748. N-*Oxides and Related Compounds. Part XVI.*[1] *Infrared Spectra of 3-Substituted Pyridine* 1-*Oxides.*

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The positions and intensities of ten characteristic bands are recorded and discussed for nineteen 3-substituted pyridine 1-oxides. The preparation of several new oxides is described.

PREVIOUS Parts have recorded the spectra of 2-[2] and 4-substituted pyridine 1-oxides;[3] we now report on some 3-analogues. For reasons which have been given[4] the spectra were measured at 0·2M concentration in purified chloroform in a 0·117 mm. cell and apparent molecular extinction coefficients were recorded. The errors and approximations involved therein have been noted,[4] as has the reproducibility to be expected on different machines under these conditions.[5] The infrared spectra of eleven 3-substituted pyridine 1-oxides (variously in CCl_4, $CHCl_3$, CS_2, or as mulls) have been discussed by Shindo;[6] this work is compared with ours below.

The 3000 cm.$^{-1}$ *Region.*—The hydrogen-bonded chloroform CH stretching frequency (cf. refs. 1, 2) is found at 3020—2965 cm.$^{-1}$ (70—170) [2985 ± 15 cm.$^{-1}$ (120 ± 30)].*

Ring CC *and* CN *Stretching Frequencies in the* 1600—1400 *cm.*$^{-1}$ *Region.*—The four bands expected in this region are found (Table 1, cols. 2—5) at 1612—1598 [1605 ± 4] cm.$^{-1}$, 1570—1558 [1565 ± 3] cm.$^{-1}$, 1490—1468 [1480 ± 6] cm.$^{-1}$, and 1440—1425 [1434 ± 5] cm.$^{-1}$ (except that the final band absorbs at 1417 in the 3-phenyl-compound). These positions agree reasonably well with those found by Shindo:[6] 1610—1587, 1573—1538, 1499—1471 and 1456—1427 cm.$^{-1}$.

The intensities of the first three of these bands depend on the nature of substituent (electron-donor substituents increasing the intensity) but the intensity of the fourth band varies comparatively little (Table 2). These intensity variations have already been discussed and correlated with the symmetry of the particular vibration and the charge distribution in the ring.[7]

N^+–O^- *Stretching Band.*—This is found at 1308—*ca.* 1230 cm.$^{-1}$ (Table 1, col. 6). The intensity is (185—370) [(275 ± 65)]. The position of the band rises in general with increasing electron-acceptor properties of the substituent, but detailed correlation is difficult for the band is split into two components in the methyl-, chloro-, cyano-, and nitro-derivatives and is overlapped by strong substituent absorption in the carbonyl compounds.

CH *In-plane Bending Modes.*—Of the four possible modes of this type, only one is identified at 1160—1150 [1156 ± 2] cm.$^{-1}$ (Table 1, col. 8). The intensities depend on the electron-donor power of the substituent: OR (390—400) > Me (290) > unsaturated carbon (220—230) > chloro (70) > strong electron-acceptors (30—45) except that the cyano- (185) and phenyl compound (125) are respectively stronger and weaker than expected. This mode was found by Shindo[6] at 1191—1153 (m—s) and probably corresponds to that in *meta*-disubstituted benzenes at [1157 ± 5] cm.$^{-1}$,[8] the intensity of which

* Parentheses enclose apparent extinction coefficients; square brackets enclose arithmetical means and standard deviations. The position of shoulders and the intensity of shoulders and superimposed bands were not used in the statistical treatment.

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[1] Part XV, Katritzky, Monro, and Beard, *J.*, 1958, 3721.
[2] Katritzky and Hands, *J.*, 1958, 2195.
[3] Katritzky and Gardner, *J.*, 1958, 2192.
[4] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.
[5] Katritzky and Lagowski, *J.*, 1958, 4155.
[6] Shindo, *Chem. Pharm. Bull. Japan*, 1958, **6**, 117; 1956, **4**, 460.
[7] Katritzky, *J.*, 1958, 4162.
[8] Katritzky and Simmons, *J.*, 1959, 2058

TABLE 1.

No.	Substituent	$CHCl_3$ νCH cm.$^{-1}$	ε_A	A_1 $\nu\begin{cases}\mathrm{CC}\\\mathrm{CN}\end{cases}$ cm.$^{-1}$	ε_A	B_1 $\nu\begin{cases}\mathrm{CC}\\\mathrm{CN}\end{cases}$ cm.$^{-1}$	ε_A	A_1 $\nu\begin{cases}\mathrm{CC}\\\mathrm{CN}\end{cases}$ cm.$^{-1}$	ε_A	B_1 $\nu\begin{cases}\mathrm{CC}\\\mathrm{CN}\end{cases}$ cm.$^{-1}$	ε_A	ν^+N–O$^-$ cm.$^{-1}$	ε_A	? cm.$^{-1}$	ε_A	B_1 βCH cm.$^{-1}$	ε_A	B_1 Ring cm.$^{-1}$	ε_A	B_2 γCH cm.$^{-1}$	ε_A	A_2 γCH cm.$^{-1}$	ε_A	*a*
1	OEt	2970	140	1602	115	1565	170	1490	175	1440	130	($CHCl_3$)		1179	280	1156	400	1011	80	993 987*	95 60	843	30	*b*
2	OMe	2970	120	1605	150	1566	175	1488	170	1438†	160	(1238	100)	1190	135	1169 1150	170 390	1008	140	965	115	844	30	*b*
3	Me	2970	125	1608	85	1568	20	1482	90	1428	65	1278 1268	215 190	1165*	170	1158	290	1017	125	946	75	891	15	—
4	CH_2CO_2Et	2980	150	1610	95	1560	25	1485	100	1440†	240	1270	370	($CHCl_3$)		1156†	350	1019	160	982	100	874	35	*c*
5	Ph	2980	115	1606	115	1564	45	1472†	120	1417	115	1308	185	1190	100	1160	125	1015	135	900	175	870	45	*d*
6	$CH{:}CHCO_2Et$	2975	105	1602	110	1563	35	1484	130	1433	155	1262	330	($CHCl_3$)		1157	230	1015	120	(—)		857	70	*c*
7	$CH{:}CHCO_2Pr^n$	2975	145	1598	90	1562	30	1482	105	1430	130	1262	320	(—)		1155	230	1015	160	990*	55	855	60	*e*
8	$CH{:}CHCO_2Bu^n$	2965	170	1600	80	1558	25	1482	100	1432	140	1261	330	(—)		1155	220	1015	140	(—)		856	55	*e*
9	Cl	3000	90	1600	120	1565	15	1470	160	1426	175	1293 1260 1250*	175 195 150	—		1155	70	1015	145	917	275	853	50	—
10	CN	3020	70	1605	85	1560	25	1477	75	1425	115	1307 1290	220 230	—		1153	185	1015	190	958	110	868	55	*f*
11	CO_2Me	3120 3010	30 105	1610	75	1570	35	1482	60	1442†	270	1307†	570	($CHCl_3$)		1158	40	1017	175	997	115	890	35	*c*
12	CO_2Et	2980	85	1602	45	1566	20	1475	50	1436	165	1298†	560	—		1156	40	1014†	230	952	60	889	25	*c*
13	CO_2Pr^n	2975	135	1608	45	1568	20	1480	60	1437	170	1296†	500	—		1158	40	1015	165	966	90	889	40	*e*
14	CO_2Pr^i	2995	125	1610	50	1568	25	1480	55	1436	180	1296†	510	1180*	50	1158	35	1016	170	961	165	890	25	*e*
15	CO_2Bu^n	2980	145	1607	50	1565	20	1477*	45	1435	160	1295†	510	—		1154	35	1014	160	957	65	888	25	*e*
16	CO_2Bu^i	2995	165	1612	45	1566	20	1480*	55	1437	175	1296‡	480	($CHCl_3$)		1158	35	1016	150	985	135	888	35	*e*
17	CO_2Bu^s	2980	150	1609	45	1568	25	1480	60	1436	180	1297†	480	1172*	35	1157	35	1015	175	956	105	888	30	*e*
18	COMe	2990	90	1606	45	1561	25	1477	20	1433	145	1280	280	—		1159	45	1014	125	925	30	896	70	*c*
19	NO_2	2970	70	1620*	15	(—)		1468	90	1440	160	1290 1257	300 260	—		1154	30	1012	190	949	65	873	70	*f*

* Shoulder. † Peak considered to be formed by the superimposition of two bands. ‡ Peak strongly overlapped by neighbouring band. (—) Band is masked by stronger absorption. — Absence of band. ($CHCl_3$) Band is masked by solvent absorption.

Extra bands that could not be correlated with the substituent were found for: No. 1 at 894 cm.$^{-1}$ (20), No. 3 at 1306 (55) and 855 cm.$^{-1}$ (20), No. 11 at 903 cm.$^{-1}$ (55), No. 18 at 871 cm.$^{-1}$ (30).

[a] This column gives cross references to substituent bands, details of which have been published: [b] Katritzky and Coats, *J.*, 1959, 2062. [c] Ref. 4. [d] Ref. 5. [e] Katritzky, Beard, and Lagowski, in preparation. [f] Katritzky, unpublished work.

TABLE 2. *Intensities of ring stretching frequencies at* 1600—1400 *cm.*$^{-1}$.

Nos. in Table 1	Substituent type	Band near 1605 Range	Band near 1605 Mean and deviation	Band near 1565 Range	Band near 1565 Mean and deviation	Band near 1480 Range	Band near 1480 Mean and deviation	Band near 1434 Range	Band near 1434 Mean and deviation
1—2	Donor	115—150	130	170—175	170	170—175	170	130	130
3—9	Weak	80—120	100 ± 15	15—45	30 ± 10	90—160	115 ± 25	65—175	130 ± 40
10—19	Acceptor	45—85	55 ± 15	20—35	25 ± 5	20—90	60 ± 20	115—180	160 ± 20
1—19	All substituents	45—150	80 ± 35	15—175	40 ± 50	20—175	95 ± 45	65—180	150 ± 30

varies with substituents in much the same way. As in the *meta*-benzenes, this band often shows a shoulder or subsidiary band at higher frequencies (col. 9).

Ring Breathing Mode.—This (col. 9) occurs at 1019—1008 cm.$^{-1}$ (80—190) [1015 ± 2 cm.$^{-1}$ (150 ± 25)]; the corresponding mode occurs at [995 ± 3 cm.$^{-1}$ (20 ± 15)] in *meta*-benzenes.[8] Shindo reported [6] this band at 1022—1008 cm.$^{-1}$ (m—s).

Out-of-plane CH *Bending Frequencies.*—Two of these modes are probably represented by the bands listed in Table 1, cols. 10 and 11. The position of the first mode is very variable 997—900 [957 ± 27] cm.$^{-1}$, the intensity is (30—270) [(110 ± 55)]; it probably corresponds to that absorbing at [914 ± 8 cm.$^{-1}$ (20 ± 10)] for *meta*-benzenes. The second band of intensity (15—70) [(40 ± 15)], is found at 844—843 cm.$^{-1}$ for the alkoxy-compounds (Nos. 1, 2), at 857—853 cm.$^{-1}$ for the unsaturated esters (Nos. 6—9) and otherwise at 896—868 [884 ± 9] cm.$^{-1}$; for *meta*-benzenes the corresponding band absorbs at [836 ± 5] cm.$^{-1}$ for the compounds with two donor-substituents and at [880 ± 11] cm.$^{-1}$ otherwise.

Absorption which sometimes occurs just above the solvent cut-off at 805 cm.$^{-1}$ is probably a third out-of-plane mode, reported by Shindo [6] at 817—743 cm.$^{-1}$. We find

TABLE 3. *Esters.*

		Found			Quoted			
Ester *	Yield	B. p.	mm.	n_D †	B. p.	*mm.*	n_D †	Ref.
3Py·CO_2Pr^n	81	138·5—139·5°	25	1·4984(18·5)	134°	23	1·4964(25)	*a, b*
3Py·CO_2Pr^i	33	125—127	30	1·4931(18·5)	131	27	—	*b*
3Py·CO_2Bu^n	68	144	20	1·4950(19)	130	11	1·4933(25)	*a, b*
3Py·CO_2Bu^i	57	126	17	1·4950(14·5)	110—111	8	—	*b*
3Py·CO_2Bu^s	50 ‡	101·5	0·3	1·4816(16)	—	—	—	
3Py·CH:CH·CO_2Pr^n	45 §	172	25	1·5504(15)	—	—	—	
3Py·CH:CH·CO_2Bu^n	50 ¶	173—174	15	1·5450(17·5)	—	—	—	

* 3Py denotes 3-pyridyl radical. † Temperature of determination given in parentheses. [a] Badgett, Provost, Ogg, and Woodward, *J. Amer. Chem. Soc.*, 1945, **67**, 1135. [b] Charront, Harispe, Harispe, and Chevillard, *Bull. Soc. chim. France*, 1948, 1014. ‡ Found: C, 66·6; H, 7·5; N, 7·7. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3; N, 7·8%. § Found: C, 69·0; H, 7·0; N, 7·5. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·8; N, 7·3%. ¶ Found: C, 70·1; H, 7·6; N, 7·1. $C_{12}H_{15}O_2N$ requires C, 70·2; H, 7·4; N, 6·8%.

TABLE 4. 3-*Substituted pyridine* 1-*oxides.*

							Found (%) Required (%)		
Subst.	M. p.	Crystal form	Yield (%)	Solvent	*a*	Formula or lit. m. p.	C	H	N
CO_2Pr^n	49—50·5°	rhombs	71	Pet.	D, E	$C_9H_{11}O_3N$	59·6 59·7	6·2 6·1	— —
CO_2Pr^i	70	cubes	82	EtOAc	—	$C_9H_{11}O_3N$	59·5 59·7	6·2 6·1	7·7 7·7
CO_2Bu^n	30—33	plates	48	[b]	D, E	$C_{10}H_{13}O_3N$	62·1 61·5	6·6 6·7	6·9 7·2
CO_2Bu^i	62—62·5	rhombs	62	EtOAc	D	$C_{10}H_{13}O_3N$	62·0 61·5	6·8 6·7	7·2 7·2
CO_2Bu^s	43—46	—	49	[c]	D, E	$C_{10}H_{13}O_3N$	61·2 61·5	6·4 6·7	7·3 7·2
CH:CH·CO_2Pr^n	89—91	rhombs	70	EtOAc	—	$C_{11}H_{13}O_3N$	63·7 63·7	6·6 6·3	6·6 6·8
CH:CH·CO_2Bu^n	69—71	rhombs	93	EtOAc	D, E	$C_{12}H_{15}O_3N$	64·9 65·1	6·8 6·8	6·2 6·3
CN	174—175	—	47	EtOH	—	175—176 [d]	—	—	—
Cl	57—58	cubes	80	C_6H_6	D	C_5H_4ONCl	46·6 46·3	3·1 3·1	— —
NO_2	169—169·5	yellow needles	40	EtOH	—	$C_5H_4O_3N_2$ 167—169 [e]	43·1 42·9	2·6 2·9	— —
Me	37—38	—	—	[g]	D, E	33—36 [f]	—	—	—

[a] In this column D indicates that the compound was deliquescent, E that the m. p. was determined in an evacuated tube. [b] Distilled, b. p. 146—148°/0·15 mm.; Jaffe and Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441, give b. p. 135—139°/0·16 mm., but no m. p. [c] Distilled, b. p. 180·5/2 mm. [d] Jujo, *J. Pharm. Soc. Japan*, 1946, **66**, 21; *Chem. Abs.*, 1951, **45**, 6200. [e] Ochiai and Kaneko, *Pharm. Bull. Japan*, 1957, **5**, 56. [f] Hevy and Tsai, *J. Amer. Chem. Soc.*, 1954, **76**, 4184. [g] Distilled, b. p. 114—115°/1·5 mm. Pet = light petroleum. b. p. 60—80°.

absorption for Nos. 1, 2, 12, 13, 14, 15, 19 at respectively 819 (35), 828 (55), 822 (35), 807 (45), 805 (30), 805 (25), 818 cm.$^{-1}$ (250).

Substituent Bands.—All the remaining bands in the spectra with $\varepsilon_A > 10$ of these compounds could be assigned to substituent absorption (the few exceptions are given in footnotes to Table 1). Many of them have been published; cross references are given in col. 12.

Preparation of Compounds.—The following compounds have already been described (Nos. refer to Table 1); Nos. 4, 12, 18;[9] No. 5;[10] No. 6;[11] No. 11.[4] The other compounds were prepared by standard methods as indicated in the Experimental section.

EXPERIMENTAL

Esters of Nicotinic Acid.—Thionyl chloride (11·9 g.) was added with stirring below 0° to nicotinic acid (12·3 g.) under pyridine (16 c.c., previously dried by successive treatment with KOH pellets and freshly calcined CaO). The whole was then stirred for 1½ hr. at 100°, the alcohol (0·1 mole) added, and the heating continued for 3 hr. more. The mixture was added to water (160 c.c.) and just basified with aqueous ammonia (*d* 0·088). Ether-extraction (3 × 50 c.c.) gave, from the dried ($MgSO_4$) extracts, the ester by distillation. Details are given in Table 3.

Esters of β*-Pyridylacrylic Acid.*—The acid (10 g.), alcohol (25 c.c.), and sulphuric acid (10 c.c.) were heated for 18 hr. at 100°. The mixture was worked up as above. Details of the *products* are given in Table 3.

Conversion of Pyridines into their N*-Oxides.*—The pyridine (0·01 mole) in acetic acid (6 c.c.) and 30% aqueous hydrogen peroxide (1·5 c.c.) was heated at 70° and volatile material then removed to 100°/20 mm. The residue in chloroform (5 c.c.) was treated with potassium carbonate (2 g.) and the oxide recovered from the filtered solution by evaporation. Details are recorded in Table 4. 3-Ethoxy-, m. p. 85—86°, b. p. 175° (bath)/0·05 mm. and 3-methoxypyridine 1-oxide, m. p. 100—101°, were prepared by refluxing 3-chloropyridine 1-oxide overnight with the corresponding alcoholic sodium alkoxide: they were characterised as picrates (Table 5), prepared in and recrystallised from ethanol.

TABLE 5. *Picrates.*

Base †	M. p.	Crystal form	Formula or lit. m. p.	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
$3PyCO_2Pr^n$	129—130°	—	129·5—130 [a]	—	—	—	—	—	—
$3PyO{\cdot}CO_2Pr^n$	91·5—92	prisms	$C_{15}H_{14}O_{10}N_4$	44·2	3·3	13·8	43·9	3·4	13·7
$3Py{\cdot}CO_2Pr^i$	145·5	rhombs	$C_{15}H_{14}O_9N_4$	46·1	3·6	14·3	45·7	3·6	14·2
$3Py{\cdot}CO_2Bu^n$	113—114	—	113·5—114 [a]	—	—	—	—	—	—
$3PyO{\cdot}CO_2Bu^n$	84—85·5	needles	$C_{16}H_{16}O_{10}N_4$	45·3	3·7	13·3	45·3	3·8	13·2
$3Py{\cdot}CO_2Bu^i$	124	needles	$C_{16}H_{16}O_9N_4$	47·2	3·8	—	47·1	3·9	—
$3PyO{\cdot}CO_2Bu^i$	90	prisms	$C_{16}H_{16}O_{10}N_4$	45·7	3·9	13·5	45·3	3·8	13·2
$3Py{\cdot}CO_2Bu^s$	99·5—100·5	needles	$C_{16}H_{16}O_9N_4$	47·0	3·9	13·7	47·1	3·9	13·7
$3PyO{\cdot}CO_2Bu^s$	94·5—95·5	rhombs	$C_{16}H_{16}O_{10}N_4$	45·3	3·7	12·9	45·3	3·8	13·2
$3Py{\cdot}CH{:}CH{\cdot}CO_2Pr^n$	128—128·5	prisms	$C_{17}H_{16}O_9N_4$	48·6	3·9	13·0	48·6	3·8	13·3
$3Py{\cdot}CH{:}CH{\cdot}CO_2Bu^n$	100	rods	$C_{18}H_{18}O_9N_4$	49·9	4·2	13·3	49·8	4·2	12·9
$3PyO{\cdot}CH{:}CH{\cdot}CO_2Bu^n$	109—110	rhombs	$C_{18}H_{18}O_{10}N_4$	47·8	3·8	12·8	48·0	4·0	12·4
$3PyO{\cdot}Me$	149—151	plates	$C_{12}H_{10}O_8N_4$ 138—139 [b] 141—143 [c]	42·9	3·0	16·2	42·6	3·0	16·6
$3PyO{\cdot}OMe$	155—156	needles	$C_{12}H_{10}O_9N_4$	41·1	3·0	15·6	40·7	2·8	15·8
$3PyO{\cdot}OEt$	125—125·5	needles	$C_{13}H_{12}O_9N_4$	43·0	3·4	14·9	42·5	3·3	15·2

† 3Py indicates 3-substituted pyridine ring, 3PyO indicates 3-substituted pyridine 1-oxide ring.
[a] Footnote *a* of Table 3. [b] Bockelheide and Linn, *J. Amer. Chem. Soc.*, 1954, **76**, 1290. [c] Footnote *f* of Table 4.

Part of this work was done during the tenure (by A. R. K.) of an I.C.I. Fellowship.

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[*Received, May* 15*th*, 1959.]

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[9] Katritzky, *J.*, 1956, 2404.
[10] Hands and Katritzky, *J.*, 1958, 1754.
[11] Katritzky and Monro, *J.*, 1958, 150.