SHORT COMMUNICATIONS

INFRARED ABSORPTION OF SOME 3,4-DISUBSTITUTED PYRIDINES AND PYRIDINE 1-OXIDES*

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During work in this department on the synthesis of 1,4,6-triazanaphthalenes,[1] 5-azaindoles,[2] and pyrazolo[4,3-*c*]pyridines,[3] we measured the spectra of several 3,4-disubstituted pyridines and pyridine 1-oxides. In this paper we record and make tentative assignments for the absorption bands which are characteristic of these rings.

3,4-Disubstituted Pyridines

Ring CC and CN Stretching Vibrations in the 1620–1400 cm^{-1} Region.—It has been established[4] that the intensities of the bands due to ring stretching vibrations of substituted pyridines depend upon the electronic nature of the substituent, whereas the positions of the bands are relatively invariant. For the 3,4-disubstituted pyridines four bands are found in this region at 1617–1580 cm^{-1} (50–500) [1594±10 cm^{-1} (200±160)],§ 1580–1550 cm^{-1} (15–190) [1566±9 cm^{-1} (100±60)], 1525–1482 cm^{-1} (30–270) [1516±6 cm^{-1} (200±40) for compounds 1–6 and 1488±6 cm^{-1} (60±30) for compounds 9–16], and 1404–1436 cm^{-1} (25–125) [1416±10 cm^{-1} (65±30)] (see Table 1).

The variations in the position and intensity of the bands with the change in substituent type are similar to the variations observed for the corresponding 3- and 4-monosubstituted pyridines.[5] However, as expected, the substituent in the 4-position has a greater effect on the band positions and intensities compared with that of the 3-substituent (cf. Katritzky[4]) owing to the greater interaction between the ring and the substituent (particularly when it is electron-donating) in the 4-position. This is particularly noticeable with the third band. Compounds having electron-donating substituents in the 4-position absorb at *c.* 28 cm^{-1} higher than those

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§ Apparent extinction coefficients are enclosed in parentheses. The mean and standard deviations of the position and intensity of the bands are given in brackets.

[1] Clark-Lewis, J. W., and Singh, R. P., *J. Chem. Soc.*, 1962, 3162.

[2] Badger, G. M., and Rao, R. P., *Aust. J. Chem.*, 1964, **17**, 1399.

[3] Badger, G. M., and Rao, R. P., *Aust. J. Chem.*, 1965, **18**, 379.

[4] Katritzky, A. R., *J. Chem. Soc.*, 1958, 4162.

[5] Katritzky, A. R., Hands, A. R., and Jones, R. A., *J. Chem. Soc.*, 1958, 3165; Katritzky, A. R., and Gardner, J. N., *J. Chem. Soc.*, 1958, 2198.

having electron-withdrawing substituents. Also, the intensity of this band is higher for those compounds having an electron-donating substituent.

TABLE 1

RING STRETCHING VIBRATIONS IN THE 1650–1400 cm^{-1} REGION

ϵ_A values for compounds 12, 20, and 23 should be halved for comparison with other compounds. s, strong; m, medium; w, weak; sh, shoulder

	Substituent		ν(CC) / ν(CN)		ν(CC) / ν(CN)		ν(CC) / ν(CN)		ν(CC) / ν(CN)	
	3	4	cm^{-1}	ϵ_A	cm^{-1}	ϵ_A	cm^{-1}	ϵ_A	cm^{-1}	ϵ_A
					3,4-Disubstituted Pyridines					
1	NH_2	NHMe[a]	1594	280	—	—	1525	180	1432sh	50
2	NH_2	NH_2[b]	1580	m	—	—	1512	s	1432	m
3	NHMe	NH_2	1586	150	—	—	1516	200	1436sh 1422	40 70
4	NH_2	OEt	1587	170	—	—	1516	270	1436	95
5	Me	NHMe	1602	450	1580	190	1521	180	1414	35
6	Me	NH_2	1598	160	1578	100	1507	180	1417	40
7	NO_2	NHMe	1617	500	1567	190	1526[h]	230	1425[h]	130
8	NO_2	NH_2[b]	[g]		1557	m	1517[h]	s	1422	w
9	NO_2	OEt	1599	450	1563	140	1495	90	1416	25
10	Me	Me	1599	90	1563	15	1496	40	1412	60
11	Me	Cl	1584	75	1566	95	1483	120	1404	65
12	Me	–N=N–[c]	1585	120	1574	125	1482	50	1409	110
13	Me	NO_2	1607	50	1569	90	1484	40	1405	35
14	CN	CN	1580	105	1550	35	1486	40	1407	125
15	CO_2Me	CO_2Me	1593	65	1565	50	1490	30	1413	80
16	CO_2Et	CO_2Et	1592	80	1564 1553sh	50 45	1488	35	1411	75
					3,4-Disubstituted Pyridine 1-Oxides					
17	Me	NHMe[d]	1632	s	1566	s	1486	s	1415	s
18	Me	Me	1620	35	—	—	1489	210	1430	35
19	Me	Cl	1605	25	—	—	1474	240	1422	115
20	Me	–N=NO–[be]	1597	s	—	—	1477	s	1414	m
21	NHMe	NO_2[a]	1616	520	1585	600	1495[h]	220	1413	285
22	Me	NO_2	1606	210	1573	220	1477	100	1417	20
23	$-(CH_2)_2-$	NO_2[df]	1603	s	1567	vs	1465	s	1436	m
24	Br	NO_2	1594	260	1563sh	200	1471	120	1427	110

[a] Measured as 0·104M solution. [b] Measured as a saturated solution. [c] 3,3′-Dimethyl-4,4′-azopyridine. [d] Measured as Nujol mulls. [e] 3,3′-Dimethyl-4,4′-azoxypyridine-1,1′-dioxide. [f] 4,4′-Dinitro-1,1′-dioxy-3,3′-dipicolyl. [g] Band obscured by stronger absorption. [h] Band considered to be superimposition of two peaks.

CH In- and Out-of-Plane Deformations.—By analogy with the CH deformation frequencies of 1,2,4-trisubstituted benzenes,[6] we have assigned the bands in Table 2 to CH deformations. The band near 1000 cm^{-1} is due to the ring breathing mode.

TABLE 2

CH DEFORMATION AND RING BREATHING FREQUENCIES OF 3,4-DISUBSTITUTED PYRIDINES

	Substituent		β(CH)		β(CH)		Ring		γ(CH)		γ(CH)		γ(CH)	
	3	4	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	NH_2	NHMe	1196	80	1066*	110	—	—	897	35	856	90	813	135
2	NH_2	NH_2	1191	m	1070	w	986	w	—	—	851	w	812	s
3	NHMe	NH_2	1192	50	1083	35	—	—	885sh	25	860	60	817	125
4	NH_2	OEt	1187	95	1060sh	40	—	—	890	25	841	45	804	90
5	Me	NHMe	1195	140	1068	105	994	35	913	10	839	50	814	120
6	Me	NH_2	1192	85	1079	30	996	35	915	10	865	70	820	100
7	NO_2	NHMe	1197	80	1062	45	—	—	—	—	867*	240	814	105
8	NO_2	NH_2	1198	m	1075	w	—	—	928	w	854	w	824	s
9	NO_2	OEt	1195	140	†		—	—	928*	105	854*	185	812	90
10	Me	Me	1195	40	1070	40	1000	10	—	—	841	55	823	85
11	Me	Cl	1190	25	†		997	25	—	—	—	—	825 817	110 95
12	Me	–N=N–‡	1189	30	1054	100	994	25	—	—	857	50	837	190
13	Me	NO_2	1183	25	1058	40	1005	10	—	—	843	85	—	—
14	CN	CN	1187	40	1050	10	—	—	—	—	843	135	815	55
15	CO_2Me	CO_2Me	1196	100	1053	75	—	—	—	—	840	40	823	40
16	CO_2Et	CO_2Et	1180	80	1051	130	—	—	—	—	840	45	—	—
			[1191±5 cm^{-1} (70±40)]		[1072±7 cm^{-1} (50±30)]§		[996±5 cm^{-1} (25±10)]		[911±15 cm^{-1} (20±10)]		[848±9 cm^{-1} (65±35)]		[818±8 cm^{-1} (100±40)]	

* Band considered to be superimposition of two peaks. † Band obscured by stronger absorption. ‡ ϵ_A value should be halved for comparison with other compounds. § For electron-donating 4-substituent. For electron-withdrawing 4-substituent, 1053±3 cm^{-1} (70±50).

With few exceptions all the remaining bands in the spectra with $\epsilon_A \geqslant 10$ were found to be characteristic of the substituents.

3,4-Disubstituted Pyridine 1-Oxides

With only five of the eight available compounds soluble in chloroform, it is not feasible to discuss in detail the absorption bands (Tables 1 and 3) characteristic

TABLE 3

CH DEFORMATION AND $^{+}N-O^{-}$ STRETCHING FREQUENCIES OF 3,4-DISUBSTITUTED PYRIDINE 1-OXIDES

Substituent		$\nu(^{+}N-O^{-})$		β(CH)		β(CH)		γ(CH)		γ(CH)	
3	4	cm^{-1}	ϵ_A	cm^{-1}	ϵ_A	cm^{-1}	ϵ_A	cm^{-1}	ϵ_A	cm^{-1}	ϵ_A
Me	NHMe	1270	m	1151	s	1112	w	886	s	817	s
Me	Me	1292	210	1150	65	1124	200	867	65	818	90
		1258	240								
Me	Cl	1292	310	1152	105	1130	20	866	95	817	100
		1252	240								
Me	$-N=N^{+}-O^{-}$	1294	vs	1157	s	1118	vs	860	m	803	s
	|	1255	vs								
NHMe	NO_2	1310	330	1150	60	1125	50	—	—	824	180
		1244	660								
Me	NO_2	1307	600	1155	30	1120	10	864	120	825	60
		1260	280								
$(CH_2)_2$	NO_2	1300	vs	1142	m	—	—	864	s	840	m
		1270	vs								
Br	NO_2	1300	400	1158	50	1123	70	858	110	824	50
		1255	100								

of the 3,4-disubstituted pyridine 1-oxide ring. Assignments have been made by analogy with those for 3- and 4-monosubstituted pyridine 1-oxides,[7] and 1,2,4-trisubstituted benzenes.

The majority of the remaining bands in the spectra with $\epsilon_A \geqslant 10$ could be assigned to the substituent absorption. Notable exceptions were those at 1097 cm^{-1} (300) for 3-methylamino-4-nitropyridine 1-oxide; 1091 (450) for 3-methyl-4-nitropyridine 1-oxide; 1082 cm^{-1} (vs) for 4,4′-dinitro-1,1′-dioxy-3,3′-dipicolyl; and 1050 cm^{-1} (300) for 3-bromo-4-nitropyridine 1-oxide. Bands of similar intensity and position have been observed, but not assigned, for other nitroheterocycles.[8] It is probable, however, that the band is associated with the C–N stretching vibration coupled with a ring stretching mode (cf. Stephenson *et al.*[9]).

[6] Randle, R. R., and Whiffen, D. H., "Molecular Spectroscopy." p. 111. (Institute of Petroleum: New York 1954.)

[7] Katritzky, A. R., Beard, J. A. T., and Coats, N. A., *J. Chem. Soc.*, 1959, 3680; Katritzky, A. R., and Gardner, J. N., *J. Chem. Soc.*, 1958, 2192.

[8] Katritzky, A. R., and Simmons, P., *Rec. Trav. Chim. Pays-Bas*, 1960, **79**, 361.

[9] Stephenson, C. V., Coburn, W. C., and Wilcox, W. S., *Spectrochim. Acta*, 1961, **17**, 933.

Experimental

The spectra were measured for 0·208M solutions in chloroform (unless stated otherwise) in 0·096 mm matched cells on a Perkin–Elmer Model 21 spectrophotometer with a sodium chloride prism and calibrated with a polystyrene film at 1601, 1028, and 907 cm^{-1}.

Compounds 1, 2, 3, 4, 7, 8, 9, and 21 were donated by Professor J. W. Clark-Lewis.[1,10] 3,4-Dicanopyridine was prepared by Mr. B. Paul.

3,4-Lutidine 1-Oxide

3,4-Lutidine was oxidized in the usual way with peracetic acid to give *3,4-lutidine-1-oxide* (42%), m.p. 128–130° (needles from acetone) (Found: N, 11·1. C_7H_9NO requires N, 11·4%). The picrate had m.p. 142–144° (Found: N, 15·9. $C_{13}H_{12}N_4O_8$ requires N, 15·9%).

All other compounds were prepared by methods described in the literature.

[10] Clark-Lewis, J. W., and Singh, R. P., *J. Chem. Soc.*, **1962**, 2379.