595. *Infrared Absorption of Heteroaromatic and Benzenoid Six-membered Monocyclic Nuclei. Part X.*[1] *Pyridones and Pyridthiones.*

By A. R. KATRITZKY and R. ALAN JONES.

The infrared spectra of ten pyridones and six pyridthiones are recorded. Tentative assignments for most of the bands are made on the basis of the similarity of the spectra of these with those of other heteroaromatic compounds.

PREVIOUS papers in this and a cognate series were concerned with the infrared spectra of monosubstituted pyridines[2] and pyridine 1-oxides[3] and bands were tentatively assigned to specific molecular vibration modes. The compounds were found to possess four ring-stretching modes in the 1600—1400 cm.$^{-1}$ region, the positions of which were relatively constant and the intensities of which could be correlated with the charge disturbance created in the ring by substituent and hetero-group. The in- and out-of-plane CH bending depended mainly on the number and relative orientation of the ring hydrogen atoms (for a review see ref. 4).

The present work was undertaken in an attempt to interpret the spectra of, and extend the above generalisations to, pyridones and pyridthiones. As planar six-membered ring compounds in which each annular atom possesses a *p*-orbital perpendicular to the plane of

---

[1] Part IX, Katritzky and R. A. Jones, *J.*, 1959, 3670.

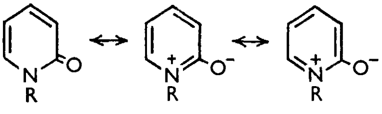
[2] (*a*) Katritzky and Gardner, *J.*, 1958, 2198; (*b*) Katritzky and Hands, *ibid.*, p. 2202; (*c*) Katritzky, Hands, and Jones, *ibid.*, p. 3165.

[3] (*a*) Katritzky and Gardner, *J.*, 1958, 2192; (*b*) Katritzky and Hands, *ibid.*, 2195; (*c*) Katritzky, Beard, and Coats, *J.*, 1959, 3680.

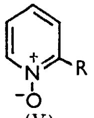
[4] Katritzky, *Quart. Rev.*, 1959, **13**, 353.

the ring and a total of six π-electrons they are aromatic and their reactions are in accordance with this.[5]

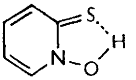
Pyrid-2- and -4-one are usually depicted by the uncharged structures (I) and (IV), but charged canonical forms (*e.g.*, II, III) are of great importance in these mesomeric compounds, and such structures demonstrate the similarity to pyridine 1-oxides (cf. V). As before, the spectra were measured as 0·189M-solutions in purified chloroform in a 0·106 mm. compensated cell. The bands in the regions 4000—3020, 3000—1240, 1200—800 cm.$^{-1}$ (*i.e.*, the region unobscured by solvent absorption) are recorded in Tables 1 and 2; tentative assignments are given at the heads of the columns to the molecular modes approximately depicted in formulæ (VI)—(XXIV). The compounds containing H or OH groups at the 1-position were less soluble: in the 2-series saturated solutions had to be used in two cases and in the 4-series satisfactory solution spectra could not be obtained.

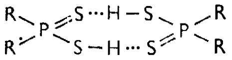

(I) (II) (III)

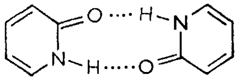

(IV)


(V)

NH *and* OH *Stretching Frequencies* (Tables 1 and 2, col. 1).—All the compounds are shown to be very strongly hydrogen-bonded, both by the positions of the peaks and by their broad nature. 1-Hydroxypyrid-2-one and -2-thione exist as monomers (cf. XXV); strong hydrogen bonds involving sulphur are known (*e.g.*, XXVI) [6] but are rare. Pyrid-2-one is a dimer, presumably (XXVII), under these conditions,[7] and pyrid-2-thione is also largely dimerised in chloroform solution (as shown cryoscopically).

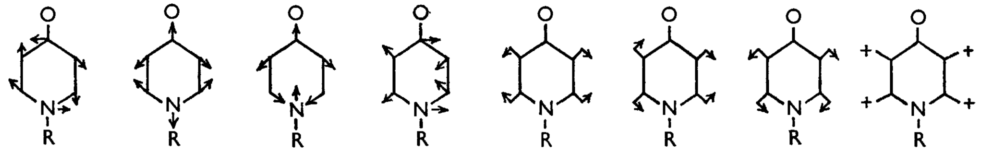

(XXV)


(XXVI)


(XXVII)

The 3000 *cm.*$^{-1}$ *Region* (Table 1, col. 2; Table 2, col. 2).—All the compounds show a

*Approximate vibration modes of pyrid-4-ones.**


(VI) (VII) (VIII) (IX) (X) (XI) (XII) (XIII)
Col. 3 4 6 7 13,14† 16 18 20

* Double bonds are omitted.

† As a Referee has commented, the assignment of the bands in *both* cols. 13 and 14 of Table 1 to mode (X) is not certain. However, as the Referee implies, it is unlikely that the fourth β_{CH} vibration [*i.e.*, that corresponding to (XIX) for the 4-series] should absorb at frequencies as low as these. Further, any assignment to νN–R frequencies would leave bands unexplained in the N–H and N–O–R compounds. We thus tentatively let the assignment of the doublet to mode (X) stand.

---

[5] Katritzky and Lagowski, " Heterocyclic Chemistry," Methuen and Co. Ltd., London, 1960, pp. 51—52.

[6] Allen and Colclough, *J.*, 1957, 3912; cf. Bellamy, " The Infra-Red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958, p. 351.

[7] Personal communication from Dr. C. A. Dekker.

TABLE 1. *Pyrid-4-ones and -thiones.*

No.	1-Subst.	1	2		3		4		5		6		7	
		νOH νNH	νCH		pyridone ring stretch				νC=O		pyridone ring stretch			
		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
Pyrid-4-ones.														
1	H (Nj)	3200m 2650m	—		(—)		1631	s	1548	s	1502	s	1384	s
2	Me	NA	2970	170	1664	165	1643	600	1575	600	1513	85	1401	155
3	CH$_2$Ph	NA	2970	150	1660 *	130	1640	650	1575	550	1500	90	1408	90
4	OMe	NA	2980	165	1650 *	290	1624	440	1577	430	1493	180	1403	25
5	OCH$_2$Ph	NA	2970	145	1645 *	195	1630	510	1575	550	1484	50	1394	25
Pyrid-4-thiones.														
6	H (Nj)	3190w	—		—		1615	vs	NA		1540	w	1458	s
7	Me	NA	2940	150	—		1635	>500	NA		1510	45	1471	330
8	CH$_2$Ph	NA	2960	135	—		1621	600	NA		1510	60	1470	340
9	OH (Nj)	3090w *ca.* 2500w broad	—		—		1613 1580 *	s s	NA		1540 *	w	1472	s

No.	8		9		10		11		12		13		14		15	
	Ph		Me		CH$_2$ wag		νNO		?		β_{CH}				νC=S	
			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
Pyrid-4-thiones.																
1	NA		NA		NA		NA		1302 1260 *	m w	1187	s	1144 *	w	NA	
2	NA		1488 1440	50 15	NA		NA		1361	45	1192	220	1144	20	NA	
3	1486 * 1456	75 90	NA		1355	60	NA		1376 1330 1300	65 30 30	1176	320	—		NA	
4	NA		1460 1445	85 75	NA		1326	60	1292	60	1179	75	1158	95	NA	
5	1456	35	NA		1350	40	1326	40	—		1174	80	1152	70	NA	
6	NA		NA		NA		NA		1373 1276	w w	1195	mw	1149	m	1106	s
7	NA		(—) —		NA		NA		—		(CHCl$_3$)		1150 *	20	1119	>550
8	1500 * 1452 *	55 70	NA		1354	25	NA		1369	30	1184	35	1160 *	25	1108	750
9	NA		NA		NA		(—)		1380	w	1194	m	1180	m	1110	s

No.	16		17		18		19		20						
	β_{CH}		Ph		β_{CH}		νC–O		γ_{CH}		Extra bands		M. p.		Ref.
	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	Found	Lit.	
Pyrid-4-thiones.															
1	1081	w	NA		1032 989	w w	NA		827 840 *	m w	907	w	146—147° 92—93	148·5° 92—94	*h* *a*
2	—		NA		1015	25	NA		845	240					
3	1093	15	1075 1027	15 25	1013	20	NA		845	200			109—111	—	*b*
4	1085	25	NA		1011	30	1027 975	65 185	843	280			60—65	60—65	*c*
5	1081 ⁑	25	1081 ⁑ 1027 *	25 5	1010	25	939 901	50 110	843	240	820 *	40	112—114	112—113	*d*
6	1079	m	NA		1040	w	NA		792	s	988 970	m w	184—186	186	*e, f*
7	1094 *	35	NA		1030	135	NA		819	135			161—163	161—163	*f*
8	(—)		1075 * (—)	40	1027	160	NA		821	160			183—185	—	*b*
9	1098 *	m	NA		1029	w	960	w	827 812	w w			140	142	*g*

TABLE 2. *Pyrid-2-ones and -thiones.*

No.	1-Subst.	1 νOH or NH cm.$^{-1}$	ε_A	2 νCH cm.$^{-1}$	ε_A	3 νC=O cm.$^{-1}$	ε_A	4 ring stretching cm.$^{-1}$	ε_A	5 ring stretching cm.$^{-1}$	ε_A
Pyrid-2-ones.											
1	H	3120 3070 2820 2490	55 50 100 20	2990 §	160	1672 * 1656	210 650	1619	330	1544	110
2	Me	NA		3000	80	1665	550	1590	370	1545	105
3	CH_2Ph	NA		2990	105	1659	600	1590	440	1541	110
4	OH (sat.)	2400	s	2940	s	1655	s	1570 *	s	1560	s
5	OMe	NA		3000	75	1664	640	1593	300	1535	140
6	OCH_2Ph	NA		3000	80	1666	700	1591	330	1539	190
Pyrid-2-thiones.											
7	H (sat.)	2900 (v. broad)	s			NA		1620 1590	m s	1560 * 1525 *	m m
8	Me	NA		2960	115	NA		1628	145	1537	220
9	CH_2Ph	NA		2960	95	NA		1624	130	1534	260
10	OH	2600 (v. broad)	30	2990	70	NA		1612	70	1572	150

No.	6 Ph cm.$^{-1}$	ε_A	7 Me cm.$^{-1}$	ε_A	8 ring stretching cm.$^{-1}$	ε_A	9 ring stretching cm.$^{-1}$	ε_A	10 Ring? cm.$^{-1}$	ε_A	11 β_{CH} cm.$^{-1}$	ε_A	12 β_{CH} cm.$^{-1}$	ε_A
Pyrid-2-thiones.														
1	NA		NA		1472	90	1444	110	1377	20	1254	75	1156	55
2	NA		1466	10	1500	15	1415	20	1387	15	1318	75	1154	85
3	1465 * 1459	35 45	NA		1501	30	1435	20	1400 1352	15 45	1242	70	(—)	
4	NA		NA		1500	m	1446	m	1367	m	1252 *	w	1182	m
5	NA		1457 1422	35 35	1500 *	40	1439	55	1364	10	1272	80	1160	60
6	1492 ⁑ 1455 ⁑	60 75	NA		1492 ⁑	60	1455 ⁑	75	1345	55	1255	125	1159	50
7	NA		NA		1490 *	w	1443	mw	1368	m	1250 *	mw	1179	w
8	NA		1460	35	1485 * 1473	35 155	1417	240	1350	5	1306	35	1193	60
9	1500 1465	50 95	NA		1488 * 1470	35 145	1422	185	1337	10	1252	50	1184	80
10	NA		NA		1486 1458	185 200	1416	280	1350	10	1263	110	1189 1165	65 85

No.	13 β_{CH} cm.$^{-1}$	ε_A	14 νC=S cm.$^{-1}$	ε_A	15 νNO cm.$^{-1}$	ε_A	16 Ph cm.$^{-1}$	ε_A	17 Me cm.$^{-1}$	ε_A	18 β_{CH} cm.$^{-1}$	ε_A	19 Ring breathing? cm.$^{-1}$	ε_A
Pyrid-2-thiones.														
1	—		NA		NA		NA		NA		1012 *	25	993	100
2	1138 *	25	NA		NA		NA		1050	45	—		NA	
3	1144	110	NA		NA		1074 1028	25 20	NA		1018	20	NA	
4	1148	m	NA		1110	w	NA		NA		—		NA	
5	1141	90	NA		1104	80	NA		—		1010	15	NA	
6	1141	80	NA		1102	80	1073 * 1025	5 5	NA		1010	20	NA	
7	(—)		1135	s	NA		NA		NA		1040	m	998	m
8	(—)		1142 1112	230 440	NA		NA		1053	45	1020	25	NA	
9	1150	45	1113 * 1104 1086	150 175 240	NA		(—) 1027 ⁑	 130	NA		1027 ⁑	130	NA	
10	(—)		1142	290	1112 1081	35 50	NA		NA		1024 1013	10 15	NA	

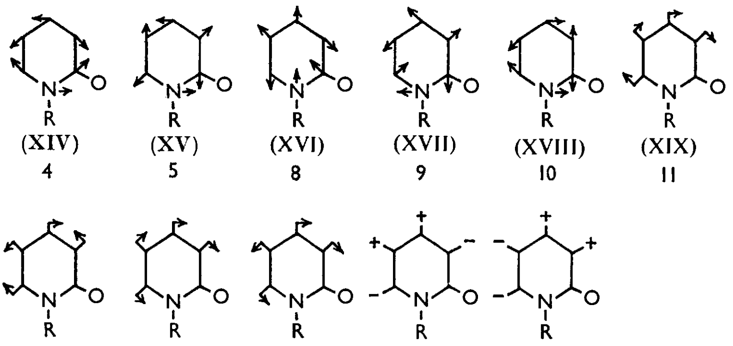
TABLE 2. (*Continued.*)

No.	20 νC–O cm.$^{-1}$	ε_A	21 γ_{CH} cm.$^{-1}$	ε_A	22 γ_{CH} cm.$^{-1}$	ε_A	Extra bands cm.$^{-1}$	ε_A	M. p. or b. p./mm. Found	Lit.	Ref.
1	NA		917	35	845 837	20 20	1097	15	105—107°	106—107°	*h*
2	NA		876	50	842	40			† 98—100°/2	122—124°/11	*i*
3	NA		873	45	842	75	953	10	74—75°	75—76°	*j*
4	NA		894 888	m m	835	m			148—149°	149—150°	*k*
5	980	115	871	30	832	60			† 130°/0·05	130°/0·05	*c*
6	960 939	40 40	912 867	70 45	834	85			76—78°	76—78°	*c*
7	NA		874	w	<800?				124—126	125	*l, f*
8	NA		—		804	45			88—90	89—90	*m, f*
9	NA		—		830	25	990 952	15 15	85—87	—	*b*
10	NA		—		813	45			63—64	65—67	*n*

Nj = Nujol mull (insoluble in $CHCl_3$). sat. = saturated solution in $CHCl_3$. * Shoulder. ⁑ Band considered to be the superimposition of two bands. — Absence of band. (—) Band masked by stronger absorption. ($CHCl_3$) Band masked by solvent. NA = Band neither found nor expected. § Band the intensity of which is markedly raised by overlap with neighbouring band. † B. p.

Refs.: *a*, Tschitschibabin and Ossetrowa, *Ber.*, 1925, **58**, 1711. *b*, This work. *c*, Gardner and Katritzky, *J.*, 1957, 4375. *d*, Cunningham, Newbold, Spring, and Stark, *J.*, 1949, 2091. *e*, King and Ware, *J.*, 1939, 873. *f*, Jones and Katritzky, *J.*, 1958, 3610. *g*, Ochiai, *J. Org. Chem.*, 1953, **18**, 534. *h*, Königs and Geigy, *Ber.*, 1884, **17**, 589. *i*, Prill and McElvain, *Org. Synth.*, Coll. Vol. II, John Wiley and Son Inc., New York, 1946, p. 419. *j*, Fischer, *Ber.*, 1899, **32**, 1302. *k*, Shaw, *J. Amer. Chem. Soc.*, 1949, **71**, 67. *l*, Philips and Shapiro, *J.*, 1942, 584. *m*, Gutbier, *Ber.*, 1900, **33**, 3359. *n*, Shaw, Bernstein, Losee, and Lott, *J. Amer. Chem. Soc.*, 1950, **72**, 4362.

*Approximate vibration modes of pyrid-2-ones.**



(XIV) (XV) (XVI) (XVII) (XVIII) (XIX)
Col. 4 5 8 9 10 11

(XX) (XXI) (XXII) (XXIII) (XXIV)
Col. 12 13 18 21 22

* Double bonds are omitted.

strong band at 3000—2940 [2975 ± 20] * cm.$^{-1}$ of intensity (135—170) [(155 ± 15)] * for the 4-series and (70—115) [(85 ± 15)] for the 2-series. This band was not present for a carbon tetrachloride solution of 1-benzylpyrid-2-one and for a tetrachloroethylene solution of 1-methylpyrid-2-thione, which indicates that it was due to the H-bonded chloroform C–H stretching band (cf. refs. 2, 3).

C=O *and* C=S *Stretching Modes* (Table 1, cols. 5, 15; Table 2, cols. 3, 14).—These modes are found (see Table 3). In the 4-series earlier workers [8] assigned the band at *ca.* 1630 cm.$^{-1}$ (Table 1, col. 4) to the νC=O; the present assignment is in better agreement with the pyrid-4-thione spectra and we have been informed by Dr. L. J. Bellamy [9] that application

---

* Parentheses signify apparent molecular extinction coefficients and square brackets denote arithmetical means and standard deviations, calculated by omitting shoulders and, in the case of ε_A, overlapped bands.

[8] Leonard and Locke, *J. Amer. Chem. Soc.*, 1955, **77**, 1852.

[9] Personal communication, cf. Bellamy and Rogasch, *Spectrochim. Acta*, 1960, **16**, 30.

TABLE 3.

	νC=O	νC=S
4-Series	1577—1575 cm.$^{-1}$ (430—600)	1119—1108 (>550)
2-Series	1666—1655 cm.$^{-1}$ (550—700)	1142—1112 (290—440)

of his method of solvent shifts led him independently to the same assignment. The low positions of the C=O stretching bands are in accord with the expected high contribution of single-bond character of this link. Our data for the C=S bands are in reasonable agreement with those of Spinner [10] who has discussed this region for pyrid-2- and -4-thione and their 1-methyl derivatives.

Ring-stretching Modes (Table 1, cols. 3, 4, 6, 7; Table 2, cols. 4, 5, 8, 9).—The bands are assigned to these modes as in Table 4. These compounds show the usual four ring-stretching bands, at positions not very different from those in pyridines and benzenes.[4] The 4-series compounds are of C_{2v} symmetry and there is a very large disturbance of charge symmetry co-directional with the symmetry axis; the fact that one of the pair of higher-frequency bands is much stronger than the other is in agreement with this.[11] As expected, for the 2-series compounds of C_s symmetry, the difference in the intensities of the pair of higher-frequency bands is less. Changes in the position and intensity of the pairs of bands of lower frequency are less easy to explain: these bands are considerably stronger in the pyridthiones than in the oxygen compounds.

TABLE 4.

4-*Series*: *ring-stretching modes.*

ca. 1650 cm.$^{-1}$ shoulder.
1643—1621 cm.$^{-1}$ (440—650) [1630 ± 10 cm.$^{-1}$ (555 ± 90)]
1510—1484 cm.$^{-1}$ (45—180) [1502 ± 11 cm.$^{-1}$ (80 ± 50)]
1408—1394 cm.$^{-1}$ (25—155) for CO compounds;
1471—1470 cm.$^{-1}$ (330—340) for CS compounds.

2-*Series*: *ring-stretching modes.*

1628—1590 [1603 ± 17] cm.$^{-1}$; (300—370) for CO, (70—145) for CS
1572—1535 cm.$^{-1}$ (105—220) [1545 ± 12 cm.$^{-1}$ (160 ± 55)]
1500—1458 [1479 ± 17] cm.$^{-1}$; (15—90) for CO, (155—200) for CS
1455—1415 [1429 ± 12] cm.$^{-1}$; (20—110) for CO, (240—280) for CS.

Vibration of the Benzyl Groups.[12]—The benzene ring vibrations near 1600 cm.$^{-1}$ are doubtless hidden by stronger absorption; those near 1490 and 1450 cm.$^{-1}$ can be distinguished (Table 1, col. 8; Table 2, col. 6), as can the phenyl β_{CH} frequencies near 1070 and 1028 cm.$^{-1}$ (Table 1, col. 17; Table 2, col. 16). A band at 1355—1350 cm.$^{-1}$ is possibly the CH_2 wagging mode.

Vibrations of the Methyl Groups (Table 1, col. 9; Table 2, cols. 7, 17).—Some bands in the 1450 and 1050 cm.$^{-1}$ regions are very tentatively assigned to methyl bending and rocking modes.

Ring Modes.—The band for the 2-series compounds at 1387—1345 cm.$^{-1}$ (5—45) [1358 ± 17 (20 ± 15)] (Table 2, col. 10) is possibly the ring vibration (XVIII). A band has been reported at 1315 ± 11 cm.$^{-1}$ in *ortho*-disubstituted benzenes [12] but is usually not easily detected in heterocyclic compounds. In the 4-series the compounds also show some unexplained bands hereabouts (Table 1, col. 12). Aromatic compounds in which the ring is free from heavy substituents in the 1,3,5-positions show a ring breathing mode near 1000 cm.$^{-1}$; such are possibly the bands of Table 2, col. 19.

In-plane CH *Deformation Modes* (Table 1, cols. 13, 14, 16, 18; Table 2, cols. 11—13, 18).—These bands have been assigned (see Table 5) by comparison with other compounds containing the same orientation of ring hydrogen atoms.

The NO *Stretching Vibration*.—This will absorb at fairly high frequencies because the

[10] Spinner, *J. Org. Chem.*, 1958, **23**, 2037.

[11] Katritzky, *J.*, 1958, 4162.

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

TABLE 5.

4-*Series*	para-*Disubst. benzenes*[13]
Obscured	[1258 ± 11 cm.$^{-1}$ (*ca.* 15)]
Doublet at 1192—1174 [1185 ± 7] cm.$^{-1}$ 1158—1144 [1151 ± 7] cm.$^{-1}$ variable ε_A	[1176 ± 6 cm.$^{-1}$ (var.)]
1093—1081 [1089 ± 4] cm.$^{-1}$; (*ca.* 20)	[1111 ± 7 cm.$^{-1}$ (20 ± 15)]
1030—1010 [1018 ± 8] cm.$^{-1}$ (20—30) for CO, (135—160) for CS	[1013 ± 5 cm.$^{-1}$ (var.)]
2-Series	ortho-*Disubst. benzenes*[12]
1318—1254 cm.$^{-1}$ (35—125) [1270 ± 32 cm.$^{-1}$ (80 ± 30)]	[1269 ± 17 cm.$^{-1}$ (*ca.* 15)]
1193—1154 cm.$^{-1}$ (50—85) [1168 ± 15 cm.$^{-1}$ (70 ± 15)]	[1160 ± 4 cm.$^{-1}$ (20 ± 10)]
1150—1141 [1145 ± 4] cm.$^{-1}$, ε_A variable	[1125 ± 14 cm.$^{-1}$ (25 ± 15)]
1040—1010 cm.$^{-1}$ ($\leqslant$25) [1019 ± 11 cm.$^{-1}$]	[1033 ± 11 cm.$^{-1}$ (50 ± 40)]

NO bond has some double-bond character in these compounds (overlap of oxygen *p*-orbitals with the aromatic ring). Bands near 1325 cm.$^{-1}$ (Table 1, col. 11) and 1100 cm.$^{-1}$ (Table 2, col. 15) have been provisionally assigned to these modes, but the first is doubtful.

Alkyl–Oxygen Stretching Mode.—This has been assigned bands near 950 cm.$^{-1}$ (Table 1, col. 19; Table 2, col. 20).

Out-of-plane CH *Deformations.*—The characteristic in-phase mode of four hydrogen atoms in 2,3,5,6-positions is shown in the 4-series at 845—843 cm.$^{-1}$ (200—280) [844 ± 1 cm.$^{-1}$ (240 ± 35)] for the oxo-compounds and at 821—819 cm.$^{-1}$ (135—160) for the thio-analogues (Table 1, col. 20).

In the 2-series (Table 2, cols. 21, 22) there is a band at 917—871 cm.$^{-1}$ (30—70) (absent for two of the thio-compounds) and another at 845—832 cm.$^{-1}$ (20—85) for the oxo-compounds and at 813 cm.$^{-1}$ for the thio-analogues. *ortho*-Disubstituted benzenes with two donor substituents absorb at 916—906 cm.$^{-1}$ (10—25) and many *ortho*-substituted benzenes show a band in the 900—800 cm.$^{-1}$ region.[1]

General Conclusions.—The spectra of pyridones and pyridthiones have been shown to resemble those of other heteroaromatic compounds. The generalisations established for pyridines, etc., apply to these compounds and it has been possible to give a tentative assignment to nearly all the bands. The spectra reported here for potentially tautomeric pyridones and pyridthiones support the conclusion[14] that these compounds exist predominantly as such and not in the hydroxy- or mercapto-pyridine form.

Experimental.—1-*Benzylpyrid*-4-*one*. Pyrid-4-one (0·95 g.), benzyl chloride (1·25 g.), and sodium in ethanol (0·22 g. in 25 c.c.) were refluxed for 1 hr. The solid was filtered off and the filtrate evaporated to give 1-*benzylpyrid*-4-*one* (1·1 g., 60%) which crystallised from benzene as deliquescent plates, m. p. 109—111° (Found: C, 77·7; H, 6·3; N, 7·7. $C_{12}H_{11}NO$ requires C, 77·8; H, 6·0; N, 7·6%).

1-*Benzylpyrid*-4-*thione*. 1-Benzyl-4-pyridone (0·4 g.) was heated with phosphorus pentasulphide (0·8 g.) for 3 hr. at 130°. Aqueous sodium hydroxide (10% *ca.* 10 c.c.) was added and the alkaline solution extracted with chloroform (2 × 20 c.c.). The extracts were dried and evaporated to give 1-*benzylpyrid*-4-*thione* (0·19 g., 45%) which crystallised from ethanol as yellow plates, m. p. 183—185° (Found: C, 71·3; H, 6·0; N, 7·0. $C_{12}H_{11}NS$ requires C, 71·6; H, 5·5; N, 7·0%).

1-*Benzylpyrid*-2-*thione* was prepared by a method analogous to that of the 4-compound and crystallised from benzene as yellow needles (40%), m. p. 85—87° (Found: C, 71·0; H, 5·56%).

Other compounds were prepared by recorded methods and recrystallised or distilled immediately before use.

The spectra were measured under the same conditions as before.[1]

We thank Dr. L. J. Bellamy for an interesting discussion and for communicating to us his unpublished results. This work was carried out during the tenure (by R. A. J.) of a D.S.I.R. maintenance grant.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November* 18*th*, 1959.]

---

[13] Katritzky and Simmons, *J.*, 1959, 2051.

[14] Gardner and Katritzky, *J.*, 1957, 4375; R. A. Jones and Katritzky, *J.*, 1958, 3610; Mason, *J.*, 1957, 4874, 5010; 1958, 674.