247. N-*Oxides and Related Compounds. Part IX.* The Electric Dipole Moments of Pyridine– and Trimethylamine–Boron Trihydride and Trihalide Complexes.*

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The mesomeric moments in pyridine–boron trihydride and trihalide complexes are large, negative, and approximately constant. From these and the positive mesomeric moment in pyridine 1-oxide, the moment due to the inward drift of electrons from the oxygen atom can be estimated.

The variation of moment change due to complex formation by both trimethylamine and pyridine is in the order: $BF_3 < BH_3 \lessgtr BCl_3 < BBr_3$. The reasons for this are discussed.

In the preceding paper, the mesomeric moments for 4-substitution into the pyridine–boron trichloride complex were measured and compared with those for 4-substitution into pyridine and pyridine 1-oxide. Such complexes are interesting for other reasons, and some of these are pursued in this paper. In particular, the mesomeric moments in the aromatic system for attachment of the acceptor molecules are derived, and the magnitudes of the moments due to formation of complexes involving trimethylamine or pyridine are estimated when the acceptor molecules are boron trihydride, trifluoride, trichloride, and tribromide.

EXPERIMENTAL

Trimethylamine–Borane.—The following simplification of Schaeffer and Anderson's method [1] was convenient: aqueous trimethylamine (25—30%; 10 c.c.) and concentrated hydrochloric acid (10 c.c.) were mixed and evaporated at 100°/13 mm. for 30 min. after solidification had taken place. Then a slurry of lithium borohydride (0·84 g.) in ether (150 c.c.) which had been refluxed for 30 min. was added. The whole was refluxed for 30 min., filtered, and evaporated to give the adduct (1·5 g., 60%), m. p. 92—93° (lit.,[1] yield 85%, m. p. 93°). The compound was purified by sublimation.

Pyridine–Borane.—This was prepared as described in ref. 2 and distilled. The compound is evidently subject to superheating for at constant pressure (0·15 mm.) six fractions were collected: the b. p. rose from 58° to 78° for the third fraction, and fell to 68° again; n_D^{20} was 1·5315 for the first fraction and 1·5310 for all of the others [ref. 2 gives n_D^{25} 1·5280; ref. 3 gives v. p. (mm.) 0·1 at 25°, 0·15 at 45°, 0·35 at 60°, 0·9 at 85°, 1·8 at 99°; the increase in pressure seems unduly small for the temperature range quoted].

Pyridine–Boron Trifluoride.—This was prepared as in ref. 4. It sublimed at 100°/0·15 mm. and then had m. p. 46—47° (lit.,[4,5] m. p. 45°, 47—48°). It was not possible to recrystallise it from ethyl alcohol.

Trimethylamine–Boron Tribromide.—To 25—30% (w/v) aqueous trimethylamine (25 c.c.), benzene (25 c.c.), and light petroleum (b. p. 40—60°; 25 c.c.) was added sodium hydroxide (25 g.). After 10 min. the organic layer was separated and dried (NaOH). Boron tribromide (25 c.c. of 0·5M-solution in light petroleum) was added slowly with cooling in solid carbon dioxide–ethanol. The *adduct* (3·1 g., 80%), crystallised five times from ethanol, formed needles, m. p. 230—232° (Found: C, 11·8; H, 2·7; N, 4·2; Br, 77·2. $C_3H_9NBBr_3$ requires C, 11·6; H, 2·9; N, 4·5; Br, 77·4%). Only an abortive attempt to prepare this compound has been previously recorded.[6]

Pyridine–Boron Tribromide.—Boron tribromide (10 c.c. of 0·5M-solution in light petroleum) was added in 5 min. to pyridine (0·5 c.c.) in light petroleum (10 c.c.) with cooling as above.

* Part VIII, preceding paper.

[1] Schaeffer and Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 2143.
[2] Taylor, Grant, and Sands, *ibid.*, 1955, **77**, 1506.
[3] Brown, Schlesinger, and Cardon, *ibid.*, 1942, **64**, 325.
[4] van der Meulen and Heller, *ibid.*, 1932, **54**, 4404.
[5] Brown and Holmes, *ibid.*, 1956, **78**, 2174.
[6] Johnson, *J. Phys. Chem.*, 1912, **16**, 1.

The adduct (1·35 g., 80%), twice recrystallised from ethanol, had m. p. 127—128° not raised by further recrystallisation (Found: C, 18·3; H, 1·6; N, 4·1. Calc. for $C_5H_5NBBr_3$: C, 18·2; H, 1·5; N, 4·2%) (ref. 5 reports m. p. 128—129°; ref. 6 says that it becomes " brown and crispy " at 120°).

Physical Measurements.—For details see preceding paper. The results are recorded in Table 1.

TABLE 1.

Pyridine–borane				Pyridine–boron trifluoride			
10^6W	ε	V	$10^5\Delta n_D$	10^6W	ε	V	$10^5\Delta n_D$
3959	2·4315	1·1443	19	1230	2·3179	1·1443	—
5577	2·4967	1·1441	30	1997	2·3438	1·1438	—
7328	2·5678	1·1438	37	2191	2·3499	1·1438	—
9504	2·6563	1·1437	46	2771	2·3696	1·1436	—

$\varepsilon = 2\cdot2722 + 40\cdot35W$; $V = 1\cdot1446 - 0\cdot10W$; $\Delta n_D = 0\cdot00001 + 0\cdot05W$; $_TP = 734\cdot1$ c.c. $_EP = 30\cdot1$ c.c. $\mu = 5\cdot86 \pm 0\cdot01$ D

$\varepsilon = 2\cdot2736 + 34\cdot94W$; $V = 1\cdot1446 - 0\cdot38W$; $_TP = 999\cdot0$ c.c. $_EP = 26\cdot8$ c.c.^{a} $\mu = 6\cdot90 \pm 0\cdot05$ D

Trimethylamine–borane				Pyridine–boron tribromide			
2523	2·3520	1·1451	−28	1665	2·3070	1·1433	9
5596	2·4490	1·1461	−62	1831	2·3125	1·1433	11
6227	2·4681	1·1459	−68	2619	2·3288	1·1428	15
7920	2·5218	1·1465	−85	4365	2·3629	1·1414	23

$\varepsilon = 2\cdot2727 + 31\cdot45W$; $V = 1\cdot1445 + 0\cdot24W$; $\Delta n_D = -0\cdot11W$; $_TP = 461\cdot6$ c.c.; $_EP = 25\cdot1$ c.c. $\mu = 4\cdot62 \pm 0\cdot01$ D

$\varepsilon = 2\cdot2734 + 20\cdot72W$; $V = 1\cdot1446 - 0\cdot73W$; $\Delta n_D = 0\cdot05W$; $_TP = 1322\cdot9$ c.c. $_EP = 50\cdot5$ c.c. $\mu = 7\cdot90 \pm 0\cdot06$ D

Trimethylamine–boron tribromide			
2146	2·3058	1·1432	10
2794	2·3155	1·1428	13
3274	2·3228	1·1425	22

$\varepsilon = 2\cdot2728 + 15\cdot31W$; $V = 1\cdot1446 - 0\cdot64W$; $\Delta n_D = -0\cdot00001 + 0\cdot06W$; $_TP = 938\cdot3$ c.c. $_EP = 56\cdot2$ c.c. $\mu = 6\cdot57 \pm 0\cdot01$ D

^{a} It was impossible to measure refractive indices because the solute crystallised in the refractometer cell. The following values were used to obtain $_EP$: R_D (pyridine) = 24·07 c.c. (Landolt–Börnstein Tabellen) and $R_D(BF_3)$ = 2·7 c.c. (Phillips, Hunter, and Sutton, *J.*, 1945, 146).

DISCUSSION

As in previous treatments, the algebraic difference of electric dipole moment between a pyridine complex and a trimethylamine complex may be taken as an approximate value for the contribution to the former moment of electron drifts induced by the highly polar dative link which joins the pyridine to the acceptor molecule. This statement assumes that the moments of the dative link and of the co-ordinated acceptor molecule are the same in the aromatic and the aliphatic compounds, which cannot be entirely true; but the errors which arise are probably small.

These differences appear in column 4 of Table 2 and show interesting features: for the boron compounds as adducts, the differences are all (*a*) roughly constant, (*b*) less than the difference between pyridine and trimethylamine, and (*c*) in the opposite sense from that of the oxygen atom as adduct.
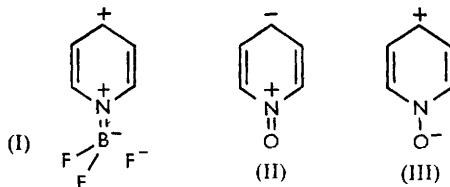
(*a*) This observation indicates that the polarising power of the dative link plus co-ordinated adduct are much the same in all four cases, although the gross moments of the compounds increase by 35—40% in the series BH_3, BF_3, BCl_3, BBr_3. It is likely that the

polarisation is almost wholly an inductive effect in the aromatic ring, for canonical structures such as (I) are probably unimportant. This may be contrasted with the varying effect that the corresponding CX_3 groups have when attached to benzene, as shown by the differences between $C_6H_5 \cdot CX_3$ and $CH_3 \cdot CX_3$ in column 8. These indicate that the CF_3

TABLE 2.

1	2	3	4	5	6	7	8	9	10
			Pyridine adduct *less*				Substd. benzene *less*	NMe₃ adduct *less*	Pyridine adduct *less*
Adduct for cols. 2 and 3	NMe₃ adduct	Pyridine adduct	NMe₃ adduct	Subst. for cols. 6 and 7	Substd. methane	Substd. benzene	substd. methane	substd. methane	substd. benzene
Nil	$-0\cdot65^a$ $\pm0\cdot03$	$-2\cdot22^b$ $\pm0\cdot02$	$-1\cdot57$	—	—	—	—	—	—
O	$-5\cdot02^c$ $\pm0\cdot02$	$-4\cdot24^c$ $\pm0\cdot02$	$+0\cdot78$	—	—	—	—	—	—
BH_3	$-4\cdot62^d$ $\pm0\cdot01$	$-5\cdot86^d$ $\pm0\cdot01$	$-1\cdot24$	CH_3	0	$+0\cdot40$	$+0\cdot40$	$-4\cdot62$	$-6\cdot26$
BF_3	$-5\cdot63^e$ $\pm0\cdot03$	$-6\cdot90^d$ $\pm0\cdot05$	$-1\cdot27$	CF_3	$-2\cdot34^g$	$-2\cdot56^h$	$-0\cdot22$	$-3\cdot29$	$-4\cdot34$
BCl_3	$-6\cdot31^e$ $\pm0\cdot03$	$-7\cdot70^d$ $\pm0\cdot02$	$-1\cdot39$	CCl_3	$-1\cdot59^j$ $\pm0\cdot01$	$-2\cdot02^j$ $\pm0\cdot01$	$-0\cdot43$	$-4\cdot72$	$-5\cdot68$
BBr_3	$-6\cdot57^d$ $\pm0\cdot01$	$-7\cdot90^d$ $\pm0\cdot06$	$-1\cdot33$	CBr_3	Not available		—	—	—

A positive sign means that the positive pole of the dipole is towards the adduct or the corresponding group. [a] Groves and Sugden's figures recalculated (*J.*, 1937, 1779). [b] Curran and Leis's figures recalculated (*J. Amer. Chem. Soc.*, 1945, **67**, 79). [c] Linton's figures recalculated (*ibid.*, 1940, **62**, 1945). [d] Present investigation. [e] Philips, Hunter, and Sutton's figures recalculated, neglecting $_AP$ (*J.*, 1945, 146). [f] Selected from data in Wesson's tables (Wesson, "Tables of Electric Dipole Moment," The Technology Press, Massachusetts Institute of Technology, Cambridge, Mass. U.S.A., 1948). [g] Fuoss's value (*J. Amer. Chem. Soc.*, 1938, **60**, 1633) recalculated by Conradi and Li (*ibid.*, 1953, **75**, 1785). [h] Frieser, Hobbs, and Gross (*ibid.*, 1949, **71**, 111). [j] Sutton's figures recalculated (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668); see also ref. *h* for a value for benzotrichloride.

group is less effective than the CCl_3 in polarising; but it must be emphasised that the value for $CH_3 \cdot CF_3$ is a vapour-phase determination which may not be strictly comparable with the other values which are for benzene solutions. This point will be taken up below.

(*b*) This decrease is not what would at first be expected, because the polarisation of the aromatic system by the dative link and the adduct molecule ought to be greater than that due to the polarity within the pyridine ring. The differences are not, however, truly comparable; for in the trimethylamine complexes the bonding orbitals of the nitrogen atom used in the N–C bonds have more *s* character than have those in trimethylamine itself. If hybridisation in the latter could be changed to that in the former, the dipole moment of the lone pair, and hence of the whole molecule, would increase markedly; and the apparent mesomeric moment in pyridine would correspondingly decrease.

(*c*) The third observation again emphasises the great difference between the boron compounds and the oxygen atom as adducts, only the latter having unshared electrons which by delocalisation in a molecular π-orbital can drift into the ring. The algebraic difference between the two mesomeric moments, *viz.*, between $+0\cdot78$ and $-1\cdot24$ to $-1\cdot39$, which is *ca.* $2\cdot1$ gives some measure of this drift against the polarising action of the $^+N\!-\!O^-$ bond in the 1-oxide. It is remarkably large, although smaller than the estimate of $2\cdot35$ D which Linton [7] obtained as the difference between the moment predicted for pyridine 1-oxide ($6\cdot59$ D) and that observed ($4\cdot24$ D), *i.e.*, as:

$$\Delta\mu = \mu(\text{pyridine oxide}) - \mu(\text{pyridine}) - [\mu(\text{trimethylamine oxide}) - \mu(\text{trimethylamine})]$$

This implies that the effect of different hybridisations of the nitrogen atom in trimethylamine and its oxide can be ignored, which, as has been emphasised above, is probably untrue. The larger the moment taken for trimethylamine, the smaller are both the

[7] Linton, *J. Amer. Chem. Soc.*, 1940, **62**, 1945.

predicted value and the difference. The present estimate, using only tetrahedrally hybridised aliphatic compounds, should avoid this difficulty.

Further, Linton's value should give the differential effect of contributions by structures (II) and (III) and was surprisingly large in view of chemical [8] and dipole-moment [9] evidence that forms (II) and (III) are of comparable importance. Our estimate should represent the moment due to the inward drift of electrons (II) only (within the limitations which apply to all comparisons between tetrahedrally and trigonally hybridised compounds), because the induced polarisation due to the external polar bond (cf. III) is present both in the complexes and in the *N*-oxide, and should cancel approximately in our calculation. This may be seen from the explicit statement:

$$\Delta'\mu = \mu\text{(pyridine 1-oxide)} - \mu\text{(trimethylamine oxide)}$$
$$- [\mu\text{(pyridine boron complex)} - \mu\text{(trimethylamine boron complex)}]$$

$^+$N$^-$B$^-$ *Moment.*—The second main matter is that of the magnitude of the moment change due to co-ordination, and its connection with the nature of the X atom in the acceptor BX_3 molecule.

The most interesting quantity to evaluate would be the moment of the $^+$N$^-$B$^-$ bond; but this is always difficult because of the contribution from the tetrahedrally hybridised BX_3 group, which cannot be directly observed. The simplest way of allowing for it is to compare the moments of the complexes with those of the $\geqslant$C$^-$CX_3 compounds. The available differences are given in Table 2, for aliphatic pairs in column 9 and for aromatic ones in column 10.

In the aromatic series they are complicated by the changes in mesomeric moment, especially for the case of X = H. In the aliphatic series, there is the possible incompatibility of the moment for CH_3·CF_3, from vapour measurements, with the others which are all from solution measurements. Nevertheless, both series show that the differences are roughly the same for X = H and for X = Cl, but are less for X = F. Subtraction of the moments of HCX_3 compounds from those of either the pyridine or the trimethylamine complexes, as is shown in Table 3, gives differences that increase in the order F, H, Cl, Br. Acceptor power, therefore, appears to be in the order:

$$BF_3 < BH_3 \leqslant BCl_3 < BBr_3$$
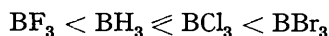
For the halides, this is qualitatively the same as that found by H. C. Brown and Holmes [5] from the heats of formation of the complexes.

TABLE 3.

X	$\mu(Me_3N\text{-}BX_3)$	$\mu(CHX_3)$	$\mu(Me_3N\text{-}BX_3) - \mu(CHX_3)$	$\mu(C_5H_5N\text{-}BX_3)$	$\mu(C_5H_5N\text{-}BX_3) - \mu(CHX_3)$
H	4·62	0	4·62	5·86	5·86
F	5·63	1·59	4·04	6·90	5·31
Cl	6·31	1·18	5·13	7·70	6·52
Br	6·57	1·0	5·57	7·90	6·90

Acceptor power can be regarded as being due to the possession by the boron atom of an unfilled, low-lying orbital, and to any formal positive charge which the atom bears because of the polarity of the B–X links.

It can hardly be given a precise and general definition, because different methods of assessing it would require different definitions. In relation to the thermodynamic stability of the complex, there would, for example, certainly have to be reference to the steric effects between donor and acceptor molecules,[10] which effects, however, may not enter,

[8] Katritzky, *Quart. Rev.*, 1956, **10**, 395.
[9] Katritzky, Randall, and Sutton, *J.*, 1957, 1769; see also preceding paper.
[10] *Inter al.*, Brown and Nakagawa, *ibid.*, p. 2197; Brown and Barbaras, *ibid.*, 1947, **69**, 1137; Brown and Taylor, *ibid.*, p. 1332; Brown and Horowitz, *ibid.*, 1955, **77**, 1733.

at least not in the same way, into the definition from dipole-moment change. We need more information on this point. Exact parallels between estimates of acceptor power from different means of determination are therefore not to be expected; but qualitative agreement is probably significant.

Two explanations may be offered for the order observed from dipole-moment changes:

(*a*) Back-co-ordination from the X atoms, involving structures of type $\begin{matrix} X \\ \diagdown \\ X \diagup \end{matrix} \bar{B}{=}\overset{+}{X}$

with π-bonds, will reduce the net formal positive charge and also saturate the spare orbital. Decrease of back-co-ordination in the order $BF_3 > BCl_3 > BBr_3$ would then explain the acceptor order observed for the halides. The relative position of the BH_3 complex could hardly be predicted; but it may be noted that, although the low polarity of the B–H bonds may give little positive charge to the boron atoms, there is no back-co-ordination at all.

(*b*) From simple electrostatic considerations, it can be seen that, although the formal positive charge on the B atom attracts lone-pair electrons, the negative ones on the X atoms repel them. Hence, for a given formal charge on the B and the X atoms, the repulsion would decrease as the B–X distance increases, and so the acceptor power might increase in the observed order. Again, the relative position of the BH_3 complex could hardly be predicted, but neither positive nor negative formal charges would be large.

The bond lengths in the free halides are all less than would be predicted by the simple addition of covalent radii: B–F is 19%, B–Cl is 6·9%, and B–Br is 7·4% less. This indicates that back-co-ordination is much greater in the first than in the other two where it is roughly the same.

It is likely that both explanations have partial validity.

[*Note Added January 20th*, 1958.—In a personal communication, Dr. N. N. Greenwood and his colleagues have informed us of recent results on the electrical conductivity of the molten pyridine–boron trichloride complex. These show that there is about 1% dissociation into kinetically free ions which are thought to be $[Py_2BCl_2]^+$ and $[BCl_4]^-$. If this substance retains the ionic dimerised form in dilute solution in benzene, our conclusions from the electric polarisation measurements would need drastic revision. It is probable, *a priori*, that the equilibrium form would be different, because the much smaller concentration of the benzene solutions used would not favour dimerization; and the lower dielectric constant would not favour an even more highly polar form (μ probably 10—15 D) than the simple monomer. If there were an equilibrium between these two forms over the range of weight fraction used (0·001—0·005), it would be expected that the proportions would change and that the $ε/w_2$ curve would not be the normal rectilinear one but would show a positive curvature. In fact, the departures from rectilinearity are within the known experimental error generally found, *viz.*,

$10^6 w_2$	0	1048	2140	3756	4763
Δ	+0·0002	−0·0001	−0·0001	−0·0008	+0·0004

They show negligible curvature. There is therefore no indication of a change of solute form.

Measurements of molar electrical conductivity in benzene solution made by Mr. E. W. Randall (*ca.* 10^{-6} cm.² ohm⁻¹ mole⁻¹) combined with the analysis used by N. N. Greenwood and K. Wade (*J.*, in the press) for pyridine complexes with gallium trichloride, indicate that the solute is dissociated into kinetically free ions only to the extent of about 1 part in 10^8. Therefore if it were in the suggested ionic form it would be effectively dimeric. Measurements of molecular weight in benzene by the Beckmann method, made by Mr. M. Hely Hutchinson, give a value of 186 ± 30 (twice standard deviation) which is sufficient proof that the substance is monomeric (*M*, 197) and not dimeric.

These results confirm that the form assumed for the solution, *viz.*, Py,BCl_3, is correct in our solutions.]

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