448. *Infrared Studies of Heterocyclic Compounds. Part II.*[1] *2-Monosubstituted Pyridines.*

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The positions and intensities of ten characteristic bands are recorded and discussed for thirty-five 2-substituted pyridines.

AFTER our work [1] on 4-substituted pyridines, we now report on some 2-analogues. 2-Picoline has been studied in detail,[2] but the only previous comparative work was that by Cook and Church [3] on 2-benzyl- and five 2-alkyl-pyridines; bands were reported at 1603—1597, 1577—1575, 1477—1474, 1468—1437, 1311—1299, 1152—1146, 1052—1050, and 995 cm.$^{-1}$ corresponding to those now discussed, except that at *ca.* 1093 cm.$^{-1}$. Bands noted [3] at 1225 and 750—743 cm.$^{-1}$ are obscured by solvent in our work; other absorption found [3] has been shown [4] due to the substituent: *e.g.*, that at 1501 and 1458 cm.$^{-1}$ is due to the benzene ring in 2-benzylpyridine.

The 3000 *cm.*$^{-1}$ *Region.*—The hydrogen-bonded chloroform CH stretching frequency [1] occurs at 3000—2940 cm.$^{-1}$ (10—100) [2980 ± 15 cm.$^{-1}$ (50 ± 25)].*

The 1650—1550 *cm.*$^{-1}$ *Region.*—Two bands occur. The first (col. 2 of the Table) is at 1616—1573 cm.$^{-1}$, but only strong electron-donor substituents cause absorption above 1600 cm.$^{-1}$. When the ring is attached to a saturated carbon atom (Nos. 10—14, 23—24) the band is at 1600—1595 cm.$^{-1}$; the frequency is lowered by carbon–carbon multiple bonds (Nos. 15—22 at 1593—1585 cm.$^{-1}$), electron-accepting substituents (Nos. 27—35 at 1590—1585 cm.$^{-1}$), and heavy atoms (Cl and Br; Nos. 25, 26; at 1586—1573 cm.$^{-1}$). Intensities tend to decrease from electron-donor to electron-acceptor substituents; they are (100—290) [(170 ± 65)] in Nos. 1—9 (65—150) [115 ± 25)] in Nos. 10—26 (except Nos. 18, 19, and 22 strongly overlapped by substituent absorption), and (50—100) [(75 ± 20)] with electron-withdrawing substituents (Nos. 27—34; the nitro-compound is lower still).

The second band (col. 3) is at 1581—1562 [1572 ± 4] cm.$^{-1}$. Intensity variation is similar to that for the previous band: (80—235) [(160 ± 55)] for Nos. 1—9; (30—75) [(50 ± 10)] for Nos. 10—24 (except Nos. 18, 19, 21, and 22 overlapped); and (25—45) [(35 ± 10)] for Nos. 27—35.

* Arithmetical means and standard deviations: see footnote, *J.*, 1958, 2182.

[1] Part I, Katritzky and Gardner, preceding paper.
[2] Long, Murfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171, and references therein.
[3] Cook and Church, *J. Phys. Chem.*, 1957, **61**, 458.
[4] Katritzky *et al.*, preceding papers and unpublished work.

The 1500—1400 *cm.*$^{-1}$ *Region.*—Two bands are found. One (col. 4) is at 1483—1460 [1471 ± 6] cm.$^{-1}$ except in the halogeno-compounds where it is considerably lower (cf. other cases [4]). Intensities are (140—340) with the strongest electron-donors (Nos 1—4), (10—35) with stronger electron-acceptors (Nos. 29—35), and for the rest (30—125) [(80 ± 25)].

The other band is at 1443—1420 [1433 ± 5] cm.$^{-1}$ except in the bromo-compound at 1414 cm.$^{-1}$ (cf above). Electron-donor substituents (Nos. 1—9), and especially amido-compounds with adjacent NH (Nos. 6—9), raise the intensity, which otherwise (Nos. 10—35) is (20—145) [(70 ± 30)].

The 1300—1240 *cm.*$^{-1}$ *Region.*—Nine compounds absorb weakly at 1293—1250 cm.$^{-1}$ (10—35); for others there is a shoulder hereabouts.

The 1200—990 *cm.*$^{-1}$ *Region.*—Four bands are found. The first (col. 7) is at 1152—1140 [1147 ± 3] cm.$^{-1}$. Electron-donor substituents (Nos. 1—9) give intensities of (35—80) [(60 ± 15)], acceptor substituents (Nos. 27—35) give intensities of (5—25) [(15 ± 5)], and the remainder (Nos. 10—26) intensities of (10—50) [(25 ± 10)].

Another band (col. 8) is at 1102—1083 cm.$^{-1}$ (5—70) [1093 ± 4 cm.$^{-1}$ (15 ± 15)] except for the halogeno-compounds (Nos. 25, 26) which both show two strong bands hereabouts (cf. other cases [4]).

A third band is at 1059—1039 [1048 ± 5] cm.$^{-1}$. Its intensity is (5—50) [(20 ± 10)], except for Nos. 9 and 23 (strongly overlapped by substituent-absorption) and for the esters (Nos. 29 and 30).

		1 [a]		2		3		4		5	
		$CHCl_3$		A_1		B_1		A_1		B_1	
		νCH		νCC, νCN		νCC, νCN		νCC, νCN		νCC, νCN	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	NH_2	2960	40	1616 ‡	460	1574	115	1483	220	1443	240
2	OMe	3000	65	1610 / 1590 *	165 / 95	1578	150	1483	340	1420	185
3	OEt	2990	100	1600	180	1574	125	1470	240	1433	250
4	O·CH_2Ph	3000	40	1601	125	1573	80	1475	140	1433	155
5	NMe·COPh	3000	80	1592	230	1573	165	1472 ‡	260	1442	160
6	NH·COMe	2980	50	1600	120	1580	220	1460	60	1434	325
7	NH·COPh	3000	35	1601	140	1581	200	(—)		1434	335
8	NH·CO·Morph [b]	2980	90	1599	100	1580	235	(—)		1432 ‡	380
9	NH·CO_2Et	2980	95	1593	290	(—)		1480 *	45	1443	330
10	Me	2960	65	1595	70	1571	40	1478	85	1430	40
11	Et	2950	90	1595	110	1570	45	1476	85	1431	60
12	CH_2·CH_2Ph	2950	60	1598	125	1574	45	1478	85	1436	75
13	CH_2Ph	2940	35	1596	130	1571	50	1473	75	1432 ‡	80
14	CH_2·C_6H_4·NO_2-*p*	2940	45	1590	140	1571	75	1472	70	1432	80
15	C:CPh	2970	40	1585	150	1563	45	1463	125	1428	60
16	CH:CHPh	2970	50	1592 ‡	180	1566	55	1471	110	1431	60
17	CH:CH·CO_2Et	2990	75	1587	85	1570	45	1468	80	1432	100
18	C_6H_4·NH_2-*p*	2980	40	1598	190	1570	80	1471 ‡	220	1428 *	40
19	C_6H_4·NH_2-*m*	2980	50	1595	195	1570	105	1478 *	70	1424	60
20	Ph	2970	50	1592	105	1568	45	1470 ‡	130	1427	60
21	C_6H_4·NO_2-*m*	2950	35	1593	130	1575	70	1473	70	1431 *	85
22	C_6H_4·NO_2-*p*	2990	30	1591	170	1573	90	1468	115	1438	85
23	CH_2·OH	2950	25	1600	65	1573	30	1476	30	1439	40
24	CHPh·OH	3000	20	1599	90	1577	50	1473	45	1438	85
25	Cl	2980	30	1586	130	1562 *	55	1451	95	1420	110
26	Br	2980	40	1573	115	1562	145	1444	115	1414	145
27	CH:N·OH	2970	60	1590	80	1571	45	1475	55	1436	50
28	CN	3000	20	1585	90	(—)		1462	65	1431	65
29	CO_2Me	3000	90	1590	50	1575	35	1470	30	1433	115
30	CO_2Et	2980	95	1590	70	1572	40	1465 ‡	55	1438	80
31	CHO	2980	30	1590	75	1578 *	20	1470	10	1438	20
32	COMe	2980	35	1586	55	1571	25	1467	20	1436	45
33	CO·C_6H_4·NO_2-*m*	2990	20	1588	90	(—)		(—)		1436	55
34	CO·C_6H_4·NO_2-*p*	2990	10	1588	100	1560 *	35	1468	15	1434	30
35	NO_2	3000	20	1595 *	10	1567 *	50	1460	35	1430	80

[a] See footnote, p. 2192, and also for meaning of other symbols. [b] Morpholide.

		6		7		8		9		10	
		A_1		A_1		B_1		A_1		A_2	
		?		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
1	NH_2	1270 *	35	1149	70	—		1043	20	990	35
2	OMe	1270 *	115	1141	70	1097	10	1045 ‡	110	987	50
3	OEt	(—)		1140	80	(—)		(—)		988	40
4	O·CH_2Ph	(—)		1140	35	1090 *	50	1040	40	988	60
5	NMe·COPh	(—)		1150	35	1094 *	30	1051	40	993	25
6	NH·COMe	1280 *	25	1149	60	1092	10	1050	20	1000	30
7	NH·COPh	(—)		1149	60	1093	45	1049	20	992	25
8	NH·CO·Morph [b]	1265 *	115	1148	65	(—)		1047	25	986	65
9	NH·CO_2Et	1282 *	120	1152	75	1098 *	85	1050	70	995	40
10	Me	1293	35	1147	30	1099	10	1049	30	999	20
11	Et	—		1146	30	1102	5	1047	25	995	30
12	CH_2·CH_2Ph	1258 *	15	1149	10	—		1051	10	996	15
13	CH_2Ph	1270 *	10	1146	10	1091	10	1050	10	997	30
14	CH_2·C_6H_4·NO_2-*p*	(—)		1144	15	(—)		1048	20	996	35
15	C:CPh	1285	15	1145	25	1090	10	1042	10	990	30
16	CH:CHPh	—		1148	50	1092	5	1048	10	992	30
17	CH:CH·CO_2Et	(—)		1148 *	105	1092 ‡	55	1038 *	90	993	55
18	C_6H_4·NH_2-*p*	1267 *	90	1152	25	1095	10	1059	10	990	20
19	C_6H_4·NH_2-*m*	1274	15	1151	35	1094	20	1059	10	992	40
20	Ph	1292	10	1150	20	1094	10	1059 *	5	998	15
21	C_6H_4·NO_2-*m*	(—)		1144	15	(—)		1050	20	997	30
22	C_6H_4·NO_2-*p*	1270	10	1151	30	1097	35	1059	5	991	20
23	CH_2·OH	—		1145	20	1095	10	1053	70	996	20
24	CHPh·OH	—		1149	30	1098 *	15	1051 *	70	1000	30
25	Cl	1282	20	1147	50	1121 1083	190 75	1044	35	991	45
26	Br	1280	15	1144	25	1108 1076	215 145	1040	50	989	55
27	CH:N·OH	(—)		1149	25	1093	20	1048	10	995 *	90
28	CN	1281	10	1150	15	1090	15	1044	25	992	60
29	CO_2Me	1282 *	140	(—)		1089 ‡	45	1046	65	998	55
30	CO_2Et	1282 *	180	(—)		(—)		1045	90	995	100
31	CHO	(—)		1149	10	1088	15	1040	20	994	50
32	COMe	(—)		1146	15	1100	70	1043	35	996	30
33	CO·C_6H_4·NO_2-*m*	1274 *	85	1150	15	(—)		1046	20	997	115
34	CO·C_6H_4·NO_2-*p*	(—)		(—)		1090	30	1044	10	997	95
35	NO_2	1250	20	1145	5	1083	10	1039	30	996	65

The final band in this region (col. 10) is at 1000—986 cm.$^{-1}$ (15—115) [1094 ± 4 (45 ± 25)] cm.$^{-1}$.

Assignments.—Comparison with Randle and Whiffen's data [5] for *ortho*-substituted benzene derivatives suggests the assignments indicated at the head of the Table. The means are usually within 20 cm.$^{-1}$ and all our bands are accounted for; of the bands reported for the benzene derivatives, only those at [934 ± 11 (w) and 865 ± 14 (w)] cm.$^{-1}$ have no analogues.

Experimental.—See Part I [1] for sources of specimens and measurement of spectra.

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[5] Randle and Whiffen, Paper No. 12, Report on Conference of Molecular Spectroscopy, 1954, Institute of Petroleum, p. 111.