446. N-*Oxides and Related Compounds. Part XIV.*[1] *Infrared Spectra of 2-Substituted Pyridine 1-Oxides.*

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The positions and intensities of twelve characteristic bands are recorded and discussed for twenty-four 2-substituted pyridine 1-oxides.

After our work[1] on 4-substituted pyridine 1-oxides we report the spectra of some 2-analogues. Only the 2-methyl compound had been investigated previously.[2, 3]

The 3000 *cm.$^{-1}$ Region.*—The hydrogen-bonded chloroform CH stretching frequency[1] is found at 3010—2950 cm.$^{-1}$ (40—175) [2985 ± 15 cm.$^{-1}$ (95 ± 30)].

The 1650—1550 *cm.$^{-1}$ Region.*—The main band (col. 2 of the Table) is at 1640—1596 cm.$^{-1}$. Electron-donors tend to raise, and electron-attracting groups and heavy atoms (S, Cl) to lower, the frequency. Intensity variation is also significant; electron-donors increase markedly the low values observed with saturated substituents (*e.g.*, No. 11). Increase of the intensity by electron-acceptors is less (contrast 4-substituted pyridine 1-oxides[1]; cf. the reluctance of pyridine 1-oxides to release electrons at the 2-position[4, 5]).

A second band sometimes found (col. 3) is strong only with electron-donating substituents; in the amido-compounds it is stronger than the band just discussed. The position is 1577—1550 cm.$^{-1}$ except for the esters.

The 1500—1400 *cm.$^{-1}$ Region.*—Two bands are shown. The first (col. 4) occurs above 1500 cm.$^{-1}$ for the ether and amines (Nos. 1—5), otherwise at 1500—1470 cm.$^{-1}$ [1483 ± 9]. Its intensity falls from *ca.* (200) in the compounds with strongly electron-donating substituents (except No. 1 where the band is split) to low values for electron-attractors; chlorine and sulphur here appear to act as electron-donors.

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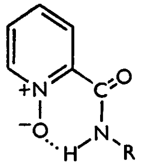
[1] Part XIII, Katritzky and Gardner, *J.*, 1958, 2192.
[2] Shindo, *Pharm. Bull.* (*Japan*), 1956, **4**, 460.
[3] Wiley and Slaymaker, *J. Amer. Chem. Soc.*, 1957, **79**, 2233.
[4] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 2182.
[5] Hands and Katritzky, *J.*, 1754.

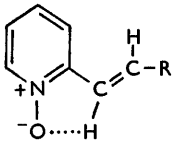
		1[a]		2		3		4		5		6	
		CHCl$_3$		A_1		B_1		A_1		B_1		—	
		νCH		νCC νCN		νCC νCN		νCC νCN		νCC νCN		?N$^+$–O$^-$	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	NH$_2$	2970	70	1640	190	1577	100	1548 1503	45 55	1449	80	—	
2	NHMe	2950	65	1628	230	1574	160	1533	145	1453	60	(—)	
3	NMe$_2$	2970	90	1618	230	1560	115	1510	220	1444 ‡	150	—	
4	OMe	2970	130	1613	105	1570	95	1503	200	1446	160	—	
5	OEt	2990	175	1617	175	1570	160	1504	290	1441	175	(—)	
6	NH·COMe	3000	90	1617	145	1572	280	1478	135	1428	350	(—)	
7	NH·COPh	2990	70	1612	140	1574	330	1482	200	1430	320	(—)	
8	NH·CO·Morph[b]	2990	140	1620	165	1577	370	1492 *	310	(—)		(—)	
9	NH·CO$_2$Et	3000	130	1620	140	1578	340	1487	175	1435	280	(—)	
10	NMe·COPh	3000	100	1610	90	1551	45	1500	280	1435	175	(—)	
11	Me	2970	110	1615	15	—		1491	105	1456	135	—	
12	CH$_2$·CH$_2$Ph	2970	100	(—)		—		1491 ‡	105	1441	170	1273 *	45
13	CH$_2$Ph	2970	85	(—)		—		1490 ‡	105	1437	185	1282	55
14	CH$_2$·C$_6$H$_4$·NO$_2$-*p*	2990	105	(—)		—		1490	145	1438	210	1282 *	60
15	CH:CHPh	2970	85	1610 ‡	50	1550	20	1484	95	1431	150	1303	45
16	Ph	2970	70	(—)		—		1478 ‡	130	1417	110	1295 *	20
17	C$_6$H$_4$·NO$_2$-*m*	2980	50	(—)		—		1471	60	1415	100	1290 *	35
18	S·CH$_2$Ph	3000	135	1594	35	1556	25	1471	220	1425	175	1270	125
19	Cl	3000	85	1602	5	—		1470	180	1427	150	1272	280
20	CH:CH·CO$_2$Et	2990	100	1610	25	—		1482	60	1431	185	(—)	
21	CN	3000	40	1602	15	—		1485	85	1430	240	1295	230
22	CO$_2$Et	2990	95	1610	30	1535	15	1483 *	25	1431	210	1270 *	155
23	CO$_2$Me	3010	90	1610	40	1537	15	1483	25	1430	200	1278 *	140
24	COMe	3000	80	1606	60	—		1479 *	10	1432	230	1284 *	60

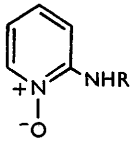
		7		8		9		10		11		12	
		—		?		A_1		B_1		A_1		A_2	
		νN$^+$–O$^-$		?		βCH		βCH		βCH		γCH	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	NH$_2$	(CHCl$_3$)		1190	95	1152	20	1128	70	—		866	45
2	NHMe	(CHCl$_3$)		1189	95	1157 ‡	150	1100	20	1039	10	839	40
3	NMe$_2$	(CHCl$_3$)		1176 ‡	280	1143 ‡	95	1110	60	1055 ‡	60	839	160
4	OMe	(CHCl$_3$)		1179	95	1153	30	1118	140	1052	45	843	80
5	OEt	(CHCl$_3$)		1195 *	120	1156	35	1120 ‡	230	1052	40	836	120
6	NH·COMe	(1235	230)	1198 *	220	1150	35	1105	60	1040	30	853 821	45 95
7	NH·COPh	1260	245	1175 *	55	1150	25	1107	35	1040	20	863 810	70 20
8	NH·CO·Morph[b]	(CHCl$_3$)		1175 *	80	1150	30	(—)		(—)		840	80
9	NH·CO$_2$Et	1252 ‡	530	1180 *	130	1150 *	140	1104	80	1040 ‡	100	854	75
10	NMe·COPh	1268	320	1174	60	1150	25	1122	90	1043	25	834	100
11	Me	1244	230	(CHCl$_3$)		1150	10	1111	40	1049	25	851	185
12	CH$_2$·CH$_2$Ph	1245	185	1174	25	1142	35	1103	5	1048	15	877 847	20 60
13	CH$_2$Ph	1247	190	1175	55	1153	20	1100	10	1047	10	861	110
14	CH$_2$·C$_6$H$_4$·NO$_2$-*p*	1250	260	1180 *	95	1155	35	1112 ‡	80	1048	25	871 861 *	90 120
15	CH:CHPh	(1235	180)	1177	85	1150	40	1097	10	1045	15	856	80
16	Ph	1242	230	1185 *	40	1150	20	1111	30	1039	10	846	135
17	C$_6$H$_4$·NO$_2$-*m*	1245	230	(—)		1153	20	1113	30	1037	35	842	120
18	S·CH$_2$Ph	1248	150	(CHCl$_3$)		1144	145	1092	95	1044	35	839	115
19	Cl	1257	200	1167	15	1145	190	1085	115	1042	25	849	145
20	CH:CH·CO$_2$Et	1268	250	(—)		1152	90	1110	25	1038	100	854 822	35 20
21	CN	1265	135	1190	70	1150	85	1100	5	1038	20	857	155
22	CO$_2$Et	1250	200	(—)		1150 *	110	1094 ‡	120	1044	50	853 831	30 20
23	CO$_2$Me	1255	200	1165 *	35	1151	75	1094 ‡	90	1045	50	856 815	110 10
24	COMe	1257	110	(—)		1148	50	1113	50	1042	50	851	110

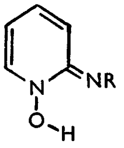
[a] See footnote p. 2187 and also for meaning of other symbols. [b] Morpholide.

The second band (col. 5) occurs at 1456—1415 cm.$^{-1}$. Amines and ethers (Nos. 1—5) absorb at 1453—1441 cm.$^{-1}$, but amido-compounds (Nos. 6—10) at 1435—1428 cm.$^{-1}$, near the compounds with electron-attracting substituents (Nos. 21—24) at 1432—1430 cm.$^{-1}$. The band for the methyl compound is at 1456 cm.$^{-1}$, and for the methylene compounds (Nos. 12—14) at 1441—1437 cm.$^{-1}$; the position is lowered by attachment to a double bond (Nos. 15, 20; at 1431 cm.$^{-1}$), a heavy atom (Nos. 18, 19; at 1427—1425 cm.$^{-1}$), and an aromatic ring (Nos. 16, 17; at 1417—1415 cm.$^{-1}$). The intensity is (60—350) [(185 ± 70)].


(I)


(II)


(III)


(IV)

The 1300—1240 *cm.*$^{-1}$ *Region.*—The $^{+}$N^{-}O^{-} stretching band (col. 7) occurs at 1274—*ca.* 1220 cm.$^{-1}$. Compounds with weakly conjugating substituents (Nos. 11—14, 16—18) absorb at 1250—1242 cm.$^{-1}$; the frequency is raised by electron-acceptors (Nos. 21—24), and apparently lowered for the amines and ethers (Nos. 1—5). The position is variable for amido- (Nos. 6—10) and ethylenic compounds (Nos. 15 and 20), probably because of varying importance of interactions as in (I) and (II). The intensity is (110—320); [(210 ± 55)].

Compounds with saturated or electron-attracting substituents show a shoulder or subsidary band (col. 6) at higher frequencies than those of the main $^{+}$N^{-}O^{-} stretching band; in the chloro- and cyano-compounds it is stronger than the " main " band.

The 1200—1000 *cm.*$^{-1}$ *Region.*—Four bands are shown. The first (col. 8) is unobscured by solvent or substituent absorption in only nine compounds, 1190—1165 cm.$^{-1}$ (15—95) [1178 ± 8 cm.$^{-1}$ (65 ± 30)].

The second band (col. 9) is at 1157—1142 cm.$^{-1}$ [1150 ± 4]; the intensity is moderate for the chloro- and benzylthio-compounds (known to have nuclear bands strengthened in this region [6]) and where electron-accepting substituents are present (Nos. 20—24), but otherwise weak (10—40) [(25 ± 10)].

The third band (col. 10) is at 1128—1085 [1106 ± 10] cm.$^{-1}$; higher frequencies are found with electron-donating substituents (Nos. 1—10), and lower with heavy atoms (S, Cl). The intensity is (20—140) [(75 ± 35)] with electron-donating substituents, including chlorine and benzylthio (*i.e.*, Nos. 1—10, 18, 19), but in the other compounds (5—50) [(25 ± 20)].

The fourth band (col. 11), absent for the amino-compound, is otherwise at 1055—1037 [1044 ± 5] cm.$^{-1}$; the intensity is (10—50) [(25 ± 15)] (except in No. 19, strongly overlapped by a substituent band).

The 800 *cm.*$^{-1}$ *Region.*—All the compounds show one band at 866—834 cm.$^{-1}$ (30—185) [849 ± 9 cm.$^{-1}$ (95 ± 40)]. Often a subsidary band or shoulder is shown.

Assignments.—Comparison with Randle and Whiffen's data [7] on *ortho*-substituted benzene derivatives suggests the assignments at the head of the Table. Nothing corresponding to the bands from these benzene derivatives at [1315 ± 11 (m), 977 ± 9 (w), 934 ± 11 (w) cm.$^{-1}$] was found, and the band in col. 8 does not correspond to a band in these compounds, but otherwise agreement is quite good (means usually within 15 wave numbers). Absorption analogous to that below 800 cm.$^{-1}$ in *ortho*-substituted benzene derivatives would be obscured by the solvent in our work.[4]

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[6] Katritzky *et al.*, preceding and following papers and unpublished work.

[7] Randle and Whiffen, Paper No. 12, Conference on Molecular Spectroscopy, 1954, Institute of petroleum, p. 111.

This work supports our conclusions[8] that 2-methylamino- and 2-amino-pyridine 1-oxide exist as (III) and not in the imino-forms (IV) and indicates that acylamino-compounds behave similarly.

Experimental.—See ref. 1 for sources of specimens and measurements of spectra.

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[8] Gardner and Katritzky, *J.*, 1957, 4375.