0·00538	5164	55·2	−108·0	

Estimation of the moles of reactant used in each experiment was made by volumetric analysis of the hydrolysis products for (*a*) total chlorine-ion content, and (*b*) free hydrochloric acid. These analyses generally agreed with each other within 1%, establishing the purity of the dimethylaminodichloroborine at >99%. The overall error of the thermochemical study—with allowance of an error of 1% in analysis, and an error of similar order in the calorimetry—is estimated at ±1 kcal./mole. The overall error in ΔHf° includes the errors that may rest in the subsidiary thermochemical data required in eqn. (2), and amounts to ±1·5 kcal./mole.

(2) *Bisdimethylaminochloroborine.* This substance is hydrolysed with moderate speed in water, and rapidly in N-hydrochloric acid. The acid hydrolysis has advantages from the thermochemical standpoint, in that the free dimethylamine produced on hydrolysis is completely held in solution as the salt, NH_2Me_2Cl. The experiments were performed by breaking weighed ampoules directly into 500 ml. of N-hydrochloric acid:

$$B(NMe_2)_2Cl(liq.) + 3H_2O(liq.) + (n+1)HCl(54H_2O) \longrightarrow (H_3BO_3 + 2NH_2Me_2Cl,27H_2O),nHCl(54H_2O) \quad . \quad . \quad (3)$$

where the excess of hydrochloric acid is denoted by n. The values of $\Delta Hf^\circ[B(NMe_2)_2Cl,liq.]$ were derived from the thermochemical equation corresponding to eqn. (3), *viz.*,

$$\Delta Hf^\circ[B(NMe_2)_2Cl,liq.] = \Delta Hf^\circ[H_3BO_3,54(n+1)H_2O] + 2\Delta Hf^\circ[NH_2Me_2Cl,27(n+1)H_2O] - 3\Delta Hf^\circ(H_2O,liq.) - \Delta Hf^\circ(HCl,54H_2O) - \Delta H_{obs.} \quad . . . . . \quad . \quad . \quad (4)\ *$$

A selection from the results obtained is given in Table 2.

TABLE 2. *Acid hydrolysis of* $B(NMe_2)_2Cl$.

Expt.	$B(NMe_2)_2Cl$ (moles)	n	$-\Delta H_{obs.}$ (kcal.)	$\Delta Hf^\circ[B(NMe_2)_2Cl]$ (kcal./mole)	Mean values
1	0·004857	102	59·0	−95·3	
2	0·005179	95	59·15	−95·2	$-\Delta H_{obs.} = 59\cdot1$ kcal.
3	0·004978	99	58·95	−95·4	$\Delta Hf^\circ = -95\cdot25$ kcal./mole
4	0·004651	106	59·25	−95·1	

The moles of reactant used in each experiment were calculated from the weight of the sample; analyses were not made on the calorimeter contents after each run. Analyses, both of chlorine ion and of dimethylamine content, were made on chosen samples from the stock of bisdimethylaminochloroborine, which generally agreed with one another satisfactorily, indicating purity † of 99—100% of the reactant. The overall error in $\Delta H_{obs.}$ is estimated at ±1 kcal./mole.

DISCUSSION

Table 3 lists the values we have obtained for the heats of formation of each member of the group $B(NMe_2)_nCl_{3-n}$. The latent heats of vaporisation ($\Delta H_{vap.}$) are from data by Wiberg and Schuster (*loc. cit.*), Burg and Randolph (*J. Amer. Chem. Soc.*, 1951, **73**, 953), and the N.B.S. tables (Circular 500).

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* Eqn. (4) neglects the heats of mixing of the products of reaction (3), which are small at the dilutions employed.

† It is possible that bisdimethylaminochloroborine disproportionates in the sense $2B(NMe_2)_2Cl \longrightarrow B(NMe_2)Cl_2 + B(NMe_2)_3$. Analysis of hydrolysis products would not reveal such disproportionation, but no evidence was found of dimer formation $[B(NMe_2)Cl_2]_2$, even on long standing.

From the ΔHf°(g.) values in Table 3, we may calculate the heats of the two following redistribution reactions,* *viz.*,

$$(a)\ \tfrac{2}{3}\mathrm{BCl_3(g.)} + \tfrac{1}{3}\mathrm{B(NMe_2)_3(g.)} \longrightarrow \mathrm{B(NMe_2)Cl_2(g.)} \quad \Delta H = -12{\cdot}1(\pm1{\cdot}4)\ \text{kcal./mole}$$

and

$$(b)\ \tfrac{1}{3}\mathrm{BCl_3(g.)} + \tfrac{2}{3}\mathrm{B(NMe_2)_3(g.)} \longrightarrow \mathrm{B(NMe_2)_2Cl(g.)} \quad \Delta H = -8{\cdot}9(\pm1{\cdot}6)\ \text{kcal./mole}$$

According to the postulate of constant transferable bond energy term values, redistribution reactions such as (*a*) and (*b*) should be thermoneutral (cf. Mortimer and Skinner, *J.*, 1953, 3189; Skinner and Tees, *J.*, 1953, 3378). The data show that the bond-energy terms $\bar{D}$(B–Cl) and $\bar{D}$(B–NMe$_2$) are *not* constant in the group $\mathrm{B(NMe_2)_nCl_{3-n}}$, and that there is an overall enhancement in the bond-energy term values of 12·1 kcal./mole in dimethylaminodichloroborine, and of 8·9 kcal./mole in bisdimethylaminochloroborine. Alternatively expressed, the dimethylaminodichloroborine molecule is more stable by 12·1 kcal./mole than would be the case if the B–Cl bonds should have the same mean energy as in boron trichloride, and the B–NMe$_2$ bond the same energy as in trisdimethylaminoborine; correspondingly, the bisdimethylaminochloroborine stability is enhanced by 8·9 kcal./mole over the value calculated in like manner.

TABLE 3.

Compound	ΔHf°(liq.)	$\Delta H_{\text{vap.}}$	ΔHf°(g.)
$\mathrm{BCl_3}$	$-103{\cdot}0 \pm 1$	$5{\cdot}5$	$-97{\cdot}5 \pm 1$
$\mathrm{BCl_2NMe_2}$	$-108{\cdot}0 \pm 1{\cdot}5$	$8{\cdot}9 \pm 0{\cdot}3$	$-99{\cdot}1 \pm 1{\cdot}8$
$\mathrm{BCl(NMe_2)_2}$	$-\ 95{\cdot}2_5 \pm 1{\cdot}5$	$10{\cdot}0 \pm 0{\cdot}5$	$-85{\cdot}3 \pm 2$
$\mathrm{B(NMe_2)_3}$	$-\ 77{\cdot}1 \pm 1$	$11{\cdot}2 \pm 0{\cdot}2$	$-65{\cdot}9 \pm 1{\cdot}2$

We have sought an explanation of these results by applying a simple molecular-orbital treatment of π-bonding ("back-co-ordination") to this group of molecules. It is generally accepted that in molecules of type $\mathrm{BX_3}$ (X = halogen, $\mathrm{NR_2}$, OR) there is some measure of π-bonding (occasioned by the existence of a vacant $2p_z$ orbital on the boron atom) which is superimposed on the trigonal B–X σ-bonding. Little is known, however, of the relative importance of such π-bonding in different $\mathrm{BX_3}$ systems. We find that the pattern of the present set of results is satisfactorily reproduced if we assume that back-co-ordination from nitrogen to boron is more powerful than from chlorine to boron.

The problem is one of six electrons, extending over four atoms in a plane. The localised reference system is considered to have the $2p_z$ boron orbital vacant, and to have p_z^2 pairs localised on each nitrogen and/or chlorine atom; we are interested in the energy stabilisation resulting from the delocalisation of the three pairs (p_z^2) of electrons. The procedure may be illustrated by the particular case of $\mathrm{B(NMe_2)Cl_2}$, for which the secular determinant is shown below:

$$\begin{vmatrix} \alpha_{\mathrm{B}} - \varepsilon & \gamma^* - S^*\varepsilon & \gamma - S\varepsilon & \gamma - S\varepsilon \\ \gamma^* - S^*\varepsilon & \alpha_{\mathrm{N}} - \varepsilon & 0 & 0 \\ \gamma - S\varepsilon & 0 & \alpha_{\mathrm{Cl}} - \varepsilon & 0 \\ \gamma - S\text{ɜ} & 0 & 0 & \alpha_{\mathrm{Cl}} - \varepsilon \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

α_{B}, α_{N}, and α_{Cl} are coulomb integrals, γ and γ^* are exchange integrals, and S^* and S are overlap integrals (cf. Roothaan and Mulliken, *J. Chem. Physics*, 1948, **16**, 118; γ and S refer to B–N bonds, γ^* and S^* to B–Cl bonds). Solution of eqn. (5) yields the energy levels, and the total electronic energy of the delocalised system is obtained by filling the lowest three of these. The energy stabilisation, relative to the localised reference system, is symbolised by $R_\pi(\mathrm{BNCl_2})$ and is given by $2[\sum_{i=1}^{3} \varepsilon_i - 2\alpha_{\mathrm{Cl}} - \alpha_{\mathrm{N}}]$.

Eqn. (5) (and the similar equations relating to the systems $\mathrm{BN_2Cl}$, $\mathrm{BN_3}$, and $\mathrm{BCl_3}$) may be simplified by assuming $\alpha_{\mathrm{Cl}} = \alpha_{\mathrm{N}}$—a reasonable approximation in view of the

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* The limits of error quoted are standard deviations. It should be noted that part of the error (*ca.* ±0·5 kcal./mole) included in the ΔHf°(g.) values of Table 3 arises from uncertainties in *assumed* thermochemical data, *e.g.*, in $\Delta Hf^\circ(\mathrm{H_3BO_3})$; since this source of error occurs with the same sign on both sides of the redistribution reactions (*a*) and (*b*) it is not relevant to the calculation of the probable error in the ΔH values.

equal electronegativities of N and Cl. By making the substitutions, $(\gamma - S\alpha_{\text{Cl}}) = \beta$, $(\gamma^* - S^*\alpha_{\text{Cl}}) = \beta^*$, $(\alpha_{\text{N}} - \alpha_{\text{B}}) = (\alpha_{\text{Cl}} - \alpha_{\text{B}}) = \delta = m\beta^*$, and $\beta = n\beta^*$, the set of equations (6) is obtained :

$$\left.\begin{aligned} R_\pi(\text{BCl}_3) &= \beta^*(1 - 3S^2)^{-1}\{(m + 6nS) - (m^2 + 12n^2 + 12nmS)^{\frac{1}{2}}\} \\ R_\pi(\text{BNCl}_2) &= \beta^*(1 - 2S^2 - S^{*2})^{-1}\{(m + 4nS + 2S^*) - [m^2 + 4(1 + 2n^2) \\ &\qquad + 4m(S^* + 2nS) - 8(nS^* - S)^2]^{\frac{1}{2}}\} \\ R_\pi(\text{BN}_2\text{Cl}) &= \beta^*(1 - S^2 - 2S^{*2})^{-1}\{(m + 2nS + 4S^*) - [m^2 + 4(2 + n^2) \\ &\qquad + 4m(2S^* + nS) - 8(nS^* - S)^2]^{\frac{1}{2}}\} \\ R_\pi(\text{BN}_3) &= \beta^*(1 - 3S^{*2})^{-1}\{(m + 6S^*) - (m^2 + 12 + 12mS^*)^{\frac{1}{2}}\} \end{aligned}\right\} \quad (6)$$

A further assumption included in eqns. (6) is that the overlap integrals S(B–Cl) and S^*(B–N) remain constant throughout the series $\text{BCl}_3 \longrightarrow \text{BN}_3$.

Values of R_π (in units of β^*) are given in Table 4 for a range of values of the unknown parameters m and n. The overlap integrals S and S^* were calculated from the formulæ given by Mulliken, Rieke, Orloff, and Orloff (*J. Chem. Physics*, 1949, **17**, 1248) assuming * the bond distances $r_{\text{B-N}} = 1{\cdot}44$ Å ($S^* = 0{\cdot}22$), and $r_{\text{B-Cl}} = 1{\cdot}73$ Å ($S = 0{\cdot}206$).

TABLE 4. R_π *Values in units of* β^*.

$n =$	1·5	0·9	0·7	0·5	0·3	
$R_\pi(\text{BCl}_3)$	3·486	1·956	1·466	0·973	0·496	$m = 0{\cdot}5$
$R_\pi(\text{BNCl}_2)$	3·119	2·042	1·743	1·499	1·336	
$R_\pi(\text{BN}_2\text{Cl})$	2·692	2·113	1·977	1·879	1·826	
$R_\pi(\text{BN}_3)$	2·181	2·181	2·181	2·181	2·181	
$R_\pi(\text{BCl}_3)$	3·194	1·702	1·225	0·767	0·354	$m = 1{\cdot}0$
$R_\pi(\text{BNCl}_2)$	2·822	1·775	1·487	1·253	1·092	
$R_\pi(\text{BN}_2\text{Cl})$	2·406	1·845	1·714	1·617	1·561	
$R_\pi(\text{BN}_3)$	1·913	1·913	1·913	1·913	1·913	
$R_\pi(\text{BCl}_3)$	2·918	1·490	1·043	0·627	0·272	$m = 1{\cdot}5$
$R_\pi(\text{BNCl}_2)$	2·566	1·560	1·287	1·066	0·914	
$R_\pi(\text{BN}_2\text{Cl})$	2·163	1·628	1·502	1·410	1·353	
$R_\pi(\text{BN}_3)$	1·694	1·694	1·694	1·694	1·694	

Table 5 gives values of two quantities, Δ_1 and Δ_2, defined in eqn. (7) :

$$\begin{aligned} \Delta_1 &= R_\pi(\text{BNCl}_2) - \tfrac{2}{3}R_\pi(\text{BCl}_3) - \tfrac{1}{3}R_\pi(\text{BN}_3) \\ \Delta_2 &= R_\pi(\text{BN}_2\text{Cl}) - \tfrac{1}{3}R_\pi(\text{BCl}_3) - \tfrac{2}{3}R_\pi(\text{BN}_3) \quad . \quad . \quad . \quad . \quad . \quad (7) \end{aligned}$$

The entries under Δ_1 and Δ_2 in Table 5 are all of the form $x\beta^*$, where x is a positive number. The implication is that an *enhancement* of the bond-energy terms in the mixed molecules BNCl_2 and BN_2Cl is predicted over the complete range given to the parameters m and n. But whereas $\Delta_1 > \Delta_2$ in case $n < 1$, the reverse is calculated for the case $n > 1$.

TABLE 5. Δ *Values in units of* β^*.

	$n =$	1·5	0·9	0·7	0·5	0·3
$m = 0{\cdot}5$	Δ_1	0·068	0·011	0·038	0·123	0·278
	Δ_2	0·076	0·008	0·035	0·100	0·206
$m = 1{\cdot}0$	Δ_1	0·055	0·003	0·033	0·104	0·219
	Δ_2	0·067	0·0025	0·030	0·086	0·168
$m = 1{\cdot}5$	Δ_1	0·056	0·0025	0·027	0·083	0·168
	Δ_2	0·061	0·002	0·025	0·072	0·133

Experimentally, we find the enhancement larger † in $\text{B(NMe}_2)\text{Cl}_2$ than in $\text{B(NMe}_2)_2\text{Cl}$,

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* The distance $r_{\text{B-Cl}}$ in BCl_3 is given by electron-diffraction studies; $r_{\text{B-N}}$ is not known in this series of compounds. The value chosen is based on the measured values in borazole and crystalline boron nitride.

† From the experimental values $\Delta_1 = 12{\cdot}1 \pm 1{\cdot}4$ kcal./mole and $\Delta_2 = 8{\cdot}9 \pm 1{\cdot}8$ kcal./mole, we have $(\Delta_1 - \Delta_2) = 3{\cdot}2 \pm 2{\cdot}1$ kcal./mole (the quoted error is the standard deviation). The magnitude of the possible error in the value $(\Delta_1 - \Delta_2) = 3{\cdot}2$ kcal./mole is unfortunately too large to allow very definite conclusions to be drawn, and this point should be borne in mind in the ensuing discussion.

corresponding to $\Delta_1 > \Delta_2$, and $n < 1$. Moreover, it would seem that n is required to be appreciably less than unity; thus, *e.g.*, if we accept the values $m = 0{\cdot}5$, $n = 0{\cdot}3$, and $\beta^* = -43{\cdot}5$ kcal./mole, the calculated values are $\Delta_1 = 12{\cdot}1$ kcal. and $\Delta_2 = 8{\cdot}96$ kcal., in excellent agreement with the experimental values (12·1 and 8·9 respectively). This particular choice of parameter values represents only one among many that would fit the experimental data satisfactorily; the important point is that, if m is chosen $>0{\cdot}5$, the trend is for n to become $<0{\cdot}3$ if agreement with experiment is to be retained.

Values of n of the order 0·3 or less imply that the exchange integral γ^* is some three or more times larger than γ. The physical interpretation of this is that back-co-ordination from the nitrogen $2p_z^2$ electrons to boron is at least thrice as effective as from the $3p_z^2$ electron pair * in chlorine. On the other hand, the overlap integrals S^* and S are almost the same for the internuclear separations we have used. This suggests that a general proportionality between exchange and overlap integrals, $kS \sim \gamma$, does not obtain. A more limited relation, $k_{nn'}S \sim \gamma$, in which the proportionality constants depend upon the principal quantum numbers n, n' of the interacting electrons, may be more satisfactory as an approximation.

Effective back-co-ordination in a given BX_3 molecule will compensate internally the electron deficiency of the $2p_z$ orbital of trigonal boron. In this sense, one might expect that BX_3 molecules which show comparatively weak acceptor behaviour are highly compensated internally. The present results confirm this, boron trichloride (small γ) being an active acceptor molecule, and trisdimethylaminoborine (large γ) a relatively weak acceptor. On this basis we might expect a large value for γ(B–O) in the alkyl borates (weak acceptor properties), and a similar trend in the values Δ_1, Δ_2 for the molecules $B(OR)Cl_2$, $B(OR)_2Cl$, to those found here. Studies on these latter compounds are in progress.

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