445. *N-Oxides and Related Compounds. Part XIII.*[1] *Infrared Spectra of 4-Substituted Pyridine 1-Oxides.*

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In addition to bands due to the substituent, twenty-four 4-substituted pyridine 1-oxides showed, with few exceptions, ten characteristic bands in chloroform; their variations in intensity and position with the nature of the substituent are discussed.

In previous Parts of this series the NH stretching region of infrared spectra was used in studies of potentially tautomeric amines,[2] and the carbonyl stretching region was used in studies of the conjugating power of various nuclei.[1] Arising out of this work, measurement under standard conditions of monosubstituted benzenes, pyridines, pyridine 1-oxides, and pyridine–boron trichloride complexes has shown that (with few exceptions): (i) in any one compound the bands (with $\varepsilon_A \geqslant 15$) are characteristic of either (*a*) all compounds with the same nucleus or (*b*) all compounds with the same substituent; and (ii) the number, position, and intensity of the bands characteristic of any one nucleus or substituent are either reasonably constant, or vary in a regular manner with the electronic (and/or steric?) character of the nucleus to which the substituent is attached, or of the substituent to which the nucleus is attached.

This paper and the succeeding one discuss the bands characteristic of 4- and 2-substituted pyridine 1-oxides. Apparent molecular extinction coefficients are recorded (cf. ref. 1, where reference is made to the errors and approximations involved).

The infrared spectra of 4-monosubstituted pyridine 1-oxides have been little investigated previously. Costa and Blasina [3] discussed the variation of the position of the $^+N-O^-$ band in the chloro-, methoxy-, and nitro-compounds in Nujol mulls and carbon disulphide solution; the amino- and hydroxy-compounds were insoluble in suitable solvents and this hindered interpretation.[4] The methyl and ethyl compounds were measured by Shindo [5] in part of a general investigation of alkylpyridine 1-oxides; 4-picoline 1-oxide has also been measured.[6] In so far as our results are comparable with this work, good agreement is found, considering the change of state or solvent.

The 3000 *cm.*$^{-1}$ *Region.*—The sodium chloride prism resolves one band only at 3010—2940 cm.$^{-1}$ (50—145) [2980 $\pm$ 16 cm.$^{-1}$ (110 $\pm$ 23)].* As pointed out by Wiley and Slaymaker,[6] *N*-oxides in chloroform solution absorb hereabouts because hydrogen bonding lowers the solvent CH stretching frequency so that it is no longer compensated; absorption in this region is less for the corresponding pyridine which should form weaker hydrogen bands, and very weak or absent in the non-bonded pyridine–boron trihalide complexes.[7] In agreement, the band becomes on the average less intense, and occurs at slightly higher frequencies, on going from electron-donor to electron-acceptor substituents.

The 1600 *cm.*$^{-1}$ *Region.*—The position of the single band (col. 2) varies from 1647 to 1609 cm.$^{-1}$ as the substituent changes from strongly electron-donating to strongly electron-attracting: an exception is the bromo-compound (No. 18) absorbing at 1605 cm.$^{-1}$; a heavy atom attached directly often lowers the frequency of a nuclear band.[7] The pyridine 1-oxide nucleus can either accept or release electrons at the 4-position,[2, 8] and this is probably why the intensity of this band depends on the magnitude of the conjugative

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* For the significance of parentheses and brackets see Part XII (footnote p. 2187).[1]

[1] Part XII, Katritzky, Monro, Beard, Dearnaley, and Earl, preceding paper.
[2] Part V, Gardner and Katritzky, *J.*, 1957, 4375.
[3] Costa and Blasina, *Z. phys. Chem.* (*Frankfurt*), 1955, **4**, 24.
[4] Costa, Blasina, and Sartori, *ibid.*, 1956, **7**, 123.
[5] Shindo, *Pharm. Bull.* (*Japan*), 1956, **4**, 460.
[6] Wiley and Slaymaker, *J. Amer. Chem. Soc.*, 1957, **79**, 2233.
[7] Katritzky and co-workers, unpublished results.
[8] Part IX, Katritzky, Randall, and Sutton, *J.*, 1957, 1769.

ability of the substituent and not on its type. For 4-substituted pyridines, where the nucleus conjugates effectively only with electron-donating substituents,[2,8] the corresponding band is intensified by such substituents, but weakened by electron-accepting substituents.[7]

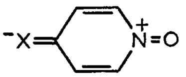
The 1500—1400 *cm.*$^{-1}$ *Region.*—Two bands are found. That of higher frequency (col. 3) is at 1492—1470 [1483 ± 6] cm.$^{-1}$, except for the amines (Nos. 1 and 2) where it is considerably higher, and for the halogen compounds (Nos. 17 and 18) where it is lower (cf. above). For the compounds without a strongly electron-withdrawing substituent (Nos. 1—19) the intensity is (170—420) [(260 ± 70)]; for the others it is lower (100—120) except for the nitro-compound (250).

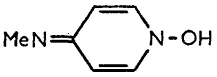
The other band (col. 4) occurs at 1456—1431 [1443 ± 7] cm.$^{-1}$; interpretation of the variable intensity (20—140) is difficult because of overlap with aliphatic CH deformations of the substituents. Absorption for, *e.g.*, the halogen compounds, and comparison with that of other nuclei shows that a nuclear bands does indeed occur here.

The 1300—1240 *cm.*$^{-1}$ *Region.*—The strong $^{+}\mathrm{N}{-}\mathrm{O}^{-}$ stretching frequency already reported[3,5] is obscured by solvent absorption for compounds with strongly electron-donating substituents (Nos. 1—5). The frequency is raised by electron-accepting substitutents; as pointed out elsewhere,[3,5] this is because canonical forms as (I) become important and increase the double-bond character of the $^{+}\mathrm{N}{-}\mathrm{O}^{-}$ linkage. The intensities are (220—400) [(310 ± 55)], and tend to increase with increasing electron-withdrawing ability of the substituent.

The 1200—1000 *cm.*$^{-1}$ *Region.*—One band (col. 6) is at 1181—1159 [1169 ± 5] cm.$^{-1}$; for amines and ethers (Nos. 1—5) the intensity is relatively low (65—80), for the esters (Nos. 19, 21, 22) it is high (420—510), otherwise it is (110—320) [(200 ± 50)].

(I)





(II)

A second band (missing from the spectrum of the dimethylamino-compound) is at 1118—1089 [1101 ± 7] cm.$^{-1}$; except for the halogeno-compounds (Nos. 17, 18) (which often have more intense nuclear bands in this region [7]) and the ethoxy- and methoxy-carbonyl compounds (strong overlap with substituent bands) the intensity is (5—35) [(20 ± 10)].

A third band is at 1044—1023 cm.$^{-1}$ (30—85) [1033 ± 5 cm.$^{-1}$ (55 ± 15)]; the frequency seems to be lowered somewhat by both strongly electron-donating and electron-attracting substituents.

The 800 *cm.*$^{-1}$ *Region.*—Two bands are generally found; probably one is a ring hydrogen deformation, and the other corresponds to the band at 838 cm.$^{-1}$ (220) for pyridine oxide itself: a band in this region was originally assigned to the $^{+}\mathrm{N}{-}\mathrm{O}^{-}$ stretching frequency; [9] it has been found in the spectrum of pyrimidine oxides.[6] The bands occur at 860—842 cm.$^{-1}$ (15—270) [852 ± 6 cm.$^{-1}$ (75 ± 60)] and at 855—820 cm.$^{-1}$ (50—250) [836 ± 9 cm.$^{-1}$ (180 ± 55)] and are considered to be superimposed in spectra of Nos. 15, 21, and 22.

Assignments.—Randle and Whiffen's work on *para*-substituted benzene derivatives[10] suggests the assignments given at the head of the Table. The mean positions of the bands are within about 20 wave-numbers in the two groups of compounds; the main difference is that there are no bands in the spectra of 4-substituted pyridine 1-oxides corresponding to those at [1571 ± 11] and [961 ± 12] cm.$^{-1}$ for the *para*-substituted benzene derivatives. It is not yet possible to compare intensities in the two groups of compounds.

This work supports the conclusion[1] that 4-methylaminopyridine 1-oxide exists as such and not in the imino-form (II).

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[9] Ito and Hata, *Bull. Chem. Soc. Japan*, 1955, **28**, 353.

[10] Randle and Whiffen, Paper No. 12, Report on Conference on Molecular Spectroscopy 1954, Institute of Petroleum.

		1[a]		2		3		4		5	
		CHCl$_3$		A_g		B_{2u}		B_{3u}		—	
		νCH		νCC νCN		νCC νCN		νCC νCN		ν$^+$N–O$^-$	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	NHMe	2960	120	1647	135	1525 1498 *	170 120	1431	50	1194	80
2	NMe$_2$	2940	135	1642	140	1517	280	1447 ‡	165	(1230	80)
3	OMe	2970	145	1635	60	1492	250	1440 ‡	135	(1232	165)
4	OEt	2960	120	1636	60	1491	250	1448 ‡	50	(1215	175)
5	O·CH$_2$Ph	2970	130	1629	45	1485 ‡	360	1456 ‡	105	(1220	160)
6	NMe·COMe	2980	105	1625	65	1483	420	1440	65	1248	260
7	NMe·COPh	3000	135	1626 *	110	1487 ‡	520	1451 ‡	100	1248	310
8	Me	2980	140	1622	5	1486	200	1442	20	1247	220
9	Et	2980	115	—		1484	190	1450	60	1242	230
10	CH$_2$·CH$_2$Ph	2960	115	(—)		1487 ‡	280	1451 ‡	90	1243	250
11	CH$_2$Ph	2960	100	(—)		1485 ‡	280	1450 ‡	80	1243	260
12	CH$_2$·C$_6$H$_4$·NO$_2$-*p*	2970	90	(—)		1484 ‡	310	1449	75	1246	260
13	C⋮CPh[b]	3000	125	(—)		1475	195	1445 ‡	50	1260	370
14	CH:CHPh	2980	100	1620 *	15	1485	300	1452 ‡	75	1251	340
15	Ph	2980	85	1622 *	15	1473	210	1431	35	1248	270
16	S·CH$_2$Ph	2990	130	(—)		1488	285	1435	95	1246	300
17	Cl	2990	115	—		1464	215	1438	85	1251	300
18	Br	2970	95	1605	30	1461	350	1432	100	1250	320
19	CH:CH·CO$_2$Et	2990	120	1618	115	1487	280	1449	140	1258	400
20	CN[c]	(CHCl$_3$)		1615	150	1472	110	(CHCl$_3$)		1282	350
21	CO$_2$Et	2980	125	1616	155	1483	120	1445	110	1258 ‡	570
22	CO$_2$Me	2980	75	1616	115	1484	100	1444	110	1261 ‡	600
23	COMe[d]	2990	95	1611	190	1481	100	1438	55	1253	390
24	NO$_2$[e]	3010	50	1609	210	1470	250	1442 *	30	1294 1283	400 400

		6		7		8		9		10	
		A_g		B_{3u}		B_{2u}		—		B_{1u}	
		βCH		βCH		βCH		? $^+$N–O$^-$		γCH	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	NHMe	1176	80	1095	5	1029	55	853	35	825	145
2	NMe$_2$	1181 ‡	120	—		1030	70	845 *	40	829 818	170 180
3	OMe	1168	75	1099	15	1027 ‡	290	856	50	835	230
4	OEt	1169	70	1102 *	20	1029 *	145	855	75	838	185
5	O·CH$_2$Ph	1166	65	1099	15	1026 *	115	857	15	834	240
6	NMe·COMe	1165	115	(—)		1030	55	844	145	836 *	110
7	NMe·COPh	1172	175	(—)		1044	45	860	15	843	200
8	Me	1173	170	1112	5	1041	60	855	75	828	200
9	Et	1170	175	1110	10	1038	55	850	80	839	185
10	CH$_2$·CH$_2$Ph	1171	220	1098	10	1038	50	844	65	832 824 *	100 70
11	CH$_2$Ph	1170	220	1098	15	1039	50	858	55	844 813	50 40
12	CH$_2$·C$_6$H$_4$·NO$_2$-*p*	1171	230	1100	25	1037	40	860	90	828	80
13	C⋮CPh[b]	1170	220	1095	25	1032 ‡	130	842	270	820	155
14	CH:CHPh	1168	260	1095	15	1032 ‡	110	860	70	844 824	45 130
15	Ph	1172	185	1100	15	1036	40	844 ‡	190	844 ‡	190
16	S·CH$_2$Ph	1175	220	1110	25	1034	70	844	100	827	155
17	Cl	1168	180	1116	55	1033	30	845	60	834	225
18	Br	1167	200	1118 1089	40 60	1032	35	849 *	20	840 832	65 240
19	CH:CH·CO$_2$Et	1165	500	1105	35	1032 ‡	185	855	25	836 815	250 65
20	CN[c]	1163	240	1097	20	1029	50	(CHCl$_3$)		(CHCl$_3$)	
21	CO$_2$Et	1159	510	1104	90	1030 *	50	855 ‡	165	855 ‡ 835	165 25
22	CO$_2$Me	1160	420	1102	50	1030	45	855 ‡	195	855 ‡	195
23	COMe[d]	1164	320	1100	15	1029	80	849 *	100	843	210
24	NO$_2$[e]	1168	110	1089	30	1023	85	(—)		852	220

* Shoulder. ‡ Absorption considered to be the superimposition of two peaks. — Absence of absorption. (—) Band masked by stronger absorption. (CHCl$_3$) Band masked by solvent.

[a] Tentative assignments of symmetry and type of vibration (cf. ref. 10) are given directly under the column numbers. [b] Extra band shown at 1145 cm.$^{-1}$ (85). [c] Measured at 0·01M-concentration in a 1 mm. cell because of low solubility. [d] Extra band shown at 1542 cm.$^{-1}$ (15). [e] Band at 1609 cm.$^{-1}$ is split, with another component at 1589 cm.$^{-1}$ (135).

EXPERIMENTAL

Preparation of Materials.—The preparation of most of the compounds has already been described.[1, 2, 8, 11] Compounds were recrystallised or distilled immediately before measurement.

4-*Benzylthiopyridine* 1-*Oxide.*—4-Chloropyridine 1-oxide was added gradually to ethanolic sodium benzyl sulphide (from 1·24 g. of toluene-ω-thiol with sodium ethoxide from 0·23 g. of sodium and 15 c.c. of ethanol). The mixture was refluxed for 45 min. Solid carbon dioxide was added, the whole filtered, and the filtrate evaporated. The residue was taken up in chloroform, centrifuged, and again evaporated, to give the *oxide* (1·0 g., 46%), yellowish plates (from ethyl acetate), m. p. 147—149° (Found: C, 66·0; H, 5·2; N, 6·4; S, 14·5. $C_{12}H_{11}ONS$ requires C, 66·3; H, 5·5; N, 6·4; S, 14·8%).

4-Ethylpyridine, oxidised by peracetic acid in the normal way, gave the 1-oxide (84%), deliquescent prisms (from ethyl acetate), m. p. 106—109° (Found: C, 68·3; H, 7·5. Calc. for C_7H_9ON: C, 68·3; H, 7·4%) (lit.,[12] m. p. 100—120°).

Measurement of Spectra.—A Perkin-Elmer Model 21 instrument was used, with a sodium chloride prism, slit programme 4, and the settings previously [1] given. The compounds were measured in purified chloroform in a 0·117 mm. cell, at 0·2M-concentration.

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[11] See also Katritzky and his co-workers, *J.*, 1956, 2063, 2404; 1957, 191, 4385; 1958, 150, 1263.

[12] Shimizu, Naito, Ohta, Yoshikawa, and Dohmori, *J. Pharm. Soc.* (*Japan*), 1952, **72**, 1474; *Chem. Abs.*, 1953, **47**, 8077.