THE INFRARED SPECTRA OF HETEROAROMATIC COMPOUNDS

By A. R. KATRITZKY, M.A., D.PHIL., PH.D., B.SC.
(THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE)

THE object of this Review is to increase the usefulness of infrared spectroscopy to organic chemists working with heterocyclic compounds (for previous reviews see refs. 1 and 2). It is felt that the best way of doing this is to attempt a simplified explanation of the spectra of compounds containing planar five- and six-membered rings. Throughout, the emphasis is on simplicity and not on rigour; thus, approximate statements are made without qualification.

This Review commences with a short introduction on the origin of infrared spectra and the classification of the relevant molecular vibrations into types. Available data on the infrared absorption of heteroaromatic nuclei in various regions of the spectrum are then discussed, and, finally, an account is given of the effect of heteroaromatic nuclei on the infrared absorption of substituents. It should be emphasised that the discussion is largely based on the fundamental work carried out on the infrared spectra of benzene and deuterobenzenes.[3]

Introduction.[4,5]

The motion of an atom is fully described by the variation of three co-ordinates, *e.g.*, the x, y, and z components of its distance from a fixed point. The motion of a molecule of n atoms is defined by the variations of $3n$ co-ordinates; *i.e.*, molecules possess $3n$ degrees of freedom. Three of these involve translational motion and three* involve rotational motion of the molecule as a whole; therefore $3n-6$ degrees of freedom are associated with changes in the relative positions of the atoms, *i.e.*, with vibration. It can be shown that for simple harmonic motion a molecule of n atoms can vibrate in just $3n-6$ ways, in which each of the atoms is moving in phase and at the same frequency. These $3n-6$ vibrations are the *normal vibrations* of the molecule, and the displacements of the atoms from their equilibrium positions are the *normal co-ordinates*. Any other molecular vibration can be represented as the superposition of two or more normal

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* Two appear in linear molecules; hence, these molecules show $3n - 5$ vibrational modes.

[1] Bellamy, "The Infrared Spectra of Complex Molecules", 2nd edn., Methuen, London, 1958, pp. 277—285.

[2] R. N. Jones and Sandorfy in Weissburger, "Techniques of Organic Chemistry. Vol. IX. Chemical Applications of Spectroscopy", Interscience Publ. Inc., London, 1956, pp. 533—537.

[3] See ref. 4 and references therein, especially papers by Ingold and his co-workers.

[4] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, London, 1945.

[5] Sheppard and Simpson, *Quart. Rev.*, 1953, 7, 19.

vibrations. Each normal vibration is quantised, and the vibrational energy levels of a molecule are given by

$$\sum_{i=1}^{i=3n-6} \nu_i w_i$$

where w represents the normal vibrational frequencies and ν the quantum numbers. In theory, infrared absorption bands could result from the promotion of a molecule from one energy level to any higher one. However, for simple harmonic motion selection rules forbid transitions in which more than one vibrational quantum number is changed (*i.e.*, combination bands), or in which the quantum number is changed by more than one unit (*i.e.*, overtone bands); bands corresponding to these abnormal transitions are therefore absent or weak, except in a few cases where Fermi resonance is important.[4] Thus, most of the strong bands in a spectrum correspond to one of the $3n-6$ transitions in which each quantum number is separately altered by one unit, *i.e.*, to *fundamentals*. However, all fundamentals do not cause strong absorption in the infrared region. The intensity of an infrared band depend upon the change of dipole moment during the vibration; for certain modes of symmetrical molecules there is no change, and the band is "forbidden". If the change in dipole moment is small, only a weak band results.*

The complete interpretation of a spectrum involves a knowledge of the normal vibrations of the molecule and of the assignment of the individual bands in the spectrum to them. For small molecules it is possible to calculate the normal vibrations from force constants, bond lengths, and atomic weights. This has not been done for heteroaromatic molecules but, by using results obtained for simpler molecules (especially benzene and deuterobenzenes[4]) and by empirical correlation of series of compounds, many spectra can be reasonably well explained. For compounds composed of a substituent and an aromatic ring, the vibrational motion is concentrated either in the ring or in the substituent for many of the normal modes; thus, series of related molecules show characteristic absorption bands. Because of the large mass difference between H and C, N, and O, the normal vibrations of a heteroaromatic ring can be roughly divided into (*a*) those in which hydrogen atoms move relatively to the heavy skeleton and (*b*) those in which each CH or NH group moves as a unit. Substitution of N for CH or of O for NH has relatively little effect upon the normal vibrations of class (*b*) because of the similar masses involved.

Vibrations of Predominantly CH *Character*.—The presence of one hydrogen atom in a planar ring means that there are three normal vibrations, in addition to those the ring would have without this hydrogen atom.

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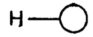
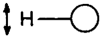
* The fundamentals which are forbidden in the infrared spectrum usually cause lines in the Raman spectrum; the simultaneous use of Raman and infrared data often simplifies the interpretation of both types of spectra.[2,4,5]

It is found that these vibrations are concentrated in the bond joining the hydrogen atom to the ring and are stretching (I), in-plane bending (II), and out-of-plane bending motions (III). Similarly, six CH-type vibrations



(I)



(II)

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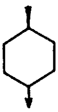
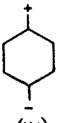


(V)

(VI)

(VII)

(VIII)



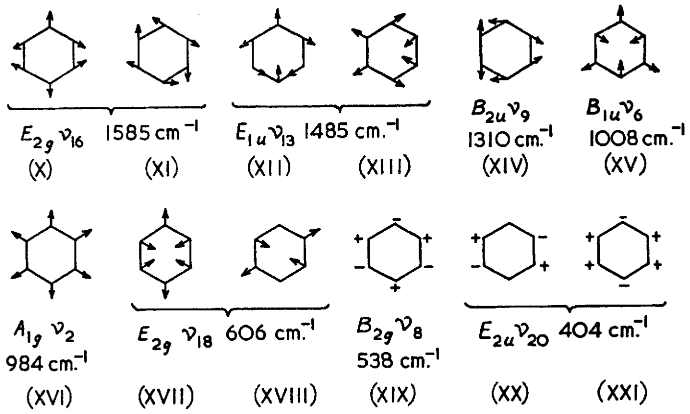
(IX)

are associated with two nuclear hydrogen atoms, but if both of these are attached to the same planar ring the two vibrations of each class interact to give in-phase (symmetrical) and out-of-phase (asymmetrical) modes, shown (IV—IX) for two *para*-hydrogen atoms. In general, if n hydrogen atoms are attached to a planar ring, there will be $3n$ CH-type modes, and in each group the n modes will be coupled. The fundamental absorption bands corresponding to the three classes occur in different parts of the spectrum: CH stretching near 3000 cm.$^{-1}$, in-plane CH bending at *ca.* 1300—1000 cm.$^{-1}$, and out-of-plane CH bending in the 1000—700 cm.$^{-1}$ region.

Vibrations of Predominantly CC, CN, *etc.*, *Character.*—The discussion of six-membered rings is most conveniently based upon the benzene molecule which has 30 (*i.e.*, $3 \times 12 - 6$) normal vibrational modes, 18 of which are of mainly CH character, as explained above. The remaining 12 modes are depicted diagrammatically in Fig. 1; because of the high symmetry of benzene some modes are "degenerate", *i.e.*, cause absorption at the same frequency. Similar vibrational modes occur for substituted benzenes, pyridines, and azines, but the degeneracy now disappears because of the lower symmetry.* It is found that the spectral positions of these modes are relatively constant, and that they can be conveniently sub-divided into C–C, etc., stretching modes (X—XIV) which absorb at *ca.* 1600—1300

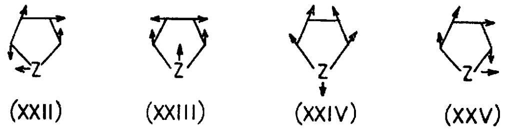
* When the only element of symmetry in an aromatic ring is the plane of the molecule (as in, *e.g.*, 2- and 3-substituted pyridines), the symmetry is denoted C_s, and the vibrational modes can be classified as those (X—XVIII) in which this plane of symmetry is preserved (denoted A') and those (XIX—XXI) in which it is not preserved (denoted A''). When the aromatic ring has an additional plane of symmetry perpendicular to the ring (as in 4-substituted pyridines or 5-substituted pyrimidines), the symmetry is denoted by C_{2v}, and the vibrational modes may be divided into (*a*) those (X, XII, XIV—XVII) which preserve both planes of symmetry (denoted A_1), (*b*) those (XI, XIII, XVIII) which preserve the symmetry plane of the molecule (denoted B_1), (*c*) those (XIX, XX) which preserve the symmetry plane perpendicular to the molecule (denoted B_2), and (*d*) those (XXI) which do not preserve any symmetry (denoted A_2). Pyrazine, 1,3,5-triazine, and benzene are examples of molecules possessing still higher symmetry; their symmetry is denoted by D_{2h} (or V_h), D_{3h}, and D_{6h}, respectively.[4]

FIG. 1. *Skeletal frequencies of benzene*

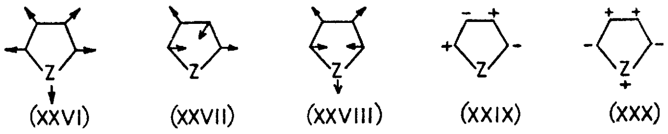


Modes which are degenerate for benzene are bracketed together. The symmetry type, position of absorption band, and notation[4] for benzene are given beneath each mode [an alternative notation of Wilson (*Phys. Rev.*, 1934, **45**, 706) is often used]. ν_{13} is infrared-active; ν_{16}, ν_2, and ν_{18} are Raman-active; ν_9, ν_6, ν_8, and ν_{20} are totally inactive (obtained by indirect means, *e.g.*, deuteration).

FIG. 2. *Skeletal modes for thiophen, furan, and pyrrole*



	$\nu_{15}B_1$	ν_6A_1	ν_5A_1	$\nu_{14}B_1$
Thiophen	1590 (8)	1404 (35)	1358 (Ra)[a]	1252 (50)
Furan	1579 (10)	1486 (60)	1381 (25)	?
Pyrrole	1530 (25)	1467 (10)	1384 (5)	1418 (20)



	ν_3A_1	$\nu_{10}B_1$	ν_1A_1	$\nu_{18}A_2$	$\nu_{23}B_2$
Thiophen	832 (95)	872 (3)	604	565	453
Furan	994 (170)	872 (75)	724	?	605
Pyrrole	1144 (10)[b]	647	711	510[c]	565[d]

Lord and Miller's notation[10] for the vibrational modes, the symmetry type (these molecules are of C_{2v} symmetry; see footnote on p. 355), and the positions (and where available intensities, determined in $CHCl_3$ solution) are given below each diagram. The assignments are essentially those given by Lord and Miller,[10] Thompson and Temple (*Trans. Faraday Soc.*, 1945, **41**, 27, and Waddington *et al.*[8] and Lecomte, *Bull. Soc. chim. France*, 1946, 415).

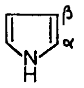
[a] Observed in Raman spectrum only. [b] This assignment is not beyond question. [c] Calculated; see ref. 10. [d] Cf. ref. 8.

cm.$^{-1}$, ring-breathing modes (XV, XVI) near 1000 cm.$^{-1}$, C–C in-plane bending modes (XVII, XVIII) in the 700—600 cm.$^{-1}$ region, and C–C out-of-plane bending modes (XIX—XXI) below *ca.* 550 cm.$^{-1}$.

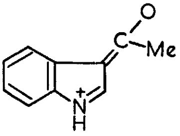
The discussion of the skeletal modes for five-membered rings is based upon thiophen, furan, and pyrrole, although the assignments for these molecules are not unquestionable. Furan and thiophen have 21 normal modes each, and pyrrole has 24; in each case 9 are skeletal, and these are shown in Fig. 2. Again, these modes can be divided into C–C, *etc.*, stretching (XXII—XXV) at *ca.* 1600—1250 cm.$^{-1}$, the breathing frequency (XXVI) at *ca.* 1150—800 cm.$^{-1}$, C–C in-plane bending (XXVII, XXVIII) at *ca.* 900—600 cm.$^{-1}$, and C–C out-of-plane bending (XXIX, XXX) at *ca.* 600—450 cm.$^{-1}$.

Characteristic absorption of heterocyclic nuclei*

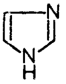
The 3000 *cm.$^{-1}$ Region.*—The CH stretching vibrations occur in much the same range, *i.e.*, *ca.* 3100—3000 cm.$^{-1}$, as they do for benzenoid compounds; this has been shown, *inter alia*, for pyridine,[7] thiophen,[8,9] pyrrole (XXXI),[9,10] thiazoles,[11] and diazines.[12] Few data have been reported on the influence of substituents on the intensity or position of these modes.



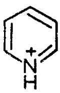
(XXXI)



(XXXII)



(XXXIII)



(XXXIV)

The NH stretching frequencies of pyrroles[13] and indoles[14,15] cause absorption at *ca.* 3450—3400 cm.$^{-1}$ (ϵ_A *ca.* 120) for dilute solutions and at

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* Throughout this Review positions of bands are quoted in cm.$^{-1}$ units. Data for a class of compounds are often expressed as arithmetical means and standard deviations (the original papers should be consulted for full details, as it was not possible to indicate many exceptions and trends here). Precise intensity data are given, where available, in parentheses after the frequencies; these data are in the form of extinction coefficients of band maxima, ε_A, where $\varepsilon_A = (1/cl).\log_{10}(I/I_0)$, c being the molar concentration and l the path length in cm. The area under the absorption peak is of greater physical significance than the peak height,[2,6] but in complex molecules band overlap often makes area measurements impracticable. Many of the ε_A values quoted are for 0·2M-chloroform solutions measured in a 0·1 mm. cell and are reproducible to an accuracy of about 10%.

[6] Brown, *Chem. Rev.*, 1958, **58**, 581.

[7] Wilmshurst and Bernstein, *Canad. J. Chem.*, 1957, **35**, 1183; Corrsin, Fax, and Lord, *J. Chem. Phys.*, 1953, **21**, 1170.

[8] Waddington *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 797.

[9] Lebas and Josien, *Bull. Soc. chim. France*, 1957, 251.

[10] Lord and Miller, *J. Chem. Phys.*, 1942, **10**, 328.

[11] Taurins, Fenyes, and R. N. Jones, *Canad. J. Chem.*, 1957, **35**, 423.

[12] Lord, Marston, and Miller, *Spectrochim. Acta*, 1957, **9**, 113; Ito, Shimada, Kuraishi, and Mizushima, *J. Chem. Phys.*, 1956, **25**, 597.

[13] Eisner and Erskine, *J.*, 1958, 971.

[14] Brown, Henbest, and E. R. H. Jones, *J.*, 1952, 3172.

[15] Millich and Becker, *J. Org. Chem.*, 1958, **23**, 1096.

ca. 3400—3100 cm.$^{-1}$ for solid compounds; the frequency lowering in the solid state has been attributed to intermolecular hydrogen bonding. Within both the ranges quoted, electron-withdrawing substituents tend to lower the frequency because of the increased importance of canonical forms of type (XXXII). Substituents in the β-position of indoles (cf. XXXII) have a larger effect on the frequency than those in the α-position, but for pyrroles (XXXI) there is little difference; these facts are in accord with the known conjugative abilities of the heterocyclic nuclei at the various nuclear positions.[16] Imidazole[17] (XXXIII) absorbs at 3125 cm.$^{-1}$.

The $\geqslant N^+$–H group in the pyridinium ion (XXXIV) causes,[18] in the solid state, one or several "immonium" bands at *ca.* 2200—1900 cm.$^{-1}$.

The 2000—1650 *cm.*$^{-1}$ *Region.*—Benzenoid compounds show overtone and combination frequencies ($\epsilon_A \sim 5$) of the out-of-plane CH bending modes in this region;[19] pyridines have been shown to possess analogous bands which depend upon the type of substitution.[19a,20]

The 1600—1350 *cm.*$^{-1}$ *Region for Six-membered Rings.*—The bands corresponding to modes (X)—(XIII) of benzene occur in this region and are relatively invariant near 1605, 1575, 1480, and 1430 cm.$^{-1}$ (Table 1). The third band is often found at lower frequencies for electron-acceptor than for electron-donating substituents; otherwise, there is usually little dependence of position on substituent type.

The intensities of these bands vary widely, but in each series the intensities can be correlated with the electronic nature of the substituent(s).[21,22,23,24]

(i) For the monosubstituted compounds, ϵ_A of the band near 1605 cm.$^{-1}$ can be high for electron-donating groups, low for weakly interacting substituents, and high again for electron-accepting groups, as in monosubstituted benzenes, 4-substituted pyridine 1-oxides, and 3-substituted pyridines. It can be very high for donors, medium for weak substituents, and low for acceptors as in 2- and 4-substituted pyridines and 3-substituted pyridine 1-oxides (2-substituted pyridine 1-oxides show intermediate behaviour). For disubstituted compounds, ϵ_A can vary directly as the algebraic sum of the electronic effects of the substituents (*e.g.*, *meta-*

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[16] Katritzky and Lagowski, "Heterocyclic Chemistry", Methuen, London, 1960.

[17] Garfinkel and Edsall, *J. Amer. Chem. Soc.*, 1958, **80**, 3807.

[18] Witkop, *J. Amer. Chem. Soc.*, 1954, **76**, 5597; *Experientia*, 1954, **10**, 420.

[19] Ref. 1, p. 67; ref. 2, p. 397.

[19a] Cook and Church, *J. Phys. Chem.*, 1957, **61**, 458.

[20] Podall, *Analyt. Chem.*, 1957, **29**, 1423.

[21] (*a*) Katritzky and Lagowski, *J.*, 1958, 4155; (*b*) Katritzky and Jones, *J.*, 1959, 3670; (*c*) Katritzky and Simmons, *J.*, 1959, 2058; (*d*) Katritzky and Simmons, *J.*, 1959, 2051.

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

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

[24] Katritzky, *J.*, 1959, 2049.

disubstituted benzenes), as the algebraic difference (*e.g.*, *para*-disubstituted benzenes), or intermediately (*ortho*-disubstituted benzenes).

(ii) In each series of compounds the band near 1575 cm.$^{-1}$ is generally weaker than the preceding band but shows similar intensity variations with the nature of the substituents.

(iii) The intensity of the band near 1480 cm.$^{-1}$ is always high for electron-donor substituents (including the *N*-oxide group) and weak or absent where these are not present.

(iv) The intensity of the band near 1430 cm.$^{-1}$ is relatively independent of the nature of the substituent.

It is possible to account for these variations,[25] particularly for the compounds of C_{2v} symmetry (cf. footnote on p. 355). The intensity of an infrared band is determined by the product of the rate of change of the dipole moment of the molecule as it undergoes the vibration in question, and by the amplitude of that vibration. Vibrations (X) and (XI) are forbidden in the infrared spectrum of benzene (no associated change of dipole moment) but vibrations (XII) and (XIV) together give a band of $\epsilon_A \sim 80$. When the combined effect of the substituent and/or heteroatom is to produce little change in the charge distribution in the ring, modes (X) and (XI) should give weak bands, whereas vibrations (XII) and (XIII) should absorb with an intensity approximately half that of benzene itself. If the substituent and/or heteroatom do produce a marked charge disturbance in the ring, this disturbance will be symmetrical with respect to the vertical plane of the molecule for C_{2v} compounds and should therefore affect the intensities of (X) and (XII) more than those of (XI) and (XIII). However, the relative change in the intensities of (X) and (XI) should be greater than those of (XII) and (XIII) because the former are allowed owing only to the presence of the heteroatom and substituent groups. Thus, in C_{2v} compounds, intensities should vary with the amount of disturbance of charge in the ring; strongly for (X), less strongly for (XI) and (XII), and comparatively little for (XIII). Moreover, in (X) the intensity should increase more or less continuously with increasing charge disturbance, but in (XII) the nature of the variation cannot be predicted. These predictions hold for monosubstituted and *para*-disubstituted benzenes and for 4-monosubstituted pyridines, pyridine 1-oxides, and pyridine–boron trichlorides (a measure of the charge disturbance of the ring was obtained from dipole-moment data).[25]

The 1600—1350 *cm.*$^{-1}$ *Region for Five-membered Rings.*—Five-membered heteroaromatic compounds generally show three bands in this region, near 1590, 1490 and 1400 cm.$^{-1}$, corresponding to modes (XXII—XXIV); available data on the positions of these bands are summarised in Table 2. The effect of the electronic nature of the substituent on the intensity of these bands has been studied for 2-substituted furans[26] and thiophens;[27] the

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

[26] Katritzky and Lagowski, *J.*, 1959, 657.

[27] Katritzky and Boulton, *J.*, 1959, 3500.

TABLE 1. *Frequencies (in cm.*$^{-1}$*) of ring-stretching bands in the* 1600—1350 *cm.*$^{-1}$ *region.*

	1	2	3	4	Ref.
Monosubstituted benzenes	1604±3	1585±3	1510→1480	1452±4	*b, a*
o-Disubstituted benzenes	1607±9	1577±4	1510→1460	1447±10	*c, a*
m-Disubstituted benzenes	1600→1620	1586±5	1495→1470	1465→1430	*d, a*
p-Disubstituted benzenes	1606±6	1579±6	1520→1480	1409±8	*e, a*
1,2,4-Trisubstituted benzenes	1616±8	1577±8	1510±8	1456±4	*a*
Pyridine	1599‡	1583	1482	1441	*f*
2-Substituted pyridines	1615→1585	1572±4	1471±6	1433±5	*g, h, i*
3-Substituted pyridines	1595±5	1577±5	1485→1465	1421±4	*j, i, h*
4-Substituted pyridines	1603±5	1561±8	1520→1480	1415±4	*k, h, i, l*
Polysubstituted pyridines	1610—1597	1588—1564	1555—1490	?	*i*
Pyridine 1-oxide	1612	—	1468	—	*m, n*
2-Substituted pyridine 1-oxides	1640→1600	1567±10	1540→1480	1435±10	*p, o, n*
3-Substituted pyridine 1-oxides	1605±4	1563±3	1480±6	1434±5	*q, o, n*
4-Substituted pyridine 1-oxides	1645→1610	—	1483±6	1443±7	*r, n, o, l*
Pyridine-boron trihalides	1636—1624	*ca.* 1590	1493—1488	1465—1459	*s*
4-Substituted pyridine-boron trichlorides ..	*ca.* 1640	1564±5	*ca.* 1500	1460→1430	*s*
Pyridazine	1572	1565	1444	1414	12
Pyrimidine	1610‡	1569	1461	1400	*t*, 12, *u*
Substituted pyrimidines	1590—1555	1565—1520	1480—1400	1410—1375	*t, u, v*
Pyrimidine oxide	1577	1534	1468	1410	*u*
Pyrazine	1584§	1523§	1490	1418	12
1,3,5-Triazine	1556	—	—	1410	*w*

‡ Probably combination bands; see refs. quoted. § Found in Raman spectrum only.

Arithmetical means and standard deviations are given for each band unless there is a marked correlation between the position of the band and the electronic nature of the substituent. In such cases a notation of the type 1510→1475 is used to indicate that electron-donor substituents, cause absorption up to *ca.* 1510 cm.$^{-1}$ and electron-acceptor substituents down to *ca.* 1475 cm.$^{-1}$. Compounds in which a heavy atom (*e.g.*, S, Cl, Br) is directly attached to the ring often absorb at approximately 10 cm.$^{-1}$ shorter wavelength than other related compounds; this is not taken into account in the Tables. In general, data are taken from the first reference in the last column.

References: a, Randle and Whiffen, Report Conf. Mol. Spectroscopy, 1954, Inst. Petroleum, paper no. 12. *b*, Katritzky and Lagowski, *J.*, 1958, 4155. *c*, Katritzky and Jones, *J.*, 1959, 3670. *d*, Katritzky and Simmonds, *J.*, 1959, 2058. *e*, *Idem*, *J.*, 1959, 2051. *f*, Wilmshurst and Bernstein, *Canad. J. Chem.*, 1957, **35**, 1183; Corrsin, Fax, and Lord, *J. Chem. Phys.*, 1953, **21**, 1170. *g*, Katritzky and Hands, *J.*, 1958, 2202. *h*, Shindo and Ikekawa, *Pharm. Bull.* (*Japan*), 1956, **4**, 192; Shindo, *ibid.*, 1957, **5**, 472. *i*, Cook and Church, *J. Phys. Chem.*, 1957, **61**, 458. *j*, Katritzky, Hands, and Jones, *J.*, 1958, 3165. *k*, Katritzky and Gardner, *J.*, 1958, 2198. *l*, Sartori, Costa, and Blasina, *Z. phys. Chem.* (*Frankfurt*), 1955, **4**, 24. *m*, Katritzky, *J.*, 1958, 4162; Sartori, Costa, and Blasina, *Gazzetta*, 1955, **85**, 1085. *n*, Shindo, *Pharm. Bull.* (*Japan*), 1956, **4**, 460. *o*, *Idem*, *ibid.*, 1958, **6**, 117. *p*, Katritzky and Hands, *J.*, 1958, 2195. *q*, Katritzky, Beard, and Coats, *J.*, 1959, 3680. *r*, Katritzky and Gardner, *J.*, 1958, 2192. *s*, Katritzky, *J.*, 1959, 2049. *t*, Short and Thompson, *J.*, 1952, 168. *u*, Wiley and Slaymaker, *J. Amer. Chem. Soc.*, 1957, **79**, 2233. *v*, Brownlie, *J.*, 1950, 3062; Blout and Fields, *J. Amer. Chem. Soc.*, 1950, **72**, 479; Lacher, Bitner, Emery, Seffl, and Park, *J. Phys. Chem.*, 1955, **59**, 615. *w*, Lancaster and Colthup, *J. Chem. Phys.*, 1954, **22**, 1149; Padgett and Hamner, *J. Amer. Chem. Soc.*, 1958, **80**, 803.

TABLE 2. *Frequencies (cm.$^{-1}$) for five-membered heteroaromatics.*

				Ref.
2-Substituted furans	1605→1570	1510→1475	1380→1400	*a*
Polysubstituted furans	*ca.* 1560	*ca.* 1510	?	*b*
2-Substituted thiophens	1523±9	1442±12	1354±7¶	*c*, *d*
3-Substituted thiophens	*ca.* 1530	*ca.* 1410	*ca.* 1370	*d*
Substituted pyrroles	*ca.* 1565	*ca.* 1500	?	13
Thiazole	1615	1485	1385	11
Substituted thiazoles	*ca.* 1610	*ca.* 1500	*ca.* 1380	11
Furoxans§	*ca.* 1610	*ca.* 1460	*ca.* 1420	*e*
Substituted isoxazoles	*ca.* 1600	*ca.* 1460	*ca.* 1420	*f*
Substituted furazans‡	*ca.* 1570	*ca.* 1425	*ca.* 1380	*g*
Imidazole	1550	1492	1451	*h*
1,2,3-Triazole	1520	1450	1410	*i*

§1-Oxa-2,5-diazole 2-oxide. ‡ 1-Oxa-2,5-diazole. ¶ Another mode, presumably (XXV), is shown at 1231±10 cm.$^{-1}$.

References: a, Katritzky and Lagowski, *J.*, 1959, 657. *b*, Kubota, *Tetrahedron*, 1958, **4**, 68; Cross, Stevens, and Watts, *J. Appl. Chem.*, 1957, **7**, 562; Daasch, *Chem. and Ind.*, 1958, 1113; Cross and Watts, *ibid.*, p. 1161. *c*, Katritzky and Boulton, *J.*, 1959, 3500. *d*, Hidalgo, *J. Phys. Radium*, 1955, **16**, 366; Hochgesang in Hartough's "Thiophene and its Derivatives", Interscience Publ. Inc., New York, 1952. *e*, Boyer, Czerniak, Gutowsky, and Snyder, *J. Amer. Chem. Soc.*, 1955, **77**, 4238. *f*, Katritzky *et al.*, unpublished work. *g*, Milone and Borello, *Gazzetta*, 1951, **81**, 368. *h*, Garfinkel and Edsall, *J. Amer. Chem. Soc.*, 1958, **80**, 3807. *i*, Hartzel and Benson, *ibid.*, 1954, **76**, 667.

TABLE 3. *Absorption bands near 1000 cm.$^{-1}$ assigned to ring-breathing modes.*

	Unsubstituted	*2-Substituted*	*3-Substituted*	*4-Substituted*
Monosubstituted benzenes[a]	*ca.* 995 (<15)[b]	?	995±3 (20±15)	?
Pyridines	$\left\{\begin{matrix}1030 & (45)\\ 993 & (45)\end{matrix}\right.$	994±4 (45±25)	1025±2 (65±35)	993±2 (35±10)[c]
Pyridine oxides	1015 (145)	?	1015±2 (150±25)	?
Pyrimidines	$991 \text{ and} \left\{\begin{matrix}1055\\ 1071\end{matrix}\right.$	*ca.* 990	—	*ca.* 990
Pyrazine	1022 m	?	?	?
Furan	994 (170)	1015±4 (85±15)[c]	?	—
Thiophen	832 (95)	823±20 (50±20)	?	—

For references see Tables 1 and 2.

[a] In this row, the column headings refer to further substitution. [b] Higher ε_A for electron-donor substituents. [c] Highe rε_A for electron-acceptor substituents.

TABLE 4. *Out-of-plane modes for six-membered rings.*

	Number and orientation of hydrogen atoms.						
	Five adjacent		Four adjacent	Four 1,2,3,5		Four 1,2,4,5	Ref.
	LIX	XIX	LXVIII	LXXIII	XIX	LXIII	
Benzenes	751±15	697±11	751±7	782±9	690±15	817±13	*a*
Pyridines	749	700	780—740	820—770	730—690	850—790	7, *b*
Pyridine 1-oxides	759	669	790—750	820—760	680—660	855—820	*c*
Azines	(Not applicable)		760 (vs)	721	680	804 (vs)	12, *d*

References: *a*, Randle and Whiffen, Report Conf. Mol. Spectroscopy, 1954, Inst. Petroleum, paper no. 12. *b*, Podall, *Analyt. Chem.*, 1957, **29**, 1423; Shindo and Ikekawa, *Pharm. Bull.* (*Japan*), 1956, **4**, 192; Shindo, *ibid.*, 1957, **5**, 472. *c*, *Idem*, *ibid.*, 1956, **4**, 460; 1958, **6**, 117. *d*, Short and Thompson, *J.*, 1952, 168.

TABLE 5. *Out-of-plane modes for five-membered rings.*

	Unsubstituted		2-Substituted		
	LXVI	LXVIII	LXIV	LXIX	LXXIV
Furan	837 (5)	744	925±9 (55±17)	884±2 (30±13)[a]	*ca.* 800
Thiophen	832 (95)[b]	710	925±8 (10±5)	853±7 (75±25)	800
Pyrrole	838 (5)	768	—	—	—

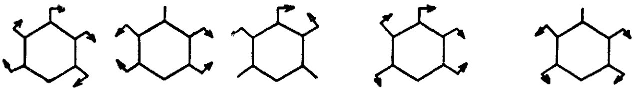
For references see Table 2.
[a] ε_A higher for electron-acceptor substituents. [b] Most of this intensity is probably due to the ring-breathing mode, see Fig. 2.

See footnotes to Table 1.

intensity of all these bands is increased by strongly electron-withdrawing substituents. This is according to expectation, since these rings can conjugate tightly with electron-accepting substituents.

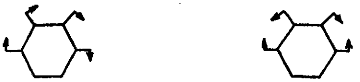
FIG. 3. *In-plane hydrogen deformation modes.*

Five adjacent hydrogen atoms.



	B_1 (XXXV)	A_1 (XXXVI)	B_1 (XXXVII)	B_1 (XXXVIII)	A_1 (XXXIX)
Monosubstituted benzenes	1240±8 w	1177±6[a]	1156±5[a]	1073±4 (20±10)	1027±3 (20±10)
Pyridine	1218	1218	1148 (20)	1085 (<5)	1068 (30)

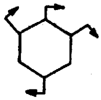
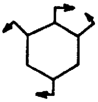
Four adjacent hydrogen atoms.

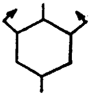
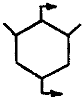


	B_1 (XL)	A_1 (XLI)
ortho-Disubstituted benzenes	1269±17 (15±5)	1160±4 (20±10)[b]
2-Substituted pyridines	1279±14 (15±5)	1147±3 (25±10)[c]
2-Substituted pyridine 1-oxides	?	1150±4 (25±10)
Pyridazine	1239[d]	1160 m
Thiophen	1283 (3)	1077 (30)
Furan	1270 (<5)	1137[d]
Pyrrole[f]	1046 (130)	1237[d]

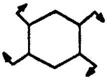
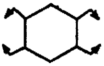
	B_1 (XLII)	A_1 (XLIII)
ortho-Disubstituted benzenes	1125±14 (25±15)	1033±11 (50±40)
2-Substituted pyridines	1093±4 (15±15)	1048±5 (20±10)
2-Substituted pyridine 1-oxides	1106±10 (25±20)[c]	1044±5 (25±15)
Pyridazine	1063 s	1063
Thiophen	909 ?	1032 (15)
Furan	?[e]	1067 (35)
Pyrrole[f]	1015 (150)	1076 (20)

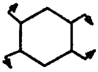
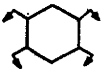
Four hydrogen atoms in the 1,2,3,5-*positions.*

	 B_1 (XLIV)	 B_1 (XLV)
meta-Disubstituted benzenes	1278±12 (30±15)	1157±5 (*ca.* 10)^{c}
3-Substituted pyridines	*ca.* 1190 ?	1124±5 (20±10)
3-Substituted pyridine oxides	?	1156±2^{c}
Pyrimidine	1220	1165

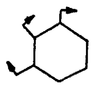
	 A_1 (XLVI)	 B_1 (XLVII)
meta-Disubstituted benzenes	1096±7 (30±15)	1076±7 (*ca.* 25)^{g}
3-Substituted pyridines	1103±5 (20±5)	1038±7 (20±5)
3-Substituted pyridine oxides	?	?
Pyrimidine	1140	1021

Four hydrogen atoms in the 1,2,4,5-*positions.*

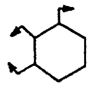
	 B_{3g} (B_1) (XLVIII)	 A_g (A_1) (XLIX)
para-Disubstituted benzenes	1258±11 (35±25)	1175±6 (var.)
4-Substituted pyridines	*ca.* 1220 m	?
4-Substituted pyridine 1-oxides	(obscured)	1169±5 (200±50)
Pyrazine	1232^{d}	1118^{d}

	 B_{2u} (B_1) (L)	 B_{1u} (A_1) (LI)
para-Disubstituted benzenes	1111±7 (25±15)^{h}	1013±5 (var.)
4-Substituted pyridines	?	1067±3 (25±10)
4-Substituted pyridine 1-oxides	1101±7 (20±10)	1033±5 (55±15)
Pyrazine	1148 (s)	1067 (vs)

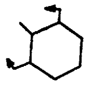
Three adjacent hydrogen atoms.



B_1 (LII)



B_1 (LIII)



A_1 (LIV)

Vicinal trisubstituted benzenes	*ca.* 1200 ?	1160±5	(w)	1073±10	(s)
2-Substituted furans	*ca.* 1220	1158±7	(95±25)	1076±3	(45±20)
2-Substituted thiophens	?	1081±3	(10±5)	1043±7	(55±40)

For references see Tables 1 and 2.

[a] These bands have $\varepsilon_A \sim 5$ for weakly interacting substituents but become stronger for electron-donor substituents. [b] Higher ε_A shown by compounds with two electron-donor substituents. [c] Higher ε_A shown by compounds with electron-donor substituents. [d] Found in Raman spectrum only. [e] Band originally assigned (Thompson and Temple, *Trans. Faraday Soc.*, 1945, **41**, 27) to this mode was later[8] suggested to be an out-of-plane mode. [f] Agreement is poor for pyrrole which may indicate coupling of the CH and NH in-plane modes or an incorrect assignment. [g] High ε_A shown for compounds with electron-acceptor substituents. [h] High ε_A for nitro-substituents.

The 1250—1000 *cm.*$^{-1}$ *Region.*—Heterocyclic compounds show series of characteristic bands in this region which are assigned to in-plane CH deformations and ring-breathing modes (XV, XVI, XXVI). Fig. 3 gives the form of the in-plane CH modes for several types of compound and a tentative assignment of the bands; data for substituted benzenes are included for comparison. There is an overall similarity in the positions of these bands for compounds with the same number of hydrogen atoms in the same orientation.

Table 3 records bands tentatively assigned to ring-breathing modes. As an empirical correlation, it can be noted that these bands are of appreciable intensity for six-membered rings, if CH groups or nitrogen atoms with lone electron pairs are present in the 1,3,5-positions. Two bands are sometimes shown by unsubstituted compounds.

The 1000—600 *cm.*$^{-1}$ *Region.*—Out-of-plane CH deformations (which are depicted in Fig. 4 for several orientations of the hydrogen atoms) and in-plane ring deformations could cause absorption in this region. The out-of-plane CH deformations of symmetry type A_2 in C_{2v} compounds (see footnote on p. 355) are forbidden in the infrared spectrum; all six-membered rings are of at least approximate C_{2v} symmetry, and these bands are therefore weak or absent. Of the B_2 type vibrations, the in-phase "umbrella" mode always results in a very strong band, but the other vibrations are usually weak and hard to detect for six-membered ring compounds. Tables 4 and 5 contain data on six- and five-membered ring compounds, respectively. The relation between the nature of the substituents and the position of a band within the range given in Table 4 is not clear; *e.g.*, changing methyl to ethyl displaces the bands for pyridines to higher frequencies.[27a] Mono- and *meta*-di-substituted benzenes show[28] an out-of-

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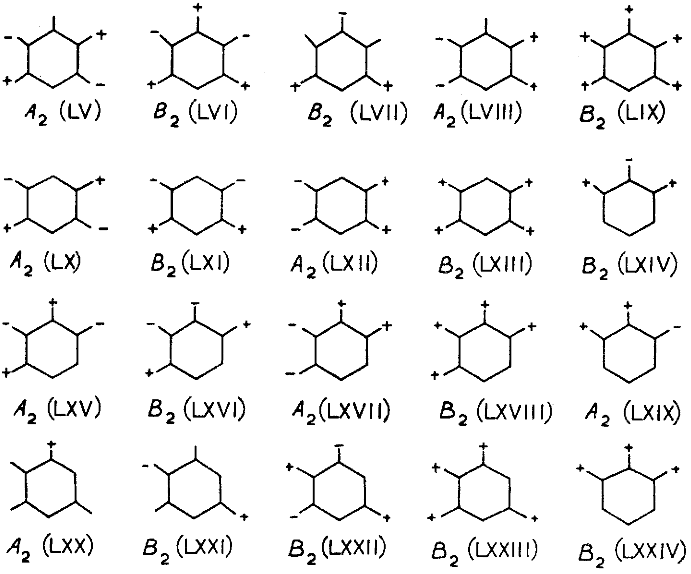
[27a] Shindo and Ikekawa, *Pharm. Bull. (Japan)*, 1956, **4**, 192.

[28] Randle and Whiffen, Conf. Mol. Spectroscopy, 1954, Inst. Petroleum, paper No. 12.

plane ring deformation mode (cf. XIX) near 700 cm.$^{-1}$, and corresponding heterocyclic compounds show similar bands (Table 4). Little is known of the remaining ring deformation modes which cause absorption below 600 cm.$^{-1}$.

FIG. 4. *Out-of-plane* CH *modes.*



Infrared Spectra of Heterocycles with Condensed Rings.—A treatment of the above type is not yet possible for condensed-ring compounds because of the paucity of data. However, it has been shown that each type of substituted naphthalene causes absorption in characteristic, narrow regions of the spectrum,[29] and that the out-of-plane CH vibration of polycyclic benzenoid compounds and of heteroaromatic compounds can be classified according to the number of adjacent hydrogen atoms present.[30] The detailed assignment of naphthalene has been discussed.[31]

Quinolines[32] show three bands near 1600 cm.$^{-1}$, five bands in the 1500—1350 cm.$^{-1}$ region, and in- and out-of-plane CH deformation frequencies in the 1300—700 cm.$^{-1}$ region; the last are determined by the number of nuclear hydrogen atoms present and can be correlated with the corresponding naphthalenes. Indoles[14] show bands at *ca.* 1460, 1420, and

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[29] Hawkins, Ward, and Whiffen, *Spectrochim. Acta*, 1957, **10**, 105; Werner, Kennard, and Rayson, *Aust. J. Chem.*, 1955, **8**, 346.

[30] Groenewege, *Spectrochim. Acta*, 1958, **11**, 579; Cannon and Sutherland, *ibid.*, 1951, **4**, 373.

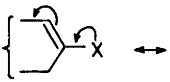
[31] Mitra and Bernstein, *Canad. J. Chem.*, 1959, **37**, 553, and references therein.

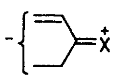
[32] Katritzky and Jones, *J.*, in the press; Shindo, *Pharm. Bull.* (*Japan*), 1956, **4**, 292; Karr, Estep, and Papa, *J. Amer. Chem. Soc.*, 1959, **81**, 152; Braunholtz and Mann, *J.*, 1958, 3368.

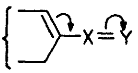
1350 cm.$^{-1}$; quinazolines[33] absorb at 1628—1612, 1581—1566, and 1517—1478 cm.$^{-1}$. Purines[34] show strong bands in this region, but some of them are due to ν C=O and NH_2 deformation modes.

Effects of heterocyclic rings on the characteristic substituent vibrations*

In general, substituents show the same characteristic bands regardless of whether they are present in heterocyclic, benzenoid, or even aliphatic compounds. The following discussion is an attempt to point out the chief changes in these vibrations caused by heterocyclic nuclei. The effect is largest when strong electronic interaction occurs between the ring and the substituent, and the magnitude of the effect can often be correlated with the degree of the interaction (*e.g.*, by using the Hammett equation). It is convenient to use the corresponding substituted benzene as a standard. Two common situations are illustrated. If an atom with a lone electron pair is adjacent to the ring, as in (LXXV), the double-bond character of the ring–X bond increases with the electron-acceptor character of the ring (cf. LXXVI), and therefore the compound absorbs at higher frequencies.

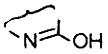

(LXXV)

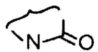

(LXXVI)

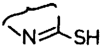

(LXXVII)

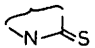
If a multiple bond is adjacent to the ring (cf. LXXVII) (with Y more electronegative than X), increasing the electron-donor properties of the ring will increase the single-bond character of the XY bond and cause absorption to occur at lower frequencies.

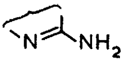
Tautomerism.—Heterocyclic compounds which contain hydroxyl, mercapto-, amino-, or acylamino-groups α or γ to ring nitrogen atoms are potentially tautomeric (cf. LXXVIII—LXXXV). Infrared spectra have

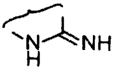

(LXXVIII)

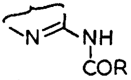

(LXXIX)

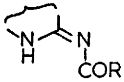

(LXXX)


(LXXXI)


(LXXXII)


(LXXXIII)


(LXXXIV)


(LXXXV)

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*Throughout this Review Py, PyO, Ph, T, Pyrr, and F denote monosubstituted pyridine, pyridine 1-oxide, benzene, thiophen, pyrrole, and furan rings, respectively, and the preceding numeral denotes the position of nuclear substitution.

[33] Culbertson, Decius, and Christensen, *J. Amer. Chem. Soc.*, 1952, **74**, 4834.

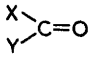
[34] Blout and Fields, *J. Amer. Chem. Soc.*, 1950, **72**, 479; Lacher, Bitner, Emery, Seffl, and Park, *J. Phys. Chem.*, 1955, **59**, 615.

been valuable in investigating this tautomerism, *e.g.*, of amino-,[35] hydroxy-,[36] mercapto-,[37] and acylamino-pyridines,[38] -pyridine 1-oxides,[39] and -pyrimidines.[40] In work of this nature, the results are most conclusive when the spectrum of the potentially tautomeric compound is compared with the spectra of derivatives of both possible forms, the structures of which are "fixed" by alkylation.

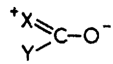
Thus, the aminopyridines show the bands expected for NH_2 groups and not those for –NH– and =NH groups (cf. LXXXIII), and the acylamino-pyridines show the bands of the particular acylamino-group; moreover all these compounds show the absorption characteristic of the appropriately substituted pyridine ring and not that of a pyridone-like molecule. The pyridones show no bands attributable to a hydroxyl group and their spectra resemble those of their *N*-methyl derivatives more than those of the *O*-methyl derivatives: *e.g.*, 4-methoxypyridine but not pyrid-4-one shows the characteristic bands of the 4-substituted pyridine nucleus, indicating that the latter does not exist as 4-hydroxypyridine; similar considerations apply to the pyridthiones. Pyridones and pyridthiones also show bands attributable to the C=O and C=S bonds, and similar to those in the corresponding *N*-methyl derivatives.*

Recent extensive work using diverse physical methods indicates that in most cases (at least in six-membered rings) amino- and acylamino-compounds exist predominantly as such, but hydroxy- and mercapto-compounds exist in the tautomeric carbonyl and thiocarbonyl forms.[16] These facts should assist in the future interpretation of infrared spectra.

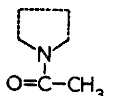
Carbonyl Compounds.—The position of the C=O stretching frequency in compounds (LXXXVI) gives a measure of the electron-releasing ability of the groups X and Y; the lower the band position the greater is the single-bond character and the importance of form (LXXXVII). If one of the groups is kept constant and the other varied through a series of heterocyclic rings, the relative electron-donating ability of these rings at



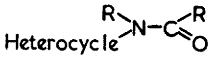
(LXXXVI)



(LXXXVII)



(LXXXVIII)



(LXXXIX)

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* Bellamy's method[41] of observing the shifts in band positions from a solvent capable of hydrogen bonding with the C=O or C=S (*e.g.*, $CHCl_3$) to one incapable of so doing (*e.g.*, C_2Cl_4) is useful in the identification of these bands.[42]

[35] Angyal and Werner, *J.*, 1952, 2911; Goulden, *J.*, 1952, 2939.

[36] Mason, *J.*, 1957, 4874.

[37] Jones and Katritzky, *J.*, 1958, 3610.

[38] Jones and Katritzky, *J.*, 1959, 1317.

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

[40] Short and Thompson, *J.*, 1952, 168; Brownlie, *J.*, 1950, 3062; Brown and Short, *J.*, 1953, 331; Brown, Hoerger, and Mason, *J.*, 1955, 4035.

[41] Bellamy *et al.*, *Trans. Faraday Soc.*, 1958, **53**, 1120; 1959, **54**, 14.

[42] L. J. Bellamy, personal communication; Katritzky and Jones, *J.*, in the press.

various nuclear positions is determined. Measurements[13,43] of methyl and ethyl esters, aldehydes, and methyl ketones (LXXXVI, Y = OMe, OEt, H, Me) show that the order is: 2-Pyrr $\sim$ 3-Pyrr $>$ 2-T $>$ 3-T $>$ Ph $>$ 4-PyO $\sim$ 3-Py $>$ 4-Py $>$ 3-PyO $>$ 3-Py–BCl_3 $\sim$ 4-Py–BCl_3; this is in agreement with other evidence.[16]

When the carbonyl group is attached directly to a nitrogen atom of a heterocyclic ring, as in (LXXXVIII), the C=O stretching frequency increases, and the C–N stretching frequency decreases, as the ring becomes increasingly electron-attracting, *i.e.*, pyrrole $<$ imidazole $<$ triazole $<$ tetrazole.[44]

In compounds of type (LXXXIX) the heterocyclic ring and the C=O group "compete" for the lone electron pair on the nitrogen atom, giving a measure of the electron-accepting power of the heterocyclic ring: Ph $<$ 3-Py $<$ 4-Py $\sim$ PyO.[45]

C≡N *Stretching Frequency.*—As the ring to which a cyano-group is attached increases in electron-donating character, the stretching frequency decreases,[46] and the intensity increases.[47,48a]

NO_2 *Frequencies.*—The asymmetrical[46] and symmetrical[48b] NO_2 stretching modes absorb at higher frequencies as the heterocyclic rings to which the group is attached become increasingly electron-demanding.

Ring–O and *Ring*–N *Stretching Modes.*—The positions of the C–O bands near 1300 cm.$^{-1}$ for ethoxyl and methoxyl compounds indicate the following order of electron-accepting ability: Ph $<$ 3-Py $<$ 4-Py $\sim$ 2-Py $<$ 4-PyO $\sim$ 2-PyO $\sim$ 4-Py–BCl_3,[49] which is in agreement with chemical evidence.[16] For amino- and dimethylamino-compounds the positions of the C–N bands, near 1280 and 1350 cm.$^{-1}$, respectively, are similarly related to the electron-accepting ability of the ring.[50]

NH *Stretching Frequencies.*—The asymmetrical and symmetrical N–H stretching modes for amino- and the N–H stretching mode in alkylamino-heterocyclic compounds increase in both wavelength and intensity as the ring becomes more strongly electron-accepting.[50,51] For compounds of type (XC),[45] just as in the corresponding acetanilides,[52] the position and

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[43] (*a*) Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182; (*b*) Katritzky, Lagowski, and Beard, unpublished work; Gronowitz and Rosenberg, *Arkiv Kemi*, 1955, **8**, 23; Shindo, *Pharm. Bull. (Japan)*, 1957, **5**, 472; 1958, **6**, 117.

[44] Otting, *Chem. Ber.*, 1956, **89**, 1940; Staab, Otting, and Ueberle, *Z. Electrochem.*, 1957, **61**, 1000; Bellamy, *Spectrochim. Acta*, 1958, **13**, 60.

[45] Katritzky and Jones, *J.*, 1959, 2067.

[46] Shindo, *Bull. Pharm. (Japan)*, (*a*) 1957, **5**, 472; (*b*) 1958, **6**, 117.

[47] Sensi and Gallo, *Gazzetta*, 1955, **85**, 235.

[48] (*a*) Katritzky, *Rec. Trav. chim.*, in the press; (*b*) Katritzky and Simmons, unpublished work.

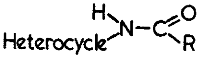
[49] Katritzky and Coats, *J.*, 1959, 2062.

[50] Katritzky and Jones, *J.*, 1959, 3674.

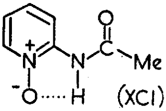
[51] Mason, *J.*, 1958, 3619; Short, *J.*, 1952, 4584; Bellamy and Williams, *Spectrochim. Acta*, 1957, **9**, 341; Osborn, Schofield, and Short, *J.*, 1956, 4191.

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

intensity of the NH stretching band are little affected by the nature of the ring unless intramolecular hydrogen bonding can occur, as in (XCI).



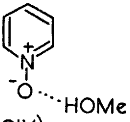
(XC)



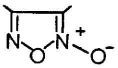
(XCI)

(XCII)

(XCIII)



(XCIV)



(XCV)

N-*Oxide Frequencies*.[23,46,53]—The N^+–O^- stretching frequency in *N*-oxides (XCII) occurs at *ca.* 1300—1200 $cm.^{-1}$ (ϵ_A *ca.* 280), but within this range the frequency is increased by the presence of electron-accepting substituents in the ring; these substituents increase the importance of canonical forms of type (XCIII) and, therefore, increase the double-bond character of the N–O bond. However, alkyl substituents in the 3-position also cause a shift towards higher frequencies; the reason for this is not known, but similar effects are observed for the C–N and C–O stretching frequencies in *meta*-substituted anilines and phenyl, methyl, and ethyl ethers.[45,49,50] The N^+–O^- stretching band shows large shifts to lower frequencies when measured in a solvent with which hydrogen-bonding can occur (*e.g.*, XCIV).

N-Oxides show another characteristic band near 850 $cm.^{-1}$ which was originally assigned[54] to the N^+–O^- stretching mode but may be the N^+–O^- in-plane bending mode.[46b]

Furoxans[55] (XCV) show bands at 1360—1300, 1190—1150, and 890—840 $cm.^{-1}$ which are analogous to the above *N*-oxide frequencies.

Summary of the principal correlations for use in diagnostic work

The presence of an aromatic ring is indicated by the appearance of four bands for six-membered rings, or three for five-membered rings, in the 1600—1350 $cm.^{-1}$ region of the spectrum. The positions of these bands give information concerning the nature of the ring and the substitution pattern. The number and positions of the in- and out-of-plane CH deformation bands in the 1200—700 $cm.^{-1}$ region indicate the number of ring hydrogen atoms, and thus the substitution pattern.

High intensity of the band near 1490 $cm.^{-1}$ for six-membered rings

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[53] Sartori, Costa, and Blasina, *Gazzetta*, 1955, **85**, 1085; *Z. phys. Chem.* (*Frankfurt*) 1955, **4**, 24; 1956, **7**, 123.

[54] Ito and Hata, *Bull. Chem. Soc. Japan*, 1955, **28**, 353.

[55] Boyer, Czerniak, Gutowsky, and Snyder, *J. Amer. Chem. Soc.*, 1955, **77**, 4238.

indicates the presence of electron-donor substituents; the intensities of the bands at *ca.* 1600 and 1580 cm.$^{-1}$ are directly related to the amount of disturbance to the charge symmetry of the ring. The electron-donor and/or electron-acceptor powers of the ring are indicated by the positions and intensities of the characteristic substituent vibration modes.

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