447. *Infrared Studies of Heterocyclic Compounds. Part I. 4-Substituted Pyridines.*

By A. R. KATRITZKY and J. N. GARDNER.

4-Monosubstituted pyridines show eight characteristic bands in chloroform; their positions and intensities are recorded and discussed for forty-eight compounds.

AVAILABLE information about the infrared spectra of heterocyclic compounds is very much less than their importance justifies. Thus in the two reviews by Bellamy[1] and by Jones and Sandorfy[2] only *ca.* 3% of the space is devoted to the topic. We considered that it was of interest to compare a large number of spectra, measured under standard conditions, in which only one parameter was being changed; after our work[3] on substituted pyridine 1-oxides this paper is devoted to the spectra of forty-eight 4-monosubstituted pyridines. Of the bands with $\varepsilon_A \geqslant 15$, eight were found to be characteristic of the nucleus and are recorded in the Table; the other bands were, with few exceptions, characteristic of the substituent. For reasons given previously[4] the spectra were all measured at 0·2M-concentration in chloroform in a 0·117 mm. cell, and apparent molecular extinction coefficients recorded.

The detailed spectrum of 4-picoline as liquid and gas is known.[5] Cook and Church[6] investigated the spectra of 4-benzyl- and six 4-alkyl-pyridines as liquid films, and recorded the positions of characteristic bands, without giving any intensities. The bands at 1613—1597, 1570—1555, 1508—1490, 1422—1406, 1072—1067, 1000—995, and 822—785 cm.$^{-1}$ which they record correspond to those discussed in this paper. They also record absorption near 1460 and 1380 cm.$^{-1}$ which may be assigned to substituent CH deformation; near 1230 cm.$^{-1}$, which would be obscured by solvent absorption in our work; and near 1300 cm.$^{-1}$ which we have not found: the last band was stated to be " of variable intensity " and assigned to an overtone. The actual positions of the bands found in the two investigations show fair agreement considering the difference in state; our compounds with a saturated carbon atom directly attached to the ring usually show a smaller range than that reported by Cook and Church:[6] *e.g.*, in the liquid, 4-picoline absorbs at 1406 cm.$^{-1}$, and 4-ethylpyridine at 1422 cm.$^{-1}$, but in chloroform solution both absorb at 1415 cm.$^{-1}$. Shindo and Ikekawa[7] discussed certain portions of the spectra of the 4-methyl and 4-ethyl compounds, in connexion with a general investigation into alkylpyridines, and the spectra of the 4-chloro-, 4-methoxy-, and 4-nitro-compound have also been recorded.[8]

The 3000 *cm.$^{-1}$ Region.*—Usually only one band is resolved, and for reasons discussed

---

[1] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1956.

[2] Jones and Sandorfy in Weissberger, " Technique of Organic Chemistry, Vol. IX. Chemical Applications of Spectroscopy," Interscience, London, 1956.

[3] Katritzky and Gardner, *J.*, 1958, 2192; Katritzky and Hands, *J.*, 1958, 2195.

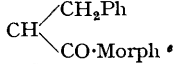
[4] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.

[5] Long, Murfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171.

[6] Cook and Church, *J. Phys. Chem.*, 1957, **61**, 458.

[7] Shindo and Ikekawa, *Pharm. Bull.* (*Japan*), 1956, **4**, 192.

[8] Costa and Blasina, *Z. phys. Chem.* (*Frankfurt*), 1955, **4**, 24.

No.	Subst.	1 $CHCl_3$ νCH cm.$^{-1}$	ε_A	2 A_g $\{\nu CC, \nu CN$ cm.$^{-1}$	ε_A	3 B_{1g} $\{\nu CC, \nu CN$ cm.$^{-1}$	ε_A	4 B_{2u} $\{\nu CC, \nu CN$ cm.$^{-1}$	ε_A
1	NMe_2	2940	110	1607	560	1550 *	80	1522	170
2	NHPh	2940	35	1595	430	1560	40	1510	185
3	NH_2	2930	55	1606	290	1573	45	1503	50
4	OMe	2960	75	1601	430	1576	155	1505	200
5	OEt	2980	90	1600	320	1570	100	1501	130
6	NH·COMe [a]	2940	55	1590	390	1570 *	30	(—)	
7	NH·COPh [a]	2960	50	1593	300	(—)		(—)	
8	Me [b]	2970	55	1610	135	1565	15	1499	15
9	Et	2970	70	1606	125	1561	15	1493	10
10	$CH_2{\cdot}CH_2Ph$	2960	75	1608	180	1563	20	(—)	
11	$CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$	2960	95	1610	185	1560 *	60	(—)	
12	$CH_2{\cdot}CH_2{\cdot}NH{\cdot}COPh$	2970	75	1608	165	(—)		(—)	
13	$CH_2{\cdot}CH_2{\cdot}NHTs$ [c]	2950	55	1609	145	1565	15	(—)	
14	$CH_2{\cdot}CH_2{\cdot}CO_2Me$	2960	85	1608	165	1560	25	1490	10
15	$CH_2{\cdot}CH_2{\cdot}CO_2Et$	2970	80	1609	160	1563	30	—	
16	CH_2Ph	2960	50	1602	180	1560	15	(—)	
17	$CH_2{\cdot}C_6H_4{\cdot}NO_2$-*p*	2960	35	1601	130	1563	25	(—)	
18	$CH_2{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CH_2Ph$	2980	85	1608	120	1565 *	25	1500 *	80
19	$CH_2{\cdot}CS{\cdot}Pip$ [d]	2950	165	1601	190	1560	15	(—)	
20	$CH_2{\cdot}CS{\cdot}Morph$ [e]	2980	115	1601	170	1560	15	(—)	
21	$CH_2{\cdot}COPh$	2980	70	1608	175	1566	35	(—)	
22	$CH_2{\cdot}CO_2Me$	2970	80	1610	135	1566	25	1496	10
23	$CH_2{\cdot}CO_2Et$	2990	75	1608	115	1568	25	—	
24	$CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$	2970	70	1603	180	1558 *	50	(—)	
25	$CH_2{\cdot}CO{\cdot}NHPh$	2950	55	1602 ‡	260	(—)		(—)	
26	 $CH\begin{matrix}/CH_2Ph\\ \backslash CO{\cdot}Morph\end{matrix}$ [e]	2980	90	1600	185	1560	20	(—)	
27	$C{\vdots}CPh$	2990	50	1600	220	1540 *	15	(—)	
28	$C{\vdots}C{\cdot}C_6H_4{\cdot}NO_2$-*p*	2980	65	1601 ‡	400	(—)		(—)	
29	$CH{:}CHPh$	2970	50	1600	290	1552	15	(—)	
30	$CH{:}CH{\cdot}C_6H_4Cl$-*p*	2980	70	1603 ‡	260	1553	15	(—)	
31	$CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$-*p*	2980	70	1601 ‡	380	1553 *	30	(—)	
32	 $C\begin{matrix}/\!\!/CHPh\\ \backslash CO{\cdot}Morph\end{matrix}$	2980	110	1600	350	1545	35	(—)	
33	$CH{:}CH{\cdot}CO_2Me$	2960	65	1600	170	1550	65	1492	15
34	$CH{:}CH{\cdot}CO_2Et$	2970	70	1601	165	1549	35	1496	10
35	Ph	2950	50	1596	130	1546	20	(—)	
36	$C_6H_4{\cdot}NO_2$-*p*	2970	40	1606	105	1551 ‡	105	(—)	
37	$CH_2{\cdot}OH$	2960	60	1610	90	1564	25	—	
38	$CHPh{\cdot}OH$	2980	55	1602	115	1562	25	(—)	
39	$CMe(CN){\cdot}OAc$	2990	40	1604	120	1568	20	—	
40	$CMe(CN){\cdot}OBz$	2980	45	1600	165	1567	20	(—)	
41	$CMe{:}N{\cdot}NH_2$	2980	45	1590	135	1545	10	—	
42	Cl	2980	35	1575	280	1565 *	115	1482	100
43	CN	2990	30	1600	90	1558	30	1490	10
44	CO_2Me	2970	60	1604	45	1565	40	1490	10
45	CO_2Et	2990	85	1602	35	1567	45	1490	5
46	CHO	2990	30	1600	15	1572	75	1490	15
47	COMe	2980	35	1600	35	1555	30	1489	15
48	NO_2	2990	20	1604	25	1575	65	1480 *	15

See footnote, p. 2192, and also for meaning of other symbols.

[a] Measured at 0·02M-concentration in 1 mm. cell because of poor solubility. [b] Measured at 0·4M-concentration. [c] Toulene-*p*-sulphonyl derivative. [d] Piperide. [e] Morpholide.

in ref. 3 this is assigned mainly to the CH stretching of the solvent, displaced by hydrogen bonding with the pyridine. The band occurs at 2990—2930 [2970 ± 15] cm.$^{-1}$; * electron attracting substituents tend to raise the frequency (cf. expected weaker H-bond formation). Compounds with weakly conjugating substituents (Nos. 8—41, except 19, 20, 26, and 32 where there is serious overlapping by substituent absorption) have intensity (35—95) [(65 ± 15)]; * when electron-withdrawing substituents are present (Nos. 42—48) this intensity is (20—35) (except for the esters). Consideration of Nos. 1—7 is complicated

---

* For the significance of parentheses and brackets see *J.*, 1958, p. 2187.

		5 B_{3u} $\{\nu CC, \nu CN$		6 ? βCH		7 A_u, B_{3g} γCH		8 B_{1u} γCH	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	NMe_2	(—)		(—)		991	300	805	105
2	NHPh	1412	30	(—)		992	105	807	50
3	NH_2	1432	25	—		991	140	815	120
4	OMe	1425	60	—		992	65	819	190
5	OEt	1415	25	—		993	95	809	105
6	NH·COMe [a]	($CHCl_3$)		—		996	80	($CHCl_3$)	
7	NH·COPh [a]	($CHCl_3$)		1072 ‡	55	994	50	($CHCl_3$)	
8	Me [b]	1415	35	1068	15	997	45	—	
9	Et	1415	40	1065	10	996	30	819	60
10	$CH_2\cdot CH_2Ph$	1418	50	1070 *	20	996	45	805	55
11	$CH_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2Ph$	1416	100	1068	25	994	45	—	
12	$CH_2\cdot CH_2\cdot NH\cdot COPh$	1418	65	1068	35	995	45	—	
13	$CH_2\cdot CH_2\cdot NHTs$ [c]	1418	125	1070 *	110	994	25	814	110
14	$CH_2\cdot CH_2\cdot CO_2Me$	1418	80	1068	20	992	35	—	
15	$CH_2\cdot CH_2\cdot CO_2Et$	1416	75	1071	25	997	40	808	40
16	CH_2Ph	1418	65	1069	30	996	40	825	20
17	$CH_2\cdot C_6H_4\cdot NO_2$-$p$	1418	45	1070	20	997	20	825	10
18	$CH_2\cdot CS\cdot NH\cdot CH_2\cdot CH_2Ph$	1418	140	1070	35	993	20	—	
19	$CH_2\cdot CS\cdot Pip$ [d]	1418	90	1070	30	995	40	—	
20	$CH_2\cdot CS\cdot Morph$ [e]	1418 *	120	1069 *	50	995	35	—	
21	$CH_2\cdot COPh$	1419	65	1071 ‡	30	995 *	90	—	
22	$CH_2\cdot CO_2Me$	1419	80	1071	25	996	50	—	
23	$CH_2\cdot CO_2Et$	1419	70	1071	25	997	30	—	
24	$CH_2\cdot CO\cdot NH\cdot CH_2Ph$	1418	80	1070	30	994	30	—	
25	$CH_2\cdot CO\cdot NHPh$	1419	80	1070	15	995	15	—	
26	$CH{<}^{CH_2Ph}_{CO\cdot Morph}$ [e]	1416 *	125	1068 ‡	70	993	35	—	
27	$C\vdots CPh$	1410	45	1068	15	990	45	820	120
28	$C\vdots C\cdot C_6H_4\cdot NO_2$-$p$	1409	70	1066	10	990	35	819	155
29	$CH{:}CHPh$	1415	30	1068	10	994	65	802	50
30	$CH{:}CH\cdot C_6H_4Cl$-p	1417	45	1065	10	992	55	(—)	
31	$CH{:}CH\cdot C_6H_4\cdot NO_2$-$p$	1417	60	1065	10	991	50	—	
32	$C{<}^{/\!/CHPh}_{CO\cdot Morph}$ [e]	1415	135	1070 ‡	65	995 *	50	813	60
33	$CH{:}CH\cdot CO_2Me$	1414	85	1066	10	990	65	812	140
34	$CH{:}CH\cdot CO_2Et$	1415	80	1067	15	992	55	813	120
35	Ph	1409	50	1068	20	990	25	827	80
36	$C_6H_4\cdot NO_2$-p	1413	30	1070	15	993	30	817	190
37	$CH_2\cdot OH$	1416	85	(—)		994	45	—	
38	$CHPh\cdot OH$	1414	95	1066 *	30	994	40	—	
39	$CMe(CN)\cdot OAc$	1416	105	(—)		996	35	818	120
40	$CMe(CN)\cdot OBz$	1415	100	(—)		995	35	818	135
41	$CMe{:}N\cdot NH_2$	1410	55	1061	30	993	45	820	90
42	Cl	1409	110	1062	40	985	10	809	110
43	CN	1412	100	1069	20	993	30	819	150
44	CO_2Me	1411	130	1065	80	995	45	829	15
45	CO_2Et	1412	105	1066	100	994	30	—	
46	CHO	1416	85	1060	20	992	25	(803	55)
47	COMe	1411	120	1064	40	993	25	813	115
48	NO_2	1405	65	1055	30	992	30	—	

by two compounds' being measured at 0·02M-concentration, and the possibility of intramolecular hydrogen-bonding.

The 1650—1550 *cm.*$^{-1}$ *Region.*—Two bands occur. The stronger (col. 2) occurs at 1610—1590 [1603 ± 5] cm.$^{-1}$ except for the chloro-compound (No. 42); halogens are known [3] to lower this band's frequency in other cases. The intensity depends on the electron-donor properties of the substituent. For amino-, amido-, alkoxy-, and chloro-substituents, it is $\geqslant 280$; for strongly electron-withdrawing substituents (Nos. 44—48) it is $\leqslant 45$. For groups with relatively weak electronic effects (Nos. 8—41) the intensity is (90—290) [(155 ± 40)] (except for No. 32 where there is strong overlapping by the carbonyl group). Phenyl groups, of course, also absorb in this region, but much less strongly;[9] however, it is possible to discern their influence. Assignment of this and the other bands is discussed at the end of the paper.

The second band in this region is usually much weaker. When the ring is attached to a saturated carbon atom (Nos. 8—26 and 37—40), position and intensity are fairly constant at 1568—1560 cm.$^{-1}$ (15—35) [1563 $\pm$ 3 cm.$^{-1}$ (20 $\pm$ 5)]. Strongly electron-donor substituents (Nos. 1—7) tend to raise both frequency and intensity (cf. the corresponding band in benzenes[10]). Carbon–carbon multiple bonds (Nos. 27—36) lower the frequency to 1553—1545 cm.$^{-1}$. Electron-acceptors (Nos. 43—48) tend to raise the intensity, but the position varies from 1575 to 1555 cm.$^{-1}$.

The 1500—1400 *cm.$^{-1}$ Region.*—A band (col. 4) frequently occurs at 1522—1480 cm.$^{-1}$; compounds with powerful electron-donor substituents (Nos. 1—5) absorb strongly at above 1500 cm.$^{-1}$, whereas those with electron-accepting substituents (Nos. 43—48) absorb weakly at 1490 cm.$^{-1}$ or below. Chlorine behaves as an electron-donor as regards the intensity, but as acceptor as regards the position of the band. The band is masked in amides and compounds with phenyl groups by substituent absorption; of the remaining compounds with weakly conjugating substituents, weak absorption is shown at 1500—1490 cm.$^{-1}$ in seven, and for five others the band is absent or too weak to be recorded.

All the compounds show a second band in this region (col. 5) at 1432—1405 [1415 $\pm$ 4] cm.$^{-1}$. Only the amino- and methoxy-compounds absorb above 1419 cm.$^{-1}$; all the nineteen compounds (Nos. 8—25, 37) in which the ring is directly attached to a CH_2 group absorb at 1419—1415 cm.$^{-1}$; carbon–carbon triple bonds and strongly electron-withdrawing substituents tend to lower the frequency to *ca.* 1411 cm.$^{-1}$. The intensity of this band is especially affected by overlap with substituent bands for Nos. 13, 18—20, 26, and 32; otherwise it is (25—130) [70 $\pm$ 25] with a definite tendency to be raised by electron-accepting substituents.

The 1080—980 *cm.$^{-1}$ Region.*—Two bands are in general found. The first (col. 6) at 1072—1055 [1067 $\pm$ 3·5] cm.$^{-1}$ is not found for compounds with strongly electron-donor substituents (Nos. 1—6); with weakly conjugating substituents (Nos. 8—40) the band is in the narrower range 1071—1065 cm.$^{-1}$ with intensity (10—35) [(20 $\pm$ 8)]; electron-attracting groups (Nos. 41—48) tend to lower the frequency, and increase the intensity.

All the compounds show a band at 997—985 [993 $\pm$ 2·5] cm.$^{-1}$ (Col. 7). The intensity is high with strongly electron-donor substituents (Nos. 1—7); otherwise it is (10—50) [(35 $\pm$ 10)], except for compounds where CH:CH-deformation absorption overlaps (Nos. 29—34).

The 800 *cm.$^{-1}$ Region.*—Many of the compounds show a band at just above 800 cm.$^{-1}$. This is probably a ring CH deformation frequency,[7] present for the remaining compounds below 805 cm.$^{-1}$, where it is obscured by solvent absorption.

Assignments.—Comparison with Randle and Whiffen's data[11] for *para*-substituted benzenes suggests the tentative assignments indicated at the head of the Table. There can be little doubt about those in cols. 2, 3, 4, and 5, where the corresponding *para*-benzene absorption is at [1620 $\pm$ 8, 1571 $\pm$ 11, 1512 $\pm$ 12, and 1450 $\pm$ 10 cm.$^{-1}$] with average intensities of m, w, vs, and m. Col. 6 probably records an in-plane CH deformation, corresponding to one of two *para*-benzene frequencies B_{3u} or B_{2u} at respectively [1125 $\pm$ 10 and 1018 $\pm$ 10 cm.$^{-1}$]. The corresponding *para*-benzenoid absorption for the two CH out-of-plane deformation modes (cols. 7, 8) is at [961 $\pm$ 12, 817 $\pm$ 13 cm.$^{-1}$].*

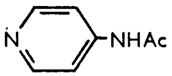
* [*Added* 28.1.1958.] A Referee has commented that, whereas for vibrations of predominately CH character the 4-substituted pyridines are correctly compared with *para*-disubstituted benzenes, for skeletal vibrations, comparison should be with monosubstituted benzenes (i.e., that, from the point of view of the ring, an electron pair is more like a hydrogen atom than a heavier substituent). As the Referee points out, this would not affect the assignments in cols. 2—5, for here the pattern of absorption is similar in both mono- and *para*-di-substituted benzenes,[11] but it suggests an alternative assignment of col. 7 to a vibration corresponding to the A_1 ring vibration at [1001 $\pm$ 4 cm.$^{-1}$] in monosubstituted benzenes.[11]

[9] Katritzky and Lagowski, unpublished results.

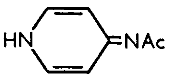
[10] Ref. 1, p. 61.

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

The above work indicates that 4-acetamido- and 4-benzamido-pyridine exist as such (as I) and not in the alternative forms (as II). Other evidence that this is so will be published separately.



(I)



(II)

Experimental.—The preparation of most of the compounds has already been described.[3,4,12] Specimens were recrystallised or redistilled immediately before measurement.

A Perkin-Elmer model 21 instrument was used with a sodium chloride prism, slit programme 4, and the settings previously given.[4]

THE DYSON PERRINS LABORATORY, THE UNIVERSITY, OXFORD.
[*Received, January 14th, 1958.*]

---

[12] See also Katritzky and his co-workers, *J.*, 1955, 2581, 2587; 1956, 2063, 2404; 1957, 191, 1769, 4375; 1958, 150, 1263.