747. *Infrared Absorption of Substituents in Heteroaromatic Systems. Part III.*[1] *Amino-, Methylamino-, and Dimethylamino-compounds.*

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The absorption due to the groups NH_2,NHMe, and NMe_2 for 57 compounds is recorded. Tentative assignments of the frequencies to specific molecular modes are made, and the dependence of the positions and intensities of the bands on molecular structure is discussed.

FOLLOWING our work on ethers [2] and amides,[1] we now report (Tables 1—3) the substituent absorption for amino-, methylamino-, and dimethylamino-compounds. Compounds of all these types had previously been examined, the NH stretching modes receiving most attention (for reviews see refs. 3*a* and 3*b*).

The 3300 *cm.*$^{-1}$ *Region.*—The amino-compounds show the NH antisymmetrical and symmetrical stretching bands at 3520—3420 cm.$^{-1}$ (10—80) * and 3420—3325 cm.$^{-1}$ (15—100) respectively (Table 1, cols. 1 and 2). For the *para*- and *ortho*-substituted anilines, the position of each band rises as the substituent becomes more electron-accepting; the apparent extinction coefficients also increase, those of the symmetrical vibration the more markedly. For the *meta*-substituted anilines the positions and intensities vary less; they are 3480—3430 cm.$^{-1}$ (15—35) [3458 ± 18 cm.$^{-1}$ (20 ± 8)] and 3400—3370 cm.$^{-1}$ (20—35) [3380 ±

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* Round brackets signify apparent molecular extinction coefficients, and square brackets signify arithmetical means and standard deviations; see footnote on *J.*, 1959 3500.

[1] Part II, Katritzky and R. A. Jones, *J.*, 1959, 2062.

[2] Part I, Katritzky and Coats, *J.*, 1959, 2067.

[3] (*a*) Bellamy, " The Infrared Spectra of Complex Molecules," 2nd Edition, Methuen, London, 1958, pp. 248—259. (*b*) R. N. Jones and Sandorfy in Weissberger, " Techniques of Organic Chemistry, Vol. IX. Chemical Applications of Spectroscopy," Interscience, London, 1956, pp. 509—531.

10 cm.$^{-1}$ (25 ± 8)] (except that the intensities for *m*-nitroaniline are higher). These results follow the findings of earlier workers.[4-6]

For the heterocyclic compounds, the positions are in the order of electron-accepting power of the rings, *viz.*, Ph $<$ 3P $<$ 2P $\sim$ 4P $<$ 2PO.* The positions for the pyridines agree with those found by Angyal *et al.*;[7a] Goulden suggested [7b] that the measurements indicated considerable $=\overset{+}{\text{N}}\text{H}_2$ character in 2- and 4-amino-pyridine. Mason [8] recently related the positions and intensity of these bands for heterocyclic amines with their molecular structure. The intensities are higher for 4- than for 3-amino-pyridine; the pyridine ring is known to withdraw electrons more readily from the 4- than the 3-position of the ring. The relatively low extinction coefficients for 2-aminopyridine and its 1-oxide are probably connected with the intramolecular hydrogen bonding in these compounds;[9,10] the ε_A values for the other heterocyclic compounds are probably affected by intermolecular hydrogen bonding (the values found by Mason [8] in dilute solution were considerably higher). In general, despite the sodium chloride prism (poor resolution) and the use of a standard concentration, our results are in reasonable agreement with others: *e.g.*, aniline showed bands at 3454 cm.$^{-1}$ (23) and 3388 cm.$^{-1}$ (30) in chloroform with a calcium fluoride prism;[11] the intensities were *ca.* (25) and (30),[3b] (20) and (28),[4] and *ca.* (30) and (35) [4b] in carbon tetrachloride (lithium fluoride prism).

For the methylamino-compounds the position of the NH stretch (Table 2, col. 1) at 3450—3420 cm.$^{-1}$ also becomes higher as the ring becomes more electron-accepting:[12] Ph $<$ 3P $<$ 4P $\sim$ 4PO. The position is relatively low in the 2-substituted pyridine and its 1-oxide, although these rings are strongly electron-accepting,[12] probably because of internal hydrogen bonding. 4-Methylaminopyridine 1-oxide shows (in 0·2M-solution) an additional band at 3240 cm.$^{-1}$ (75) due to the intramolecularly hydrogen-bonded species (cf. discussion in ref. 10). For methylaniline 3430 cm.$^{-1}$ [13] and 3433 cm.$^{-1}$ (39) [14] were previously given.

The 2800 *cm.*$^{-1}$ *Region.*—The symmetrical CH stretching frequency (possibly perturbed by Fermi resonance) reported [15] for compounds with NMe or NMe$_2$ groups directly attached to an aromatic system at *ca.* 2800 cm.$^{-1}$ (30—70) is found (Table 2, col. 2; Table 3, col. 1) at 2870—2800 cm.$^{-1}$ (25—60). It is more distinct for compounds with rings of low electron-attracting power (phenyl, substituted phenyl, and 3-pyridyl) in agreement with previous work,[15] *e.g.*, the band is absent for *N*-methylamides,[1,15b] in which a strongly electron-attracting group is attached to the nitrogen atom.

The 1650—1480 *cm.*$^{-1}$ *Region.*—The NH$_2$ scissor deformation is shown at 1632—1613 [1622 ± 4] cm.$^{-1}$ (Table 1, col. 3) except for 2-aminopyridine 1-oxide where strong intramolecular hydrogen bonding apparently shifts the mode to *ca.* 1590 cm.$^{-1}$. For the *para*-substituted compounds, increase in the electron-attracting character of the substituent raises frequencies somewhat (1613→1628 cm.$^{-1}$) and intensities markedly (60→420). *ortho*-Substituted compounds show a similar intensity variation (95 → 440) but the positions are more constant at 1626—1616 cm.$^{-1}$ [1620 ± 3]. For the *meta*-substituted anilines the positions and intensities vary less: 1632—1620 cm.$^{-1}$ (175—260) [1623 ± 3 cm.$^{-1}$ (220 ± 30)]. As expected, the intensity is higher for 4- than for 3-aminopyridine; the intensities

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* P = pyridyl; PO = pyridine oxide.

[4] Califano and Moccia, *Gazzetta*, (*a*) 1956, **86**, 1014; (*b*) 1957, **87**, 58; (*c*) 1957, **87**, 805.

[5] Flett, *Trans. Faraday Soc.*, 1948, **44**, 767.

[6] Krueger and Thompson, *Proc. Roy. Soc.*, 1957, *A*, **243**, 143.

[7] (*a*) Angyal and Werner, *J.*, 1952, 2913; (*b*) Goulden, *J.*, 1952, 2939.

[8] Mason, *J.*, 1958, 3619.

[9] Short, *J.*, 1952, 4584.

[10] Gardner and Katritzky, *J.*, 1957, 4375.

[11] Fuson, Josien, Powell, and Utterback, *J. Chem. Phys.*, 1952, **20**, 145.

[12] Katritzky, *Quart. Rev.*, 1956, **10**, 395.

[13] Richards and Burton, *Trans. Faraday Soc.*, 1949, **45**, 874.

[14] Russell and Thompson, *J.*, 1955, 483.

[15] (*a*) Hill and Meakins, *J.*, 1958, 760; (*b*) Braunholtz, Ebsworth, Mann, and Sheppard, *J.*, 1958, 2780.

TABLE 1. *Amino-compounds.*

		1		2		3		4		*Note*
		NH$_2$ stretch				NH$_2$ def.		CN stretch		*a*
		antisym.		sym.						
		cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	
para-*Substituted anilines* (*substituent is given*)										
1	NMe$_2$	3420	20	3380	20	1614	75	1260	90	*h, i*
2	OMe	3450	15	3380	15	1615	60	(—)		*h, j*
3	OEt	3430	20	3380	25	1613	60	(—)		*h, j*
4	Me	3420	10	3360	15	1623	125	1262	65	*h*
5	Cl	3430	20	3380	25	1621	160	1270	80	*h*
6	Br	3430	15	3370	25	1620	150	1270	90	*h*
7	4P §	3480 *	20	3400	45	1627	310	(CHCl$_3$)		
8	3P	3480	15	3400	45	1625	260	1280	140	*h*
9	2P	3480	15	3410	35	1628	275	1284	95	*e, h*
10	2PO §	3450 *	25	3380	60	1620	340	(CHCl$_3$)		
11	N:NPh	3500	20	3400	70	1624	340	1291	155	*h*
12	CN	3480	35	3380	70	1622	340	1303	105	*h*
13	CO$_2$Et	3480	25	3390	70	1623	410	(—)		*h*
14	COMe	3470	25	3380	55	1620	420	(—)		*h*
15	NO$_2$	3520	35	3420	90	1627	350	(—)		*h*
meta-*Substituted anilines*										
16	NH$_2$	3430	30	3380	40	1620	330	1319	70	*k*
17	OMe	3450	15	3380	20	1624	260	1329 1313 *	55 40	*j, k*
18	OEt	3460	10	3370	20	1622	220	1326 1310 *	55 40	*j, k*
19	Me	3430	20	3380	25	1622	185	1306 * 1288	20 60	*k*
20	Cl	3470	25	3380	35	1623	250	1318 1260	20 50	*k*
21	Br	3470	25	3380	35	1621	250	1315 1257	25 45	*k*
22	4P	3460	15	3380	25	1622	230	1315	50	*k*
23	2P	3470	15	3390	25	1623	175	1320	90	*e, k*
24	2PO	3450 *	15	3370	20	1622	190	1320 1296	60 40	*k*
25	CF$_3$	3470 *	20	3400	35	1628	190	1317 *	110	*k*
26	NO$_2$	3480	35	3390	55	1632	260	1332 * 1265	135 70	*k*
ortho-*Substituted anilines*										
27	NH$_2$	3400	*45*	3325	*35*	1622	*190*	1276	*175*	*l*
28	OMe	3445	25	3370	30	1616	200	(—)		*l*
29	Cl	3460	30	3385	35	1619	250	1308 1263	70 15	*l*
30	Br	3450	25	3370	30	1618	260	1311 1260	70 10	*l*
31	Me	3450	15	3380	20	1623	160	1304 1272	40 45	
32	Ph	3450	20	3370	25	1617	210	1297 1285 *	65 60	*l*
33	CO$_2$Me	3470	45	3370	50	1617	260	1317 *	110	*l*
34	NO$_2$	3515	80	3390	100	1626	440	1288 1260	180 460	*l*
Aniline and heterocyclic amines (*ring is given*)										
35	Ph	3455	20	3375	25	1622	185	1268	55	*g*
36	4P[m]	3480	30	3400	45	1625	310	1314 1254	45 35	*d*
37	3P	3460	20	3380	25	1622	125	1282 1250	60 50	*f*
38	2P	3470	20	3390	35	1614 ‡	465	1317 1250	90 40	*e*
39	2PO	3500	25	3360	20	1592 *	45	1340 1255 *	25 25	*c*

TABLE 2. *Methylamino-compounds.*

		1		2		3		4		5		6		7		8		9		10
		NH stretch		N–Me		NH in plane def.		N–Me Me sym. bend.		N–Me Me antisym. bend		Ring–N CN stretch				N–Me Me rock		N–Me CN stretch		
No.	Ring	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	*a*
1	Ph	3420	30	2820	25	1478	50	(—)		1425	30	1320	110	1263	75	1154	45	1065 *	20	*g*
2	4P	3460	45	2850 *	40	1480	35	1460	30	1417	20	1342	75	1315	80	1152	20	1068	35	
3	3P	3430	30	2825	30	1500	110	1460	45	1408	40	1340 * 1317 *	15 55	1302	70	1149	40	1069	10	*f*
4	2P	3440	30	(—)		(—)		1457	40	1410 *	55	1324	45	1285	55	1152	50	1070	15	
5	4PO	3450	55	(—)		1498 *	120	1456 *	20	(—)		1335	25	1308	15	1155	50	1065	35	*b*
6	2PO	3340	40	(—)		—		(—)		1419	35	1336	25	1267 *	20	1157 ‡	150	1070	35	*c*

TABLE 3. *Dimethylamino-compounds.*

		1		2		3		4		5		6		7		8		Note
														NMe$_2$ C–N–C stretch				*a*
		NMe$_2$		Me bend		Ring–N CN stretch		?		NMe$_2$ Me rock				antisym.		sym.		
No.	Ring	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	C_6H_4·NH_2-*p* ^{n}	2870 2800	60 60	1448	45	1332	60	(—)		1158	75	1137	70	1051	25	942	60	*i, h*
2	Ph	2870	50	1444	50	1343	105	(—)		1189	35	1130	30	1057	40	943	40	*g*
3	C_6H_4·CH:CHPh-*p*	2810	55	1449	105	1360	240	—		1187	130	1130	65	1063	35	946 §	105	
4	C_6H_4·[CH:CH·4P]-*p*	2810 *	45	($CHCl_3$)		1357	240	1330 *	100	1154	75	1124	55	1061	35	944	80	
5	C_6H_4·[CH:CH·4PO]-*p*	2820 *	60	(—)		1359	220	1330 *	70	(—)		(—)		1058	40	945	75	*h*
6	C_6H_4·NO_2-*p*	2820 *	40	1442	80	1372	100	(—)		1173 *	60	(—)		1061	55	943	90	*h*
7	4P	2840 *	45	1448	95	1380	155	1346	35	1179	35	1108	30	1063	35	951	55	*d*
8	3P	2810	25	1446	45	1358	90	1320 1306	35 40	1169	35	(—)		1063	10	944	20	
9	2P	2820 *	20	(—)		1369	40	1318	35	1174	20	—		1053	15	953	25	
10	4PO	(—)		1447 ‡	165	1379	70	1326	35	1181 *	120	(—)		1063	25	952	105	*b*
11	2PO	2820 *	50	1444 ‡	150	1356	125	—		1176 ‡	280	1143 ‡	95	1055 ‡	60	952	170	*c*

* Shoulder. ‡ Peaks considered to be formed by the super-imposition of two bands. — Absence of absorption. (—) Region obscured by other absorption. ($CHCl_3$) region obscured by solvent. § Measured in 1 mm. cell because of poor solubility.

Ph phenyl; P substituted pyridine; PO substituent pyridine 1-oxide (position of substituent denoted by a numeral).

(*a*) Many other bands found in the compounds have been published by Katritzky and his co-workers in the following papers: *J.*, 1958, (*b*) p. 2192, (*c*) p. 2195, (*d*) p. 2198, (*e*) 2202, (*f*) p. 3165, (*g*) p. 4155; *J.*, 1959, (*h*) p. 2051, (*i*) this paper, (*j*) p. 2062, (*k*) p. 2058, (*l*) preceding paper. (*m*) Extra band at 839 (40). (*n*) Extra band at 1475 (45).

of the heterocyclic compound are probably not directly comparable with the benzenoid compound because of intramolecular hydrogen bonding. This band has been previously reported at 1640—1560,[3b,16,17] and at 1650—1590 cm.$^{-1}$.[3a] Eight aromatic amines were shown [4] to absorb at 1631—1615 cm.$^{-1}$ (s).

A band at 1500—1478 cm.$^{-1}$ (35—110, but apparently absent in No. 6) for the methylamino-compound (Table 2; col. 3) is possibly the NH in-plane deformation, to which Hadži and Škrbljak [18] assigned a band near 1500 cm.$^{-1}$ for secondary aromatic amines.

The 1460—1400 *cm.*$^{-1}$ *Region.*—The methylamino-compounds show bands at 1460—1457 cm.$^{-1}$ (30—45) [1459 ± 2 cm.$^{-1}$ (40 ± 10)] and 1425—1408 cm.$^{-1}$ (20—40) [1417 ± 7 cm.$^{-1}$ (30 ± 10)] (Table 2, cols. 4 and 5). These are assigned to the antisymmetrical and symmetrical *N*-methyl CH bending modes, respectively. The positions are higher than those [1422 ± 4, 1369 ± 11 cm.$^{-1}$] for amides of the type Ar·NMe·CO·R,[1] but close to those 1465—1442, 1414—1401 cm.$^{-1}$ for amides R·CO·NHMe.[19]

The dimethylamino-compounds absorb at 1449—1442 cm.$^{-1}$ (45—95) [1446 ± 3 cm.$^{-1}$ (70 ± 20)] (Table 3, col. 2); this is probably also a methyl CH bending mode.

The 1400—1240 *cm.*$^{-1}$ *Region.*—Previous work [17,3a] had indicated that the CN stretching mode caused absorption at 1340—1250, 1350—1280, and 1360—1310 cm.$^{-1}$ for primary, secondary, and tertiary aromatic amines, respectively. Six aromatic amines absorbed [4c] at 1288—1276 cm.$^{-1}$ but *m*-chloro- and *m*-bromo-aniline each showed three bands at 1320—1261 cm.$^{-1}$. A band at 1262—1241 cm.$^{-1}$ in seven secondary aromatic amines was assigned [18] to this mode, but the published curves all show a second band at higher frequencies.

All the compounds now studied show one or two strong or medium bands (Table 1, col. 4; Table 2, cols. 6, 7; Table 3, col. 3) which are assigned to the *N*-ring CN stretching mode.

The position of the band should depend on the electron-accepting character of the ring; when this is increased, greater mesomerism, greater double-bond character, and therefore a higher frequency, should result. This is shown for the *para*-substituted anilines (Table 1, nos. 1—15) for which the frequency varies, 1260—1303 cm.$^{-1}$; the intensity is (65—155) [(105 ± 30)].

The *meta*-substituted anilines (except for the methyl, and possibly the nitro-compounds) show a band at 1329—1315 [1320 ± 6] cm.$^{-1}$ (20—90) [(50 ± 20)]; for several compounds a second band is shown at a lower frequency; this is similar to the ring-oxygen stretching frequency in *meta*-substituted anisoles and phenetoles;[2] the reason is unknown. As expected, the aminopyridines and 1-oxides all absorb at higher frequencies than aniline (Table 4), the intensity is (25—90); a weaker band at 1254—1250 cm.$^{-1}$ is also shown.

For the dimethylamino-compounds, the band occurs at 1380—1332 cm.$^{-1}$; for corresponding pairs, 16—76 [55 ± 23] cm.$^{-1}$ higher than in the amino-compounds. The intensity is (40—155) [(95 ± 35)] except in the vinyl compounds (Nos. 3—5) where it is (220—240). For the benzenoid compounds a *para*-amino-group lowers the frequency and *para*-vinyl and -nitro-groups raise it as expected. All the heterocyclic compounds absorb at higher frequencies than dimethylaniline (Table 4).

Two bands of comparable intensity at 1342—1320 and 1315—1263 cm.$^{-1}$ are shown for all the methylamino-compounds; presumably the CN stretching mode is split by interaction with another mode. The mean frequency has been taken as that for the CN stretching mode; it is 20—50 [35 ± 15] cm.$^{-1}$ higher than that for the corresponding amino-compound, and higher for each heterocyclic compound than for methylaniline (Table 4). Each component of the doublet has an intensity of (45—110) [(75 ± 15)] in methylamino-benzene and -pyridine, but (15—25) in methylaminopyridine 1-oxides.

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[16] Thompson, *J.*, 1948, 328.

[17] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

[18] Hadži and Škrbljak, *J.*, 1957, 843.

[19] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1956, **24**, 408; *J. Chem. Soc. Japan*, 1956, **77**, 171.

The increments in Table 4 (except those for 2-methylaminopyridine and its 1-oxide; these exceptions are possibly explained by proximity effects) indicate that the electron-accepting power of the various rings is in the order: Ph < 3P < 4PO ~ 4P ~ 2P < 2PO, which is in good agreement with other evidence.[2]

TABLE 4. *Nitrogen-ring stretching bands. Increments in wave-numbers over those for the corresponding benzenoid compound.*

	4P	3P	2P	4PO	2PO
Amino	46	14	49	—	72
Methylamino [a]	37	18	13	30	10
Dimethylamino	37	15	26	36	64

[a] Mean frequency of doublet used, see text.

The 1200—1100 *cm.$^{-1}$ Region.*—A band (Table 2, col. 8) for the methylamino-compound at 1157—1149 cm.$^{-1}$ (20—50) [1153 ± 2 cm.$^{-1}$ (40 ± 15)] and two bands (Table **3**, cols. 5 and 6) for the dimethylamino-compounds at 1189—1154 cm.$^{-1}$ (20—130) [1171 ± 14 cm.$^{-1}$ (60 ± 35)] and 1143—1108 cm.$^{-1}$ (30—70) [1126 ± 10 cm.$^{-1}$ (50 ± 20)] (absent in No. 9) are probably due to N-CH_3 methyl rocking frequencies by analogy with those found for N-methylamides.[1]

The 1100—900 *cm.$^{-1}$ Region.*—For dimethylamine the CNC antisymmetric and symmetric stretching modes occur at 1082 and 930 cm.$^{-1}$.[20] Bands probably due to these modes are found for the dimethylamino-compounds at 1063—1051 cm.$^{-1}$ (15—55) [1059 ± 4 cm.$^{-1}$ (35 ± 15)] and 953—942 cm.$^{-1}$ (25—170) [947 ± 4 cm.$^{-1}$ (75 ± 45)] (Table **3**, cols. 7, 8). For certain amidines containing the $\cdot NMe_2$ group these bands were found[21] at 1082—1081 (ms) and 947—936 (m) cm.$^{-1}$.

For the methylamino-compounds a band tentatively assigned to the N-methyl CN stretching frequency (Table 2, col. 9) is found at 1070—1065 cm.$^{-1}$ (10—35) [1068 ± 2 cm.$^{-1}$ (25 ± 15)]; Hadži and Škrbljak found[18] this band near 1060 cm.$^{-1}$ and suggested that it was the CN stretching or the N-Me rocking mode. The NH_2 wagging mode[4c] near 1050 cm.$^{-1}$ is apparently too weak to be detected under our conditions.

Other Bands.—Nearly all the remaining bands could be assigned to the ring or other substituents present; many of them have been published, and references are given in Tables 1—3. The small proportion of bands which could not be correlated are given as footnotes in Tables 1—3.

Experimental.—See Part I [2] for details.

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[20] Edsall, *J. Chem. Phys.*, 1937, **5**, 225.

[21] Fabian, Delaroff, and Legrand, *Bull. Soc. chim. France*, 1956, 287.