412. *Infrared Absorption of Heteroaromatic and Benzenoid Six-membered Monocyclic Nuclei. Part VI.*[1] *Pyridine–Boron Complexes.*

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The infrared spectra of the pyridine and trimethyl amine adducts of boron tri-hydride and -halides and of some substituted pyridine-boron trichloride adducts are recorded and discussed.

FOLLOWING work [1] on the characteristic ring vibrations of monosubstituted benzenes, pyridines, and pyridine 1-oxides, we have now investigated the spectra of pyridines co-ordinated with boron compounds (in these adducts a spare pair of electrons is not available for back-co-ordination into the pyridine ring; contrast pyridine 1-oxide). To facilitate assignment of the BX_3 vibrations, the spectra of trimethylamine-boron tri-hydride and -halide adducts were also determined. 0·2M-Chloroform solutions were examined in a 0·117-mm. cell.[2] Conductivity and molecular-weight measurements showed that pyridine–boron trichloride is monomeric under the conditions of measurement.[3] All the bands ($\varepsilon_A \geqslant 15$) were characteristic of the pyridine ring co-ordinately linked to boron (Tables 1 and 4), the BX_3 group (Table 3), the NMe_3 group (Table 2), or the substituent (*e.g.*, the ester bands [2b]), and tentative assignments were made as indicated in the Tables.

Trimethylamine Adducts and Boron Hydride and Halide Modes (*Tables* 2 *and* 3).—In unpublished work,[4] Peterson and Bauer tentatively assigned the bands in the infrared spectra (Nujol and halogenocarbon mulls and potassium bromide disks) of trimethylamine–boron tri-hydride, -fluoride, and -chloride using a normal co-ordinate analysis of the chloro-compound. This work, which came to our notice late, considerably assisted the assignments given in Tables 2 and 3. These are as in the previous work [4] except that the 1001 cm.$^{-1}$ band in trimethylamine–borine is assigned to the asymmetric C–N stretching mode instead of a BH bending mode because this band is absent in pyridine–borine. The frequencies agree well, considering the difference in states, with the above and other work, *e.g.*, the B–H stretching frequencies in borine carbonyl occur [5] at 2434 and 2380 cm.$^{-1}$, and in gaseous trimethylamine–borine [6] the B–H stretching frequency occurs at 2390 cm.$^{-1}$ and the BH_3 bending frequency at 1178—1169 cm.$^{-1}$.

Pyridine Adducts (*Table* 1).—As expected, changes in the ligand have relatively little effect on the ring vibrations. The ring-stretching frequencies (cols. 2—5) have been discussed.[1] The frequencies given in cols. 6, 8, and 9 are assigned to CH in-plane deformation modes corresponding to those in monosubstituted benzenes at *ca.* 1155, 1073, and 1028 cm.$^{-1}$, respectively.[2a] The B–N stretching frequency is considerably shifted from its position for the trimethylamine complexes but is remarkably insensitive to changes in the boron compound.

4-*Substituted Pyridine-Boron Trichlorides* (*Table* 4).—In the 1600—1400 cm.$^{-1}$ region the four usual ring stretching frequencies are shown (cols. 1—4). The first band occurs near 1640 cm.$^{-1}$ but is lower for the chloro-compound (cf. other series [1]); the intensity decreases as the substituent becomes more electron-attracting. The intensity of the second band, at 1570—1555 [1564 ± 5] cm.$^{-1}$,* is higher for both electron-attracting and electron-donating substituents in the 4-position than for weakly interacting groups. Another band occurs at 1511—1492 cm.$^{-1}$, except for the compounds with electron-attracting substituents; the intensity is highest for the methoxy-compound. The position of the band

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* Parentheses indicate values of ε_A and square brackets arithmetical means and standard deviations.

[1] Part V, *J.*, 1958, 4162, and references therein.

[2] (*a*) Katritzky and Lagowski, *J.*, 1958, 4155; (*b*) Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.

[3] Bax, Katritzky, and Sutton, *J.*, 1959, 1258.

[4] Peterson and Bauer, " The Infrared Spectra of Lewis Salts," Cornell University report, 1955.

[5] Taylor, *J. Chem. Phys.*, 1957, **26**, 1131.

[6] Price, Frazer, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.

TABLE 1. *Pyridine complexes.*

No.	Ligand	1 $A_1 + B_1$ νCH cm.$^{-1}$	ε_A	2 A_1 $\nu\left\{{\rm CC \atop CN}\right.$ cm.$^{-1}$	ε_A	3 B_1 $\nu\left\{{\rm CC \atop CN}\right.$ cm.$^{-1}$	ε_A	4 A_1 $\nu\left\{{\rm CC \atop CN}\right.$ cm.$^{-1}$	ε_A	5 B_1 $\nu\left\{{\rm CC \atop CN}\right.$ cm.$^{-1}$	ε_A	6 B_1 βCH cm.$^{-1}$	ε_A	7 A_1 νBN cm.$^{-1}$	ε_A	8 B_1 βCH cm.$^{-1}$	ε_A	9 A_1 βCH cm.$^{-1}$	ε_A
1	BH_3	3010	20	1624	55	1580 *	10	1488	30	1459	130	(—)		1090	155	1060	10	1020	10
2	BF_3	3020	20	1630	100	1582 *	10	1493	25	1465	140	(—)		1102 †	340	1067 †	105	—	
3	BCl_3	2960	10	1636 1621	35 35	1610 *	15	1488	25	1459	130	1158	15	1095	195	—		1024	15
4	BBr_3	3080 3020	15 20	1630	115	1610 *	20	1490	50	1460	170	1160	20	1095	310	—		1025	30

TABLE 2. *Trimethylamine complexes.*

No.	Ligand	1 CH stretch cm.$^{-1}$	ε_A	2 CH stretch cm.$^{-1}$	ε_A	3 CH bend cm.$^{-1}$	ε_A	4 CH bend cm.$^{-1}$	ε_A	5 CH bend cm.$^{-1}$	ε_A	6 CH bend cm.$^{-1}$	ε_A	7 BN stretch cm.$^{-1}$	ε_A	8 CH_3 wag cm.$^{-1}$	ε_A	9 CN stretch asym. cm.$^{-1}$	ε_A	10 CN stretch sym. cm.$^{-1}$	ε_A
1	BH_3	3000	45	2940	35	1483	110	1462	125	1435 *	20	1405	20	1250	30	1118	50	1001	135	851	110
2	BF_3	3030	25	2950	25	1485	125	1463	100	1452	80	1408	15	1249	160	1103 †	250	991	100	831	230
3	BCl_3	2970	15	—		1489	70	1460	100	1452 *	60	1408	25	($CHCl_3$)		1111	55	970	190	(—)	
4	BBr_3	2960	10	—		1485	90	1458	90	1449 *	60	1405	35	($CHCl_3$)		1110	65	964	180	820	150

TABLE 3. BX_3 *vibrations.*

	νBH_3 asym. cm.$^{-1}$	ε_A	νBH_3 sym. cm.$^{-1}$	ε_A	BH_3 bend cm.$^{-1}$	ε_A	BH_3 wag cm.$^{-1}$	ε_A	asym. ν $^{10}BF_3$, $^{11}BF_3$ cm.$^{-1}$	ε_A	asym. ν $^{10}BF_3$, $^{11}BF_3$ cm.$^{-1}$	ε_A	sym. ν $^{10}BF_3$, $^{11}BF_3$ cm.$^{-1}$	ε_A	sym. ν $^{10}BF_3$, $^{11}BF_3$ cm.$^{-1}$	ε_A	asym. νBCl_3 cm.$^{-1}$	ε_A
Trimethylamine	2360	190	2260	110	1168	190	—		1150	430	1135 *	260	933 *	160	911	350	826	170
Pyridine	2350	165	2280 *	90	1165	170	920	25	1165	310	1125	280	912 *	240	893	430	818	55

TABLE 4. *Nuclear vibration bands.*

No.	Substituent	1 A_1 $\nu\left\{{\rm CC \atop CN}\right.$ cm.$^{-1}$	ε_A	2 B_1 $\nu\left\{{\rm CC \atop CN}\right.$ cm.$^{-1}$	ε_A	3 A_1 $\nu\left\{{\rm CC \atop CN}\right.$ cm.$^{-1}$	ε_A	4 B_1 $\nu\left\{{\rm CC \atop CN}\right.$ cm.$^{-1}$	ε_A	5 A_1 νBN cm.$^{-1}$	ε_A	6 A_1 βCH cm.$^{-1}$	ε_A	7 νBCl cm.$^{-1}$	ε_A
	4-Substituted pyridine–boron trichlorides														
1	OMe	1640 1605 *	250 45	1568	75	1511	160	1460 ‡	75	1095	250	1040	85	840 823	170 70
2	Me	1641 1606 *	160 20	1562	15	1509	30	1449	110	1092	200	1038	15	835	145
3	Et	1640	190	1560	15	1500	20	1448	155	1094	260	1052	40	843 818	75 190
4	Cl	1622	140	1555	20	1492 * 1472	60 30	1433	80	1076	270	1060 *	15	838	60
5	CO_2Et	1640	90	1570	40	—		1431	170	1076	310	1057 *	40	837 *	70
6	CO_2Me	1640	95	1567	50	—		1430	210	1077	290	1057 *	45	820	70
	4-Substituted pyridine–boron tribromide														
7	CO_2Et	1640	70	1565	45	—		1431	160	1074	410	1054	55	—	
	3-Substituted pyridine–boron trichlorides														
8	CO_2Me	1631	90	1592	25	1483	40	1441 ‡	250	1096	165	861	130	818	60
9	CO_2Et	1630	80	1590	20	1484 *	40	1440	125	1093	190	889	50	820	70

* Shoulder. ‡ Band considered to be two superimposed peaks. (—) Band hidden by other absorption. ($CHCl_3$) Band hidden by solvent. — Absence band. † Indicates that the band is strongly overlapped by BF absorption.

The symmetry type of the vibration (for approximate C_{2v} symmetry) is given directly underneath the column number in Tables 1 and 4.

at 1460—1430 cm.$^{-1}$ is lowered as the electron-accepting ability of the substituent increases; the intensity is (75—210) [(140 ± 50)].* The significance of these intensity variations has been discussed.[1]

The B–N stretching frequency (col. 5) occurs at 1095—1074 cm.$^{-1}$ (200—310) [(260 ± 35)]; its position is lowered as the electron-attracting power of the 4-substituent increases; this is as expected since the B–N bond will be weaker in these compounds. A band at 1054—1038 cm.$^{-1}$ (15—85) (col. 6) is assigned to a CH in-plane bending mode analogous to that at *ca.* 1018 cm.$^{-1}$ for *para*-disubstituted benzenes. The B–Cl stretching frequency (cf. Table 3) occurs at 843—820 cm.$^{-1}$ (60—190) (col. 7).

The nuclear bands of 4-ethoxycarbonylpyridine–boron tribromide (Table 4; No. 7) closely resemble those of the analogous trichloride, and, except for the B–N band, are included in the above ranges and statistical treatment. Table 4 also gives the nuclear bands of two 3-substituted pyridine–boron trichlorides.

Experimental.—The following were prepared as previously described.[7] 4-*Ethylpyridine–*, prisms (from ethanol), m. p. 109—111° (Found: C, 37·4; H, 3·9; N, 6·1. $C_7H_9NBCl_3$ requires C, 37·5; H, 4·0; N, 6·2%) and trimethylamine–boron trichloride (from ethanol), m. p. 237—240° (decomp.) [lit.,[8] m. p. 245° (corr.; decomp.)] (Found: C, 20·5; H, 5·3. Calc. for $C_3H_9NBCl_3$ C, 20·4; H, 5·2%).

Preparation of the other compounds has been described:[3,7] they were recrystallised or redistilled before measurement. Measurements were as previously.[1b]

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[7] Bax, Katritzky, and Sutton, *J.*, 1958, 1254.
[8] Phillips, Hunter, and Sutton, *J.*, 1945, 146.