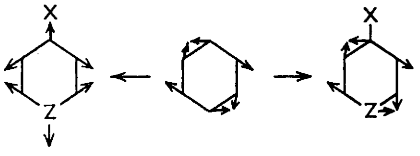
838. *Infrared Absorption of Heteroaromatic and Benzenoid Six-membered, Monocyclic Nuclei. Part V.*[1, 2] *The Correlation of Intensities of* CC *and* CN *Ring Stretching Frequencies with Charge Disturbance in the Ring.*

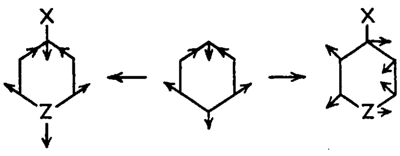
By A. R. Katritzky.

The intensities of corresponding characteristic modes in the 1600—1400 cm.$^{-1}$ region in benzene, pyridine, pyridine 1-oxide, pyridine–boron trichloride, and their monosubstituted derivatives are compared. The changes in the intensities of the bands from those in benzene are correlated with the charge disturbances created in the ring by the substituents and/or hetero-groups. Agreement is particularly satisfactory for 4-substituted compounds of C_{2v} symmetry.

In monosubstituted benzenes[1] and pyridines[3–5] and their 1-oxides[6–8] and boron trichloride adducts[9] the intensities of the characteristic bands depend on the nature of the substituent. An explanation for some of these variations is now offered.



(III) A_1 (I) E_{2g} (IV) B_1



(V) A_1 (II) E_{1u} (VI) B_1

Compounds of C_{2v} Symmetry.—Two of the normal vibrations of benzene have frequencies of 1400—1600 cm.$^{-1}$; ν_{16} (I) is infrared-inactive but occurs as a strong band in the Raman

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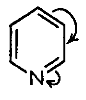
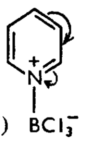
[1] Part IV, Katritzky and Lagowski, preceding paper.
[2] For other related work, see the Series " *N*-Oxides and Related Compounds," Part XV, *J.*, 1958, 3721.
[3] Katritzky and Gardner, *J.*, 1958, 2198.
[4] Katritzky and Hands, *J.*, 1958, 2202.
[5] Katritzky, Hands, and R. A. Jones, *J.*, 1958, 3165.
[6] Katritzky and Gardner, *J.*, 1958, 2192.
[7] Katritzky and Hands, *J.*, 1958, 2195.
[8] Katritzky, Beard, and Coates, unpublished work.
[9] Katritzky, unpublished work.

spectrum at 1585 cm.$^{-1}$, and ν_{13} (II) absorbs strongly in the infrared at 1485 cm.$^{-1}$.[10a] These vibrations belong respectively to the symmetry classes E_{2g} and E_{1u}, *i.e.*, they are both doubly degenerate, and when the symmetry is reduced from that of benzene (D_{6h}) to that (C_{2v}) of pyridine, pyridine–boron trihalide, or pyridine oxide, or any of the heterocyclic compounds with a 4-substituent,* or a monosubstituted benzene, each will be split into two frequencies (III—VI). One of each pair belongs to the symmetry class A_1 and is symmetric with respect to the plane of symmetry perpendicular to the ring (III and V); the others (IV and VI) are in the class B_1 and are antisymmetric with respect to this plane.

The following predictions could be made about the intensities of these bands: (i) In compounds in which the combined effect of X and Z is to produce little change in the charge distribution in the ring, vibrations (III) and (IV) should give weak bands (in the infrared) whereas vibrations (V) and (VI) should absorb with an intensity approximately half that in benzene itself. (ii) If X and Z do produce a change in the charge distribution in the ring, this change will be symmetrical with respect to the vertical plane of the molecule and therefore should affect the intensities of vibrations (III) and (V) more than those of (IV) and (VI). However, the relative change in the intensities of (III) and (IV) should be greater than those of (V) and (VI), since the former are allowed only because of the X and Z groups. Thus, intensities should vary with the amount of disturbance of the charge distribution of the ring, strongly in (III), somewhat less in (IV) and (V), and comparatively little in (VI). Moreover, in (III) and (IV) the intensity should increase more or less continuously with increasing charge disturbance, but in (V) the nature of the variation cannot be predicted.

A measure of the effect of a substituent X on the charge distribution in a monosubstituted benzene is given by the mesomeric moment of X (the algebraic difference between the dipole moments of phenyl–X and alkyl–X).[11] The concept of mesomeric moments has been extended by Katritzky and Sutton and their collaborators to include heterocyclic compounds [12,13] and thus measure the effect of the substituent X on these rings. It is more difficult to obtain a precise measure of the effect of Z. Qualitatively, in pyridine (VII) and pyridine–boron trichloride (VIII) electrons are pulled towards Z; in pyridine oxide there are two opposing effects (IX and X). Where Z is $^{+}$N–O^{-} or $^{+}$N–BCl$_3^{-}$, indications are given by taking the difference between the pyridine and trimethylamine adducts,[14] but this fails in the case of pyridine and trimethylamine themselves for the dipole moments are very sensitive to small differences of hybridisation of the lone-pair electrons.[14] The pull of electrons in pyridine is certainly less than that in the pyridine–boron trihalide adducts (*ca.* 1·3 D measured as above [14]); we have arbitrarily taken it to be 0·8 D.


(VII)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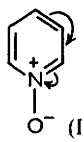
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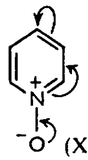
(X)

The intensity † of an infrared band is determined by the rate of change of dipole

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* If the substituent is not symmetrical, this will make little difference to the effectively localised ring vibrations.

† Strictly, integrated areas should be used in intensity correlations; however in many cases they cannot be measured because of band overlap, so apparent extinction coefficients have been used. Large irregularities in the half-band widths were not observed.

[10] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, (*a*) p. 364, (*b*) p. 241.

[11] Everard and Sutton, *J.*, 1951, 2818, and references therein.

[12] Katritzky, Randall, and Sutton, *J.*, 1957, 1769.

[13] Bax, Katritzky, and Sutton, *J.*, 1958, 1254.

[14] *Idem*, *J.*, 1958, 1258.

moment with the normal co-ordinate at the equilibrium position, *i.e.*, $\partial\mu/\partial Q$. The dipole moment of a covalent bond must reach a maximum at some internuclear distance, for it will be zero when the two atoms are infinitely near to each other or far apart.[10b] Thus, strictly, no conclusion regarding $\partial\mu/\partial Q$ can be drawn from a knowledge of the value of μ in the direction Q at the equilibrium position. However, in a series of closely related molecules, it might well be true that $(\partial\mu/\partial Q)^2$* increases continuously as some function of μ_Q.

For a qualitative comparison of the results with the predictions, substituents have been divided into three main types: (*a*) strong electron-donors, including substituted amino- and alkoxy-groups for which the average mesomeric moment has been taken as the mean of that of the dimethylamino- and methoxy-compound in each group, (*b*) substituents with a saturated carbon atom directly attached to the nucleus, which are usually weakly electron-donating and for which the mesomeric moment has been taken as that of the particular methyl compound, and (*c*) strong electron-acceptors with a carbonyl or nitro-group directly attached to the nucleus, for which the mesomeric moment has been taken as the mean of the ethoxycarbonyl, acetyl and nitro-compounds. Mean values of apparent extinction coefficients for these types of substituent (taken from refs. 1, 3, 6, 9) are given in Table 2, and average values for the disturbance of charge distribution in the ring in Table 1. Compounds with halogen or unsaturated carbon atoms directly attached to the nucleus are not included, since these substituents can be both electron donors and acceptors.

TABLE 1. *Disturbance of charge distribution in ring (Debyes).*

Type of subst.	Monosubst. benzene	4-Subst. pyridine	4-Subst. pyridine 1-oxide	4-Subst. pyridine–boron trichloride
Donor	1·3	2·5	1·2	2·6
Weak	0·3	1·2	0·3	2·0
Nil	0	0·8	0·8	1·3
Acceptor	0·6	0·4	1·6	1·1

As predicted, vibration (VI) shows (Table 2, Entries 13—16) the least variation in apparent extinction coefficients: X has little effect, Z somewhat more. Vibration (III) shows intensity variations (Table 2, Entries 1—4) which are qualitatively in good agreement with the variations in the value of charge disturbance given in Table 1. Vibration (IV) is absent or unresolved in the oxides; in the other compounds it shows intensities (Table 2, Entries 5—8) which, as predicted, are less than those of vibration (III) but are in the same relative order except that pyridines and pyridine–boron trichlorides with acceptor substituents show higher intensities than expected. The variation of vibration (V) was expected to show less correlation with the values in Table 1; it appears to become intense when any electron-donating group (including *N*-oxide) is attached to the ring.

In an attempt at quantitative correlation, extinction coefficients for the A_1 band near 1600 cm.$^{-1}$ have been plotted against the disturbance to charge distribution in the ring (Figure); there is a trend, but much scatter. The scatter is not surprising in view of the nature of the treatment and the approximations and assumptions involved.

Compounds of C_s Symmetry.—In the 2- and 3-substituted compounds the normal co-ordinates of the ring vibrations are not uniquely determined (lower symmetry), and the two charge disturbances are not collinear, cannot be algebraically added, and have no directional relation to the normal co-ordinates. Also no mesomeric moments are available.

However, intensity variations with the substituent type (Table 3) can be accounted for approximately. Replacement of H by a substituent changes masses and force constants more than replacing CH by N; thus a 2- or 3-substituted pyridine has effective C_{2v} symmetry, and in-plane vibrations are A_1 or B_1 according to their symmetry about

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* If the square is considered, the sign of $\partial\mu/\partial Q$ does not matter, and intensities are proportional to $(\partial\mu/\partial Q)^2$.

TABLE 2. *Mean positions and apparent extinction coefficients of bands in C_{2v} compounds.*

		Monosubst. benzene [a]		4-Subst. pyridine [b]		4-Subst. pyridine 1-oxide [c]		4-Subst. pyridine boron trichloride [d]	
No.	Type of subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
	A_1 Vibration near 1600 cm.$^{-1}$ (III)								
1	Donor	1603	200	1599	385	1636	85	1640	270
2	Weak	1605	15	1606	150	1622	5	1640	175
3	Hydrogen	1585 [e]	0	1588	60	1612	50	1630	90
4	Acceptor	1604	50	1602	30	1613	170	1640	90
	B_1 Vibration near 1580 cm.$^{-1}$ (IV)								
5	Donor	1586	60	1569	85	—		1568	75
6	Weak	—		1563	20	—		1561	15
7	Hydrogen	1585 [e]	0	(—)		—		(—)	
8	Acceptor	1585	35	1567	50	—		1569	
	A_1 Vibration near 1500 cm.$^{-1}$ (V)								
9	Donor	1498	155	1507	155	1489	275	1511	160
10	Weak	1495	40	1495	10	1485	195	1505	25
11	Hydrogen	1481	40 [g]	1481	15	1468 †	280	1490	30 [f]
12	Acceptor	1489	15	1490	10	1480	110	(—)	
	B_1 Vibration near 1440 cm.$^{-1}$ (VI)								
13	Donor	1451	30	1421	35	1436	60	1460	75
14	Weak	1454	45	1417	75	1447	60	1448	135
15	Hydrogen	1481	40 [g]	1439	75	1468 †	280	1461	140 [f]
16	Acceptor	1451	55	1411	100	1442	90	1430	190

Values for benzene, pyridine, and pyridine 1-oxide were obtained by measurements in chloroform solution under the usual standard conditions;[1] the assignments agree with those given by other workers.

† Indicates peak formed by the superimposition of two bands, (—) indicates band is hidden, — indicates apparent absence of band.

[a] From Ref. 1. [b] From Ref. 3. [c] From Ref. 6. [d] From Ref. 9. Frequency from Raman spectrum.[10a] [f] Mean value for pyridine–boron trihalide complexes.[9] [g] The ε_A (80) given by Jones and Sandorfy (in Weissburger, "Technique of Organic Chemistry. Vol. IX. Chemical Applications of Spectroscopy," Interscience Publ. Inc., London, 1956; p. 397) has been halved to take into account the twofold degeneracy of this band in benzene. We found ε_A (70) in benzene.

TABLE 3. *Mean positions and apparent extinction coefficients in bands of C_s compounds.*

		3-Subst. pyridine [a]		2-Subst. pyridine [b]		3-Subst. pyridine 1-oxide [c]		2-Subst. pyridine 1-oxide [d]	
No.	Type of subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
	A_1 Vibration near 1600 cm.$^{-1}$								
1	Donor	1592	100	1600	170	[e]		1620	160
2	Weak	1598	15	1596	105	1609	90	1615	15
3	Acceptor	1597	140	1589	75	1608	45	1608	45
	B_1 Vibration near 1580 cm.$^{-1}$								
4	Donor	1579	70	1577	160	[e]		1572	200
5	Weak	1581	40	1572	50	1564	25	—	
6	Acceptor	1580	20	1573	35	1567	25	1536	15
	A_1 Vibration near 1500 cm.$^{-1}$								
7	Donor	1483	165	1474	200	[e]		1500	190
8	Weak	1479	50	1475	70	1483	95	1490	125
9	Acceptor	—		1467	20	1476	50	1483	25
	B_1 Vibration near 1440 cm.$^{-1}$								
10	Donor	1429	115	1435	250	[e]		1439	200
11	Weak	1422	65	1434	65	1434	130	1443	175
12	Acceptor	1422	70	1435	50	1437	170	1431	215

[a] From Ref. 5. [b] From Ref. 4. [c] From Ref. 8. [d] From Ref. 7. Not yet available.

lines as in (XI) and (XII). 3-Substituents in pyridine are chemically similar to those in benzene, but 2-substituents to those in the 4-position;[15] *i.e.*, both electron-attracting and -donating groups conjugate in the 3-position but only the latter effectively in the 2-position

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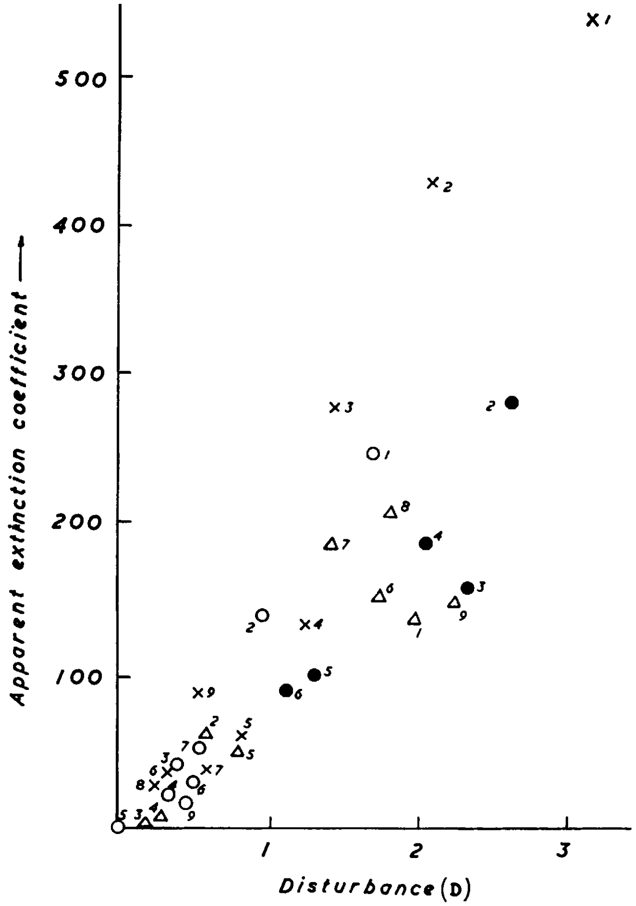
[15] Cf., *e.g.*, Mosher in Elderfield, "Heterocyclic Compounds," Wiley, New York, 1950, Vol. 1, Chap. 8.

(cf. the C:O, C·O, and C·N frequencies of carbonyl groups,[16] ethers,[17] and amines[18]). Charge disturbance by the substituent is in the direction of the vibration near 1600 cm.$^{-1}$, and these intensities (Table 3, Nos. 1—3) are explained by varying conjugation of the substituent and a constant influence of the nitrogen atom. Intensity variation is less for the band near 1580 cm.$^{-1}$ (Table 3, Nos. 4—6) as expected. The E_{1u} vibration of benzene at 1485 cm.$^{-1}$ (2 × 40) is split in pyridine as shown (XV). With normal co-ordinates symmetrical about directions intermediate to those in (XV) the nitrogen atom should have little effect on the intensities, which for the bands near 1500 and 1440 cm.$^{-1}$ in 2- and 3-substituted pyridines (Table 3, Nos. 7—12) are indeed similar to those of the corresponding benzenes, except that the B_1 band intensities are also increased by donor groups.

Extinction coefficients for band near 1600 *cm.*$^{-1}$ *plotted against disturbance of charge symmetry.*



Numbers refer to substituent: 1 NMe_2, 2 OMe, 3 Cl, 4 Me, 5 H, 6 CO_2Et. 7 COMe, 8 NO_2, 9 CN.
Ring systems are represented: ○ Benzene, × Pyridine, △ Pyridine oxide, ● Pyridine–boron trichloride.
Nitrobenzene is not included because the band is split into two components in this compound.

The 2- and 3-pyridine 1-oxides will also have approximate C_{2v} symmetry (XIII) and (XIV), both the $^+N-O^-$ and substituent influencing all the vibrations. Data in Table 2 indicate that those near 1600 and 1580 cm.$^{-1}$ should be affected mainly by the substituent

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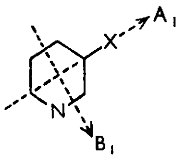
[16] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.
[17] Katritzky and Coates, unpublished work.
[18] Katritzky and R. A. Jones, unpublished work.

and those near 1500 and 1440 cm.$^{-1}$ by the $^{+}$N–O^{-} group. The 3-pyridine 1-oxide ring conjugates effectively only with electron-donor substituents,[16] in agreement with the intensity variation observed. The 2-pyridine 1-oxide ring, already known to conjugate strongly with electron donors,[17,18] is now indicated to conjugate also with acceptors (of. refs. 16 and 19). The appreciable intensity of the 1500 and 1440 cm.$^{-1}$ bands is explained by the influence of the $^{+}$N–O^{-} group.



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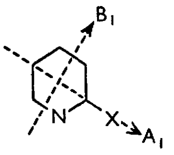

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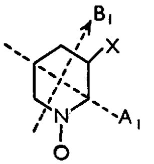

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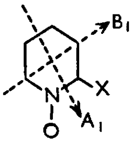

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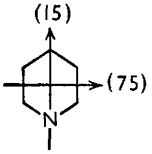

(XV)

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[19] Hands and Katritzky, *J.*, 1958, 1754.