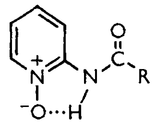
416. *Infrared Absorption of Substituents in Aromatic Systems. Part II.*[1] *Acylamino-compounds.*

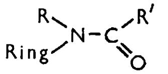
By A. R. KATRITZKY and R. A. JONES.

The absorption caused by the groups ·NH·COMe, ·NH·CO·, ·NMe·COMe, and ·NMe·CO· for a total of twenty-four acetamido-, *N*-methylacetamido-, benzamido-, and *N*-methylbenzamido-compounds is recorded. Tentative assignments are made for most of the characteristic bands, and the dependence of their positions and intensities on the structure of the compounds is discussed. More than 98% of the bands ($\varepsilon_A \geqslant 15$) for these compounds were correlated with the rings or substituent groups.

THE infrared spectra of monosubstituted amides have been extensively investigated because of the importance of the amide linkage in polypeptides and proteins, but the interest has been mainly in the NH and C:O stretching bands (" amide I " and the " amide II " bands [2,3]). Of the amido-benzenoid or -heteroaromatic compounds, acetanilide has been studied in detail,[4] and series of substituted [5] and fatty acid [6] anilides and some acetamidopyrimidines [7] have been investigated. The most comprehensive work on the assignment of skeletal frequencies is by Miyazawa *et al.*[8]

(I)





(II)

While investigating the infrared absorption of heteroaromatic rings [9-15] and the tautomerism of acylaminopyridines and their oxides, [16] we studied a series of acetamido- and benzamido-compounds and their *N*-methyl derivatives. Almost all the bands were characteristic of either the rings or the substituents; those characteristic of the groups ·NH·CO·, ·NMe·CO·, ·NH·COMe, and ·NMe·COMe are recorded in Table 1 with cross-references to the benzenoid and heteroaromatic bands (col. 19). When sufficiently soluble, the compounds were measured in 0·2M-chloroform solutions in a 0·117 mm. cell; [17] otherwise 0·02M-solutions (1 mm. cell) or, in one case, a Nujol mull were used.

The NH *Stretching Band.*—The non-bonded NH stretching frequency (possibly the *trans*-peak [18]) is shown by the compounds X·NH·COMe and X·NH·COPh in solution at 3440—3410 [3420 ± 10] * cm.$^{-1}$ (except for the 2-substituted pyridine 1-oxides); the intensities are (30—45) * in 0·2M- and (45—65) in 0·02M-solutions and are affected more by

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* Parentheses signify apparent molecular extinction coefficients, and square brackets indicate arithmetical means and standard deviations; see preceding paper.

[1] Part I, Katritzky and Coats, preceding paper.

[2] Bellamy, " The Infrared Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958, pp. 203—223.

[3] R. N. Jones and Sandorfy in Weissburger, " Technique of Organic Chemistry. Vol. IX. Chemical Applications of Spectroscopy," Interscience Publ. Inc., London, 1956, pp. 509—531.

[4] Abbott and Elliot, *Proc. Roy. Soc.*, 1956, *A*, **234**, 247.

[5] Richards and Thompson, *J.*, 1947, 1248.

[6] Dijkstra and Jonge, *Rec. Trav. chim.*, 1956, **75**, 1173.

[7] Brownlie, *J.*, 1950, 3062.

[8] Miyazawa, *J. Chem. Soc. Japan*, 1956, **77**, 171; Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1956, **24**, 408; *Spectrochim. Acta*, 1957, **10**, 217.

[9] Katritzky and Gardner, *J.*, 1958, 2198.

[10] Katritzky, R. A. Jones, and Hands, *ibid.*, p. 3165.

[11] Katritzky and Hands, *J.*, 1958, 2202.

[12] Katritzky and Gardner, *ibid.*, p. 2192.

[13] Katritzky, Beard, and Coats, unpublished work.

[14] Katritzky and Hands, *ibid.*, p. 2195.

[15] Katritzky and Lagowski, *ibid.*, p. 4155.

[16] R. A. Jones and Katritzky, (*a*) *J.*, 1959, 1317; (*b*) unpublished work.

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

TABLE 1.

No.	Ring	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
		νNH	νNH H-bonded	νCO	Amide II	N–Me Me asym bend	?	N–Me Me sym bend	COMe Me sym bend	$\overset{\|}{\underset{\|}{C}}-\overset{\|}{N}-\overset{\overset{O}{\|}}{C}\diagdown$	Two CN stretching modes		N–Me Me rock	?	N–Me Me rock	N–Me ?	COMe Me rock	N–Me N–C stretch	Un-assigned bands	Ref. to ring bands
		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	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	
Compounds X·NH·COMe																				
1	Ph	3420 45	3310 30	1688 330	1548* 95 1524 300	A	—	A	1373 95	1314 175	1297* 60	1248 135	A	—	A	A	(—)	A	1488* 70	15
2	4P[a]	3440 65	—	1711 280	(CHCl$_3$)	A	1405 50	A	1368 85	1328 150	(1277 90)	(CHCl$_3$)	A	—	A	A	(—)	A	—	9
3	3P	3425 30	3260* 35	1690 250	1538* 170 1513 200	A	1411 155	A	1369 90	1326 95	1282 120	(CHCl$_3$)	A	—	A	A	998 20	A	—	10
4	2P	3410 40	3180* 25	1694 255	1527* 120 1508 290	A	1400* 35	A	1367 80	1300 350	(CHCl$_3$)	(CHCl$_3$)	A	(—)	A	A	961 15	A	1035* 15	11
5	4PO[b]	c	c	1700 s	1500* s	A	—	A	1363 s	1320 s	1263 w	1245* w	A	1100* w	A	A	958 w	A	918 w	16*b*
6	3PO[d]	3410 w	—	1707 s	(CHCl$_3$)	A	1405 w	A	1368 w	1296 m	(CHCl$_3$)	(CHCl$_3$)	A	—	A	A	973 w	A	—	13
7	2PO	—	3280 75	1710 330	1505 400	A	1400* 95	A	1368 90	1313 110	1270 160	(—)	A	—	A	A	997 35 955 30	A A	843* 20	14
Compounds X·NMe·COMe																				
8	Ph	A	A	1653 340	A	1426 80	—)	1384 200	1356 75	1330 20	1297 70	1246* 25	1138 60	1086 40	1035* 15	—	975 35	—	—	15
9	4P	A	A	1665 310	A	1435* 45 (—)	(—)	1377 220	1352 105	1320 60	1295 100	(CHCl$_3$)	1138 50	1086 15	1030 15	—	975 30	925 10	—	16*a*
10	3P	A	A	1658 340	A	1420† 140	—	1382 170	1354 85	1325 40	1299 90	(CHCl$_3$)	1138 60	1087 30	(—)	—	973 30	—	—	10
11	2P	A	A	1660 320	A	1424* 150	—	1378 215	1349 125	1315 55	1299 70	1285* 60	1140† 90	1090† 25	1032* 25	1005* 30	978 30	—	—	16*a*
12	4PO	A	A	1668 320	A	1423 65	—	1374 170	1343 90	1308 50	1288* 60	(—)	1141 100	1092 20	(—)	1000 50	975 45	921 20	—	12
13	2PO	A	A	1682 420	A	1425* 180		1375 205	1351 160	1311 155	(—)	(—)	1143 110	1080 55	1025* 10	997 10	972 35	925 20	—	16*b*
Compounds X·NH·COPh																				
14	Ph[a]	3420 60	—	1679 310	(CHCl$_3$)	A	(CHCl$_3$)	A	A	1313 190	(CHCl$_3$)	(CHCl$_3$)	A	1096 40	A	A	A	A	1035 30	15
15	4P[a]	3430 45	—	1696 170	(CHCl$_3$)	A	1409 40	A	A	1330 175	(CHCl$_3$)	(CHCl$_3$)	A	1100* 40 1090 50	A	A	A	A	—	9, 15
16	3P	3420 45	3300* 30	1679 210	1518 220	A	1413* 120	A	A	1329 125	1280 135	(CHCl$_3$)	A	(—)	A	A	A	A	836 15	10, 15
17	2P	3430 35	—	1682 290	1515 310 1493 220	A	1402* 35	A	A	1306 450	1253* 65	(CHCl$_3$)	A	(—)	A	A	A	A	—	11, 15
18	2PO	—	3280 45	1693 290	1505 460	A	(—)	A	A	1322* 70 1310 95	1300* 80 1274 280	(—)	A	1085 35	A	A	A	A	—	14, 15
Compounds X·NMe·COPh																				
19	Ph	A	A	1641 360	A	1423 100	—	1372 280	A	1330 30	1303 115	1280 70	1108 90	(—)	1053 10	1025 60 1012 15	A	919 10	—	15
20	4P	A	A	1652 280	A	—)	—	1356 300	A	1326 115	1304 200	(CHCl$_3$)	1106 75	(—)	1043 20	1020* 35 1009 120	A	920 10	—	16*a*
21	3P	A	A	1648 350	A	1423† 120	—	1362 240	A	1326 55	1304 140	(CHCl$_3$)	1111 85	—	1050* 15	1005 30	A	918 10	—	10, 15
22	2P	A	A	1650 360	A	1416 125	—	1359 315	A	1320 90	1300 80	1288 140	1117 100	(—)	(—)	1020* 30 1012 60	A	920 10	1174 30	11, 15
23	4PO	A	A	1660 350	A	1436* 55 1423 60	—	1353 260	A	1319 90	1296 145	(—)	1109 90	(—)	(—)	1021 70 1008 155	A	922 15	1555 15 3335 20	12, 15
24	2PO	A	A	1665 370	A	1417 130	—	1355 260	A	1330 230	1255* 240	(—)	1098 95	(—)	(—)	1009 70	A	920 5	—	14, 15

* Shoulder. † Absorption considered to be the superimposition of two peaks. — Absence of absorption. (—) Band masked by stronger absorption. (CHCl$_3$) Band masked by solvent. A, Band neither expected nor found.

Ph phenyl, P substituted pyridine, PO substituted pyridine 1-oxide; the position of the substituent is indicated by a numeral.

a, 0·02M-solution in 0·1 mm. cell. *b*, Nujol mull. *c*, Broad absorption. *d*, Saturated solution (<0·02M) in 0·1 mm. cell.

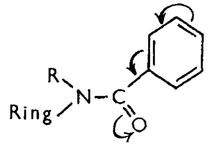
the concentration than by the nature of the ring. Thompson and his co-workers [18] found that *meta*- and *para*-substituents have little effect on the position, half band-width, and integrated intensity (and therefore also ε_A) of this band for acetanilide; concentration does affect the intensity, and at infinite dilution acetanilide absorbs at 3436 cm.$^{-1}$ (125) (lithium fluoride prism).

The compounds measured at 0·2M-concentration usually show absorption at *ca.* 3300 cm.$^{-1}$ due to the hydrogen-bonded NH groups.[2] In the 2-substituted pyridine 1-oxides intramolecular bonding (cf. I) lowers the frequency to 3280 cm.$^{-1}$.

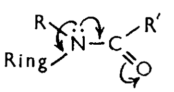
The C:O Stretching Band (Table 1, col. 3).—This, the amide I band, occurs at 1711—1641 cm.$^{-1}$; the influence of R, R′, and the ring (cf. II) can be distinguished.

(i) Changing R′ from methyl to phenyl (cf. II) increases the conjugation of the carbonyl group (III) and lowers the frequency by 8—17 [12 ± 3] cm.$^{-1}$.

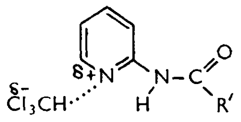
(ii) Changing R from hydrogen to methyl also increases considerably the conjugation of the carbonyl group, both because of the favourable inductive effect of the methyl group and, probably more importantly, by causing partial steric inhibition of mesomerism between the nitrogen atom and the ring for which there is independent evidence from basicities and ultraviolet spectra.[16] The frequency is lowered by 25—46 [35 ± 6] cm.$^{-1}$.



(III)



(IV)



(V)

(iii) Changing the ring from phenyl to pyridine or pyridine 1-oxide always raises the frequency (Table 2), indicating that the heterocyclic rings are all more strongly electron-accepting than phenyl and conjugate more tightly with the amide-nitrogen atom, thus causing this atom to conjugate less with the carbonyl group (cf. IV). The increment is larger for the 4- than for the 3-substituted pyridines, as expected from the relative electron-withdrawing abilities of these rings.[1,19] The large increments found for all the pyridine 1-oxides agree with the known ability of this ring to withdraw electrons strongly at each nuclear position.[1,19,20] The increments are smaller than expected in the 2-pyridyl series, possibly owing to steric inhibition of hydrogen bonding of the pyridine nitrogen atom to the solvent [11] (cf. V).

TABLE 2. *Carbonyl stretching bands. Increments in wavenumbers over that for the corresponding benzenoid compound.*

	4P	3P	2P	4PO	3PO	2PO
NH·COMe	23	2	6	(12) [a]	19	22
NH·COPh	17	0	3	—	—	14
NMe·COMe	12	5	7	15	—	29
NMe·COPh	11	7	9	19	—	24

[a] Difference obtained by using paraffin-paste spectrum. See also footnotes to Table 1.

The intensities are (170—330) [(270 ± 55)] for ·NH·COPh and ·NH·COMe compounds and (280—420) [(345 ± 40)] for ·NMe·COPh and ·NMe·COMe compounds.

The frequency range of this band agrees with previous work.[2] Similar raising of the frequency as the ring becomes increasingly electron-accepting has been noted for *meta*- and *para*-substituted acetanilides [5] and acetyl-azoles.[21]

[18] Russell and Thompson, *J.*, 1955, 483; *Spectrochim. Acta*, 1956, **8**, 138; Moccia and Thompson, *ibid.*, 1957, **10**, 240.

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

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

[21] Otting, *Chem. Ber.*, 1956, **89**, 1940.

The Amide II *Band* (Table 1, col. 4).—For the X•NH•COMe and X•NH•COPh compounds the band is found at 1524—1505 cm.$^{-1}$ (200—460) [1513 ± 7 cm.$^{-1}$ (310 ± 100)], often with a shoulder or subsidiary band. The region is obscured by chloroform when measured in a 0·1 mm. cell. This band usually occurs at 1580—1475 cm.$^{-1}$ and is due to the NH in-plane deformation frequency coupled with the N–C stretching frequency of the •NH•CO• group.[2,3,8,22]

The 1450—1400 *cm.*$^{-1}$ *Region.*—The X•NMe•COMe and X•NMe•COPh compounds show a band at 1426—1416 cm.$^{-1}$ (60—130) [1422 ± 4 cm.$^{-1}$ (90 ± 25)] (Table 1, col. 5). This is probably the asymmetric N–CH_3 CH-bending frequency which occurs at 1465—1442 cm.$^{-1}$ for compounds of type R•CO•NHMe.[8]

Some of the X•NH•COMe and X•NH•COPh compounds show a shoulder or band of unknown origin at 1413—1400 cm.$^{-1}$ (40—155) (col. 6).

The 1400—1340 *cm.*$^{-1}$ *Region.*—Absorption (col. 7) by the X•NMe•COMe compounds at 1384—1374 cm.$^{-1}$ (170—220) [1378 ± 4 cm.$^{-1}$ (195 ± 20)] and by the X•NMe•COPh compounds at 1372—1353 cm.$^{-1}$ (240—310) [1360 ± 7 cm.$^{-1}$ (275 ± 30)] is probably the CH symmetrical bending frequency previously found [8] at 1414—1401 cm.$^{-1}$ for R•CO•NHMe compounds.

The symmetrical CH bending of the acetyl-methyl group causes absorption (col. 8) at 1373—1363 cm.$^{-1}$ (80—95) [1368 ± 3 cm.$^{-1}$ (85 ± 5)] for the X•NH•COMe compounds and at 1356—1343 cm.$^{-1}$ (75—160) [1351 ± 4 cm.$^{-1}$ (105 ± 30)] for the X•NMe•COMe compounds. The ring appears to play a constant rôle in determining the position of the band, for the band is 15—20 [17 ± 2] cm.$^{-1}$ lower for the •NMe•COMe than for the corresponding •NH•COMe compound. For comparison, compounds X•COMe [17] absorb at [1359 ± 1·5 cm.$^{-1}$ (135 ± 20)], compounds R•O•COMe [23,24] at *ca.* 1375—1365 cm.$^{-1}$, and compounds R•NH•COMe [8] at 1375—1366 cm.$^{-1}$.

The 1340—1240 *cm.*$^{-1}$ *Region.*—Stretching frequencies of the two C–N partial double bonds (cf. IV) are expected in this region. Belonging to the same symmetry class, they will combine to give symmetric and asymmetric modes. With the NH-compounds, the NH in-plane deformation should also intereact with these modes.

Two or three bands are shown (Table 1, cols. 9—11). As expected from the above discussion, the absorption depends little on whether R′ is Me or Ph (II), more on the nature of the ring, and most on whether R is Me or H.

(i) The first band (col. 9) is at 1330—1300 [1319 ± 10] cm.$^{-1}$; there is no simple relation between the precise position and the structure. The intensities vary for the X•NMe•COMe and X•NMe•COPh compounds (20—230), but the band for X•NMe•COPh is always 1·4—1·9 [1·60 ± 0·2] times as intense as that for the corresponding X•NMe•COMe compounds; for these compounds the intensities increase as the rings become more electron-accepting:

$$\mathrm{Ph} < \mathrm{3P} < \mathrm{2P} \sim \mathrm{4P} \sim \mathrm{4PO} < \mathrm{2PO}$$

For the compounds X•NH•COMe and X•NH•COPh the intensities vary (95—450); for corresponding compounds, replacing NH by NMe increases the intensity 0·9—1·3 [1·15 ± 0·2] times; there is no simple relation between intensity and the ring type.

(ii) For the X•NMe•COMe and X•NMe•COPh compounds the second band (col. 10) is at 1304—1295 cm.$^{-1}$ (70—200) [1299 ± 3 cm.$^{-1}$ (110 ± 45)] except for No. 24. This band appears to occur at *ca.* 1280—1260 cm.$^{-1}$ for the X•NH•COMe and X•NH•COPh compounds, but this region is often obscured by solvent (1 mm. cell).

(iii) A third band sometimes appears (col. 11) on the edge of the region obscured by solvent absorption, *i.e.*, below 1240 cm.$^{-1}$ (0·1 mm. cell).

The 1200—1100 *cm.*$^{-1}$ *Region* (Table 1, col. 12).—The X•NMe•COMe compounds show a band at 1143—1138 cm.$^{-1}$ (50—110) [1140 ± 2 cm.$^{-1}$ (75 ± 20)], and the X•NMe•COPh

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[22] Frazer and Rice, *Nature*, 1952, **170**, 490.
[23] Francis, *J. Chem. Phys.*, 1951, **19**, 942.
[24] R. N. Jones and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 5648.

compounds one at 1117—1098 cm.$^{-1}$ (75—100) [1108 ± 6 cm.$^{-1}$ (90 ± 8)]; these are probably *N*-methyl rocking frequencies, occurring[8] at 1179—1149 cm.$^{-1}$ for R·CO·NHMe compounds.

The 1100—800 *cm.*$^{-1}$ *Region.*—A band of unknown origin is found for the compounds X·NMe·COMe and X·NH·COPh at 1096—1080 cm.$^{-1}$ (15—55) [1088 ± 5 cm.$^{-1}$ (35 ± 10)] (col. 13).

The X·NMe·COPh compounds show a band at 1053—1030 cm.$^{-1}$ (10—20) (col. 14) and a doublet at 1025—1021 and 1012—1005 cm.$^{-1}$ (30—155) (col. 15); the analogous absorption for the X·NMe·COMe compounds, which is weaker or absent, occurs at *ca.* 1030 and 1000 cm.$^{-1}$. The compounds X·NMe·COMe and X·NMe·COPh show a band at 925—918 cm.$^{-1}$ (5—20) [921 ± 2 cm.$^{-1}$ (10 ± 5)] (col. 17). Two of these bands are probably due to C–N stretching and Me rocking modes of the $N-CH_3$ group; a possible assignment is indicated in Table 1.

A band, probably an acetyl-methyl rocking mode (col. 16), occurs at 978—972 cm.$^{-1}$ (30—50) [975 ± 2 cm.$^{-1}$ (40 ± 8)] for the X·NMe·COMe compounds and at 998—958 cm.$^{-}$ (15—35) [978 ± 19 cm.$^{-1}$ (25 ± 10)] for the X·NH·COMe series. A band or oublet at 1041—987 cm.$^{-1}$ for CH_3CO·NHR compounds has been assigned[8] to a Me rocking mode, and methyl ketones show a band at [959 ± 5 cm.$^{-1}$ (35 ± 15)].[17]

Other Bands.—Nearly all the remaining bands ($\varepsilon_A \geqslant 15$) for these compounds could be assigned to the heterocyclic and/or benzenoid rings; most have been published (see refs. in col. 19). Bands which could not be correlated in this way are given in col. 18; they form 2% of the total.

Experimental.—See Part I[1] for details.

Dyson Perrins Laboratory, Oxford.
University Chemical Laboratory, Cambridge.

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