641. *Infrared Studies of Heterocyclic Compounds. Part III.*[1] *3-Monosubstituted Pyridines.*

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The positions and intensities of eleven characteristic bands are recorded and discussed for twenty-seven 3-substituted pyridines.

Following our work on 2- [1] and 4-substituted pyridines,[2] we now report spectra for some 3-analogues. Cook and Church [3] investigated the spectra of 3-picoline (which has also been studied in detail [4]) and five nicotine derivatives containing a 3-substituted pyridine ring (as liquid films) and indicated that characteristic bands were at 1605—1585, 1587—1568, 1486—1475, 1427—1416, 1383—1377, 1318—1312, 1253—1239, 1196—1180, 1131—1117, 1034—1021, 810—789, and 715—712 cm.$^{-1}$; the fifth of these was stated to be " of variable intensity," but otherwise no indication of intensities was given. Shindo [5] correlated the spectra of thirteen 3-substituted pyridines (measured in Nujol, CS_2, CCl_4, or chloroform) and found characteristic bands at 1202—1182 (vw-s), 1130—1114 (w-m), 1016—1030 (m-s), 820—770 (m-s) and 730—690 cm.$^{-1}$ (vs). He also indicated that in general pyridines showed two bands between 1630 and 1560 cm.$^{-1}$ and that, in those 3-substituted pyridines with electron-donor substituents, the band of lower frequency was the stronger of the pair, but that the reverse was true of 3-pyridines with electron-acceptor substituents.*

In the present work, for reasons already given,[6] the spectra were all measured for 0·2M-solutions in chloroform in a 0·117 mm. cell, and apparent extinction coefficients recorded in place of " strong," " weak," etc. Eleven bands were found to be characteristic of the nucleus (see Table); they include all those found by the previous workers,[3, 5] except those obscured by solvent (1240—1200 and below 805 cm.$^{-1}$), those at 1383—1377 cm.$^{-1}$ (apparently assigned to methyl absorption) and 1318—1312 cm.$^{-1}$. With very few exceptions, all other bands with $\varepsilon_A \geqslant 15$ were found to be characteristic of the substituent; they have already been published [6] for the methyl and the ethyl esters, the aldehyde, and the methyl ketone: in these seven compounds a total of 99 bands and 27 shoulders have been correlated and no band left unaccounted for.

The 3000 *cm.*$^{-1}$ *Region.*—The hydrogen-bonded chloroform CH stretching frequency [2] occurs (col. 1) at 3000—2940 [2980 ± 15] † cm.$^{-1}$; the intensity is (45—80) [(60 ± 13)] † except in the cyano- and nitro-compounds (probably less hydrogen-bonded because of low basicity) and in the ethyl and higher esters (overlapped by substituent absorption).

The 1650—1550 *cm.*$^{-1}$ *Region.*—Two bands occur. The first (col. 2) has a rather constant position at 1608—1584 [1595 ± 5] cm.$^{-1}$, but is of much higher intensity with both strong donor substituents [Nos. 1—7, (60—185)] and strong electron acceptor substituents [Nos. 17—27 (65—200)] than with substituents of a more neutral character [Nos. 8—16 (15—35)]. This intensity variation is similar to that in the corresponding band in 2- [7] and 4-substituted pyridine 1-oxides,[8] but different from those in the 2- and 4-pyridines;[1, 2] this correlates well with the relative ease of electron-donor and -acceptor power of the rings (see discussion in ref. 8).

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* In this paper, Shindo also discusses the spectra of twelve 2- and twelve 4-monosubstituted pyridines; as far as they go, his correlations are in good agreement with ours (refs. 1 and 2).

† Arithmetical means and standard deviations are given in square brackets, ε_A values in round brackets: see footnote in ref. 2.

[1] Part II, Katritzky and Hands, *J.*, 1958, 2202.
[2] Katritzky and Gardner, *J.*, 1958, 2198.
[3] Cook and Church, *J. Phys. Chem.*, 1957, **61**, 458.
[4] Long, Murfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171 and references therein.
[5] Shindo, *Pharm. Bull.* (*Japan*), 1957, **5**, 472.
[6] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.
[7] Katritzky and Hands, *J.*, 1958, 2195.
[8] Katritzky and Gardner, *J.*, 1958, 2192.

		1		2		3		4		5		6		7		8		9		10		11	
		CHCl$_3$		A$_1$		B$_1$		B$_1$		A$_1$		?		B$_1$		A$_1$		B$_1$		A$_1$		B$_2$	
		νCH		νCC, CN		νCC, CN		νCC, CN		νCC, CN		?		βCH		βCH		βCH		ring		γCH	
		—		1611 ± 9s		1590 ± 7s		1499 ± 7vs		1447 ± 15m		—		1165 ± 6var		1081 ± 10m		1045 ± 7m		995 ± 5var		782 ± 9vs	
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	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	NHMe	2950	70	1595	185	1583 *	120	1484	95	1430 *	20	1191 *	45	1123	15	1100	25	1030 *	5	1008	20	—	
2	NH$_2$	2970	65	1590	95	(—)		1486	90	1442	125	1196 *	30	1130	30	1112	15	1042	15	1019	15	—	
3	OEt	2970	80	1589	60	1578	65	1482 *	50	1425	75	1183 *	30	1130 *	25	1100 *	35	(—)		1013 *	30	—	
4	NMe·COMe	2990	75	1590	70	1581 *	50	1480	145	1420 †	140	1190 *	30	(—)		1104	25	1040 *	20	1023	60	810 *	25
5	NMe·COPh	2960	50	(—)		1580	95	1488	150	1423 †	120	1175 *	35	(—)		1102 *	70	1044	20	1023 †	80	—	
6	NH·COMe	2970	70	1599	100	(—)		1480	225	1420 *	130	(CHCl$_3$)		1124	20	1103	20	1047	15	1024	30	—	
7	NH·COPh	2990	60	1591	105	(—)		1481	290	1420	140	1190 *	40	1126	20	1098	25	1042	5	1026 †	45	—	
8	Me	2970	70	1600	15	1582	45	1479	55	1414	35	1188	20	1124	20	1102	20	1040	15	1029	55	—	
9	CH$_2$·CH$_2$·CO$_2$Et	2970	80	1600	20	1582	35	1479	55	1426	80	(—)		1124 *	40	1104 *	40	(—)		1028	75	—	
10	CH$_2$·CO$_2$Et	2970	85	1598	20	1580	40	1479	60	1426	90	1178 *	110	1117 *	35	(—)		1040 *	30	1027 †	175	—	
11	CH$_2$·OH	2940	75	1596	30	1580	45	1478	30	1424	60	1190 *	30	1122 *	15	1099	15	1042 *	50	(—)		—	
12	CH:CH·CO$_2$Et	2970	60	1592	35	1575	40	1477	50	1418	90	1186 *	200	1122	25	1111 *	20	1044	95	1025 †	110	(803	45)
13	Ph	2970	60	1584	20	(—)		1470	35	1408	85	(CHCl$_3$)		1125	10	1100	10	1023 †	30	1006	60	808	20
14	C$_6$H$_4$·NO$_2$-*p*	2970	50	(—)		1572 †	25	1471	40	1428	45	1188 †	25	1128 *	15	1109 †	50	1025	25	1001	55	(804	50)
15	Cl	3000	45	1581 *	30	1573 *	30	1472	90	1419 1407 *	85 25	(CHCl$_3$)		1120 *	35	1108 1093	125 35	—		1018	140	—	
16	Br	3000	50	1589 *	15	1576	25	1465 1440	50 30	1417	110	(CHCl$_3$)		1117 *	15	1096 1086	70 50	1025 *	20	1009	110	—	
17	CN	3000	30	1590	65	1567	25	1471	25	1418	70	1184	20	1122	15	—		—		1025	60	(803	35)
18	CO$_2$Me	2970	45	1597	105	1580 *	30	—		1421	70	1188 †	50	1122 *	140	(—)		1036	20	1025	110	—	
19	CO$_2$Et	3000	95	1598	135	(—)		(—)		1422	85	1193 *	50	(—)		(—)		1039	55	1027 †	170	—	
20	CO$_2$Pr^n	2980	130	1595	135	1578 *	25	(—)		1419	85	1191 *	45	(—)		(—)		1037	25	1024 †	140	—	
21	CO$_2$Pr^i	3000	90	1600	135	1589 *	25	(—)		1424	75	1193 *	45	(—)		(—)		1037	15	1027 †	140	—	
22	CO$_2$Bu^n	2970	125	1594	120	1578 *	25	(—)		1420	75	1190 *	50	(—)		(—)		1035	20	1025 †	135	—	
23	CO$_2$Bu^i	2950	125	1599	120	1586 *	25	(—)		1420	65	1192 *	60	(—)		(—)		1037	20	1026 †	125	—	
24	CO$_2$Bu^s	2980	95	1597	100	1580 *	20	—		1420	50	1191 *	55	(—)		(—)		1037 *	15	1025 †	115	—	
25	CHO	2990	45	1595	200	1581 *	80	—		1428	50	(—)		1120 *	15	1109	20	1035 *	20	1025	55	—	
26	COMe	2970	45	1589	170	(—)		—		1419	105	1193 *	45	1118	35	(—)		1032 *	10	1023	80	808	30
27	NO$_2$	3000	25	1608	190	1580	75	1472	20	1428	55	1192	70	1114	20	1100	20	—		1021	70	820	50

Tentative assignments of symmetry and type of vibration, and the arithmetical mean and standard deviation for the corresponding band in *meta*-disubstituted benzenes (from Ref. 9), are given immediately below the column number.

* Shoulder. † Absorption considered to be the superimposition of two bands, — absence of absorption, (—) band masked by stronger absorption, (CHCl$_3$) band masked by solvent.

The second band (col. 3) occurs at 1582—1567 [1577 ± 5] cm.$^{-1}$ with intensity (25—75) [(45 ± 15)] (except in No. 5 where it is overlapped). This band often occurs only as a shoulder on the previous band, and sometimes instead of the two bands only one is observed, usually that at higher frequencies.

The 1500—1400 *cm.*$^{-1}$ *Region.*—Usually two bands are found. One (col. 4) occurs at 1486—1480 cm.$^{-1}$ with electron donor substituents (Nos. 1—7), at 1479—1477 cm.$^{-1}$ with electronically neutral substituents (Nos. 8—12), but is lowered to 1472—1465 cm.$^{-1}$ by aryl, halogen, and electron attracting-substituents. The intensity is very high for the amides (145—290) and moderate with other electron-donor and neutral substituents (Nos. 1—3, 8—16) (30—95) [(65 ± 20)]; the band is weak or absent in compounds with electron-attracting substituents (Nos. 17—27).

Another band (col. 5) is at 1428—1414 cm.$^{-1}$ [1421 ± 4], except for the amino-compounds at 1442 cm.$^{-1}$. The intensity is (35—140) [(80 ± 25)].

The 1200—990 *cm.*$^{-1}$ *Region.*—Five bands are found. The first (col. 6) occurs at the edge of the portion of the spectrum obscured by solvent (*i.e.*, 1240—1200 cm.$^{-1}$) and usually is seen only as a shoulder.

Another band (col. 7) occurs at 1130—1114 cm.$^{-1}$ (10—35) [1124 ± 5 cm.$^{-1}$ (20 ± 10)]; it is often hidden by, or seen as a shoulder on, substituent absorption.

The third band (col. 8) is absent for No. 17, otherwise it is at 1112—1096 cm.$^{-1}$ [1103 ± 5]. The intensity is (10—25) [(20 ± 5)], except for the halogeno-compounds (Nos. 15 and 16) which cause abnormally strong absorption in this region in other series.[1, 2, 7, 8]

A weak band (col. 9) (absent in Nos. 15, 17, and 27) is found at 1047—1040 cm.$^{-1}$ with electron-donor and most neutral substituents (Nos. 1—12), at 1039—1035 cm.$^{-1}$ with electron-acceptor substituents (Nos. 18—26), but the frequency is lowered to *ca.* 1025 cm.$^{-1}$ with halogeno- and aryl substituents. The intensity is (5—25) [(20 ± 5)] except for Nos. 12 and 19 where the band is strongly overlapped by substituent absorption.

The final band in this region (col. 10) occurs at 1029—1021 cm.$^{-1}$ [1025 ± 2] except in the amino-, aryl- and halogeno-substituted compounds which all absorb at lower frequencies. The intensity is (15—140) [(65 ± 35)].

The 900—800 *cm.*$^{-1}$ *Region.*—For a few compounds a band (col. 11) occurs on the edge of the region hidden by solvent absorption below 805 cm.$^{-1}$.

Assignments.—Comparison with Randle and Whiffen's data [9] for *meta*-substituted benzenes suggests the assignments indicated at the head of the Table; the agreement is, however, not as good as for 2- and 4-substituted pyridines;[1, 2] the bands at [964 ± 10 (w), 904 ± 13 (var) and 876 ± 10 cm.$^{-1}$ (vs)] appear to have no analogues in the 3-pyridines, and the assignment of the 3-pyridine band at *ca.* 1190 cm.$^{-1}$ is uncertain.

Experimental.—See ref. 2 for sources of specimens, and conditions for measurement of the spectra.

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[9] Randle and Whiffen, Report on Conference on Molecular Spectroscopy, 1954, Inst. Petroleum, Paper No. 12, p. 111.