246. N-*Oxides and Related Compounds. Part VIII.* The Electric Dipole Moments of a Series of 4-Substituted Pyridine–Boron Trichloride Complexes.*

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The dipole moments of some compounds indicated in the title afford evidence that the pyridine–boron trichloride system can create a deficit of electrons in the 4-position, but (unlike the analogous 1-oxides) not an excess.

Katritzky, Randall, and Sutton [1] have shown that the mesomeric moments of 4-substituted pyridine 1-oxides are always greater than those of the corresponding pyridines for both electron-withdrawing and electron-releasing substituents, and have suggested that this is because electron-shifts of both type (I) and type (II) can take place in appropriate pyridine 1-oxides.

Electron shift of type (I) occurs because there is a spare electron-pair on the oxygen

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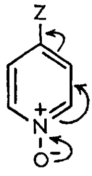
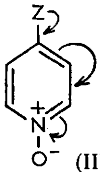
* Part VII, *J.*, 1958, 150.

[1] Katritzky, Randall, and Sutton, *J.*, 1957, 1769.

atom; therefore it should not occur in analogous compounds wherein the oxygen is replaced by an atom without such a spare electron-pair. In such compounds, the mesomeric moment should be larger for those with electron-releasing 4-substituents, but smaller for those with electron-withdrawing 4-substituents, than the mesomeric moments of the corresponding 4-substituted pyridines. To test this prediction a series of 4-substituted pyridine–boron trichloride complexes (III) has now been prepared (Table 1), and their dipole moments have been measured.



(I)



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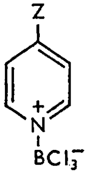

(III)

TABLE 1. *Substituted pyridine–boron trichloride complexes.*

No.	4-Subst.	Yield (%) *	M. p.	Crystal form	Solvent for recrystn.
1	OMe	63	91—93°	Needles[b]	EtOH
2	Cl	79	167·5—169	Needles	MeOH
3	Me	77	126·5—127·5	Needles	EtOH
4	H	70	113—114[a]	Plates	EtOH
5	CO_2Et	70	110—111	Plates	EtOH
6	CN	85	149—150·5	Prisms	MeOH

		Found (%)				Required (%)			
No.	Formula	C	H	N	Cl	C	H	N	Cl
1	$C_6H_7ONBCl_3$	31·9	3·3	6·0	46·4	31·8	3·1	6·2	47·0
2	$C_5H_4NBCl_4$	26·3	2·1	5·8	61·0	26·0	1·8	6·1	61·4
3	$C_6H_7NBCl_3$	34·2	3·4	6·2	—	34·3	3·4	6·7	—
5	$C_8H_9O_2NBCl_3$	35·9	3·7	4·7	39·6	35·8	3·4	5·2	39·6
6	$C_6H_4N_2BCl_3$	32·5	2·0	12·3	48·8	32·5	1·8	12·7	48·1

[a] Gerrard and Lappert, *J.*, 1951, 1020, give m. p. 114·5—115°. [b] Deliquescent.
* Prepared in light petroleum, except that no. 6 was prepared in light petroleum–benzene.

EXPERIMENTAL

Preparation of Compounds.—4-Nitro-, 4-acetyl-, 4-dimethylamino-, and 4-ethoxycarbonyl-pyridine were prepared as stated in ref. 1. 4-Cyanopyridine was purchased.

4-Chloropyridine (45%), b. p. 46°/15 mm., was prepared from 4-nitropyridine 1-oxide by Ochiai and Suzuki's method [2] (yield 58·6%; b. p. 53—55°/20 mm.).

4-Picoline, b. p. 144°, was prepared by catalytic reduction of its 1-oxide.

4-Methoxypyridine 1-oxide (7·5 g.), iron filings (6 g.), and acetic acid (30 c.c.) were kept for 4 hr. at 100°, then basified with 30% aqueous sodium hydroxide and filtered (sintered glass). The solid was washed and the solution extracted with ether. 4-Methoxypyridine (4 g., 63%), b. p. 188·5—189·5° (lit.,[3] b. p. 190°), was recovered from the dried ($MgSO_4$) extracts.

4-Cyanopyridine 1-oxide [4] had m. p. 222·5—224·5° (lit.,[4] m. p. 220—221°).

Preparation of Pyridine–Boron Trichloride Complexes.—Boron trichloride in light petroleum (b. p. 40—60°) (6 c.c. of 1·67N-solution) was added dropwise, with agitation, at 0°, to the pyridine (0·01 mole) in light petroleum (*ca.* 20 c.c.; for compound no. 6, sufficient benzene was added to bring it into solution). The adduct was filtered off and recrystallised by adding it rapidly to sufficient hot solvent, agitating the whole, and filtering it without delay into a precooled receiver. Some of the adducts decomposed very readily if the above recrystallisation procedure was not followed; even so it was not possible to purify the 4-nitro-, 4-dimethylamino-, and 4-acetyl adducts; the last gave apparently 4-*acetylpyridine hydrochloride*, plates, m. p. 150—154° (decomp.) (Found: C, 53·0; H, 5·2. C_7H_8ONCl requires C, 53·3; H, 5·1%).

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[2] Ochiai and Suzuki, *Pharm. Bull. Japan*, 1954, **2**, 247.
[3] Ochiai and Ishii, *J. Pharm. Soc. Japan*, 1951, **71**, 1092.
[4] Ochiai, *J. Org. Chem.*, 1953, **18**, 534.

Physical Measurements.—Electric dipole moments were determined by measuring the dielectric constants, specific volumes, and refractive indices (for Na_D light) of benzene solutions at 25°, by the methods described by Everard and Sutton [5] for their small scale technique, with the heterodyne capacitance meter described by Hill and Sutton.[6] The meter was calibrated by assuming the value 2·2727 for the dielectric constant of benzene at 25°.[7] The pyknometer was calibrated with air-free distilled water. The refractive index difference, Δn_D, between the solution and benzene was measured with a Pulfrich refractometer.

TABLE 2.

Pyridine–boron trichloride

10^6W	ε	V	$10^5\Delta n_D$
1048	2·3069	1·1444	6
2140	2·3430	1·1436	12
3756	2·3955	1·1429	19
4763	2·4299	1·1424	29

$\varepsilon = 2{\cdot}2725 + 32{\cdot}94W$; $V = 1{\cdot}1447 - 0{\cdot}467W$; $\Delta n_D = 0{\cdot}059W$; ${}_EP = 45{\cdot}7$ c.c.; ${}_TP = 1257{\cdot}0$ c.c.; $\mu = 7{\cdot}70 \pm 0{\cdot}02$ D

4-Chloropyridine–boron trichloride

10^6W	ε	V	$10^5\Delta n_D$
1013	2·2945	1·1441	5
1942	2·3142	1·1434	11
2116	2·3171	1·1434	11
3360	2·3446	1·1425	14

$\varepsilon = 2{\cdot}2726 + 21{\cdot}33W$; $V = 1{\cdot}1447 - 0{\cdot}63W$; $\Delta n_D = 0{\cdot}00001 + 0{\cdot}043W$; ${}_EP = 40{\cdot}51$ c.c.; ${}_TP = 960{\cdot}9$ c.c.; $\mu = 6{\cdot}71 \pm 0{\cdot}03$ D

4-Methoxypyridine–boron trichloride

10^6W	ε	V	$10^5\Delta n_D$
1044	2·3130	1·1441	8
1673	2·3373	1·1438	6
2324	2·3614	1·1432	12
2976	2·3860	1·1430	13
3714	2·4135	—	21

$\varepsilon = 2{\cdot}2733 + 37{\cdot}88W$; $V = 1{\cdot}1446 - 0{\cdot}563W$; $\Delta n_D = 0{\cdot}051W$; ${}_EP = 45{\cdot}2$ c.c.; ${}_TP = 1651{\cdot}5$ c.c.; $\mu = 8{\cdot}86 \pm 0{\cdot}02$ D

4-Ethoxycarbonylpyridine–boron trichloride

10^6W	ε	V	$10^5\Delta n_D$
995	2·2967	1·1445	4
1240	2·3019	1·1444	5
1837	2·3167	1·1440	8
2173	2·3261	1·1438	7

$\varepsilon = 2{\cdot}2722 + 24{\cdot}38W$; $V = 1{\cdot}1448 - 0{\cdot}44W$; $\Delta n_D = 0{\cdot}034W$; ${}_EP = 60{\cdot}7$ c.c.; ${}_TP = 1287{\cdot}6$ c.c.; $\mu = 7{\cdot}74 \pm 0{\cdot}07$ D

4-Methylpyridine–boron trichloride

10^6W	ε	V	$10^5\Delta n_D$
1110	2·3157	1·1441	5
1549	2·3325	1·1438	6
1858	2·3406	1·1435	10
3264	2·3928	1·1430	13
3715	2·4104	1·1427	17

$\varepsilon = 2{\cdot}2738 + 36{\cdot}69W$; $V = 1{\cdot}1446 - 0{\cdot}506W$; $\Delta n_D = 0{\cdot}044W$; ${}_EP = 44{\cdot}3$ c.c.; ${}_TP = 1477{\cdot}3$ c.c.; $\mu = 8{\cdot}37 \pm 0{\cdot}06$ D

4-Cyanopyridine–boron trichloride

10^6W	ε	V	$10^5\Delta n_D$
694	2·2783	1·1442	—
1176	2·2827	1·1441	—
1510	2·2859	1·1439	—
2053	2·2906	1·1435	—

$\varepsilon = 2{\cdot}2725 + 8{\cdot}79W$; $V = 1{\cdot}1447 - 0{\cdot}508W$; ${}_EP = 47{\cdot}2$ c.c.;[a] ${}_TP = 407{\cdot}8$ c.c.; $\mu = 4{\cdot}20 \pm 0{\cdot}05$ D

4-Cyanopyridine 1-oxide

10^6W	ε	V	$10^5\Delta n_D$
318	2·2731	1·1443	5
483	2·2734	1·1444	2
494	2·2733	1·1444	2
570	2·2737	1·1443	6

$\varepsilon = 2{\cdot}2726 + 1{\cdot}56W$; $V = 1{\cdot}1446 - 0{\cdot}427W$; $\Delta n_D = 0{\cdot}063W$; ${}_EP = 30{\cdot}31$ c.c.; ${}_TP = 58{\cdot}9$ c.c.; $\mu = 1{\cdot}22 \pm 0{\cdot}13$ D

[a] It was impossible to measure refractive indices because the solute crystallised in the refractometer cell. The following values were used to obtain ${}_EP$: pyridine = 24·07 c.c.; H = 1·10 c.c.; CN = 5·54 c.c. (Landolt–Börnstein Tabellen) and BCl_3 = 18 c.c. (Phillips, Hunter, and Sutton *J.*, 1945, 146).

The computation of moments, and the notation used here, follow the pattern set by Everard, Hill, and Sutton [8] so that no allowance has been made for atom polarisation except where specifically stated, other than that implicit in using $[R]_D$ as the distortion polarisation. For molecules of such high polarity as in the present series this is of negligible effect. In one case it was impossible to measure the refractive index, because the solute crystallised in the refractometer cell. Tables of atomic and molecular refractions were used to obtain ${}_EP$. The values used are given at the foot of Table 2.

[5] Everard and Sutton, *J.*, 1951, 16.
[6] Hill and Sutton, *J.*, 1953, 1482.
[7] Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664.
[8] Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.

DISCUSSION

The mesomeric moment in a Z-substituted pyridine–boron trichloride complex may be defined as:

$$\mu_{\mathrm{m}}(\mathrm{ZPyBCl_3}) = \mu(\mathrm{ZPyBCl_3}) + [\mu(\mathrm{PyBCl_3}) - \mu(\mathrm{AlkZ})]$$

the analogous definitions for the mesomeric moments of substituted pyridines and pyridine 1-oxides adopted by Katritzky, Randall, and Sutton[1] being used. This mesomeric moment is therefore defined as the moment arising from the redistribution of electrons when Z is substituted into an aromatic system of some kind, relative to that which occurs when Z is substituted into a paraffin. As before,[1] in order that the mesomeric moment may be calculated it is assumed to have the same direction as in the corresponding benzene compound. The direction of the total moment can then be calculated. Table 3 gives the results together with other data taken from Katritzky *et al.*[1]

TABLE 3.

	Pyridine–boron trichloride: gross moments		Angle of mesomeric moment in substd. benzene[a]	Mesomeric moment magnitudes				Vectorial difference of pyridine–BCl_3 and pyridine moments	
4-Subst.	magnitude	angle		Substd. benzene	4-Substd. pyridines	4-Substd. pyridine–BCl_3	4-Substd. pyridine 1-oxide	magnitude	angle
OMe	8·86 ± 0·02	6°	12°	0·96	1·16	1·35	1·39	6·06	1½°
Cl	6·71 ± 0·03	0	0	0·41	0·57	1·02	0·59	5·93	0
Me	8·37 ± 0·06	0	0	0·35	0·39	0·67	0·50	5·76	0
H	7·70 ± 0·02	—	—	—	—	—	—	5·48	0
CO_2Et	7·74 ± 0·07	13	180	0·50	0·47	0·17	0·93	5·75	½
CN	4·20 ± 0·05	0	180	0·45	0·27	0·10	1·5[b]	5·85	0

[a] We define the gross and the mesomeric moment angles as in ref. 1, *i.e.*, if the moment acts along the Z–C bond, Z being the positive end of the dipole, then it has angle 0°. [b] ${}_{\mathrm{T}}P - {}_{\mathrm{E}}P = 30{\cdot}3$ c.c. (${}_{\mathrm{A}}P$ being neglected), if ${}_{\mathrm{A}}P = 11{\cdot}9$ c.c. (Finn, Hampson, and Sutton, *J.*, 1938, 1254, give ${}_{\mathrm{A}}P = 11{\cdot}9$ c.c. for *p*-dicyanobenzene), then ${}_{0}P = 18{\cdot}4$ c.c. and $\mu = 0{\cdot}95$ D. This resultant moment may be at either 0° or 180° (see footnote *a*). The mesomeric moments calculated for these two alternatives are 0·3 D at 0 and 1·5 at 180°. In all known cases, the C⋮N group is electron-attracting. We therefore take the latter value as more reasonable. This provides another example where the mesomeric moment of a pyridine 1-oxide with an electron-attracting 4-substituent is greater than that of the corresponding pyridine.[1]

It is seen that for the electron-releasing substituents OMe, Cl, and Me the mesomeric moments in the pyridine–boron trichloride complexes are greater than, but for the electron-accepting substituents CO_2Et and CN are smaller than, those in the corresponding pyridines. Somewhat surprisingly, the 1-oxide with a 4-chloro-substituent does not show a corresponding large increase of mesomeric moment relative to the pyridine. As was pointed out in the previous paper, this can be attributed to the power of the $^+N{-}O^-$ group to donate electrons to the ring when required. The dual behaviour of the chlorine atom, which can attract electrons or release them according to circumstances, is shown particularly clearly in this case.

An alternative way of using the dipole-moment data is to consider the vectorial difference between the moments of the pyridine–boron trichloride complexes and those of the substituted pyridines, giving the increase in total moment due to the co-ordination of the BCl_3 group. This is greater for all the substituted compounds than for the parent one, because (*a*) electron-releasing substituents release more into the pyridine–boron trichloride system than into the pyridine system and (*b*) electron-withdrawing groups take less out.

These results support the view[1] that the pyridine 1-oxide system can produce either an excess or a deficit of electrons at the 4-position as required by the substituent there. Independent infrared evidence of this effect has now been obtained and will be published as a separate paper.

This investigation was carried out during the tenure (by A. R. K.) of an I.C.I. Fellowship.

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[*Received, July 3rd,* 1957.]