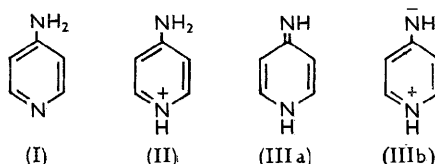


43. The Electronic Spectra of N-Heteroaromatic Systems. Part VI.* The $\pi \rightarrow \pi$ Transitions of Monocyclic Amino- and Mercapto-azines.

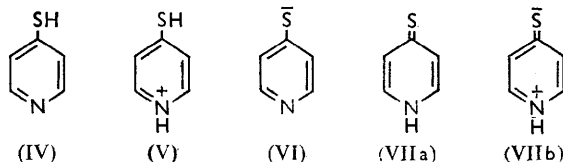
By S. F. MASON.

The ultraviolet absorption spectra of the amino-, cationic, and imino-forms of some monocyclic aminoazines have been measured in aqueous solution, and the spectra of the amines and the imines have been obtained in non-polar solvents. The results and spectroscopic data for the various ionic species of monocyclic mercaptoazines are discussed in relation to a benzyl anion and a substituted benzene charge-transfer model for these compounds. The benzyl anion model is found to be the more consistent with experiment.

RECENTLY the electronic spectra of the four ionic species of monocyclic *N*-heteroaromatic hydroxy-compounds have been interpreted in terms of a perturbed benzyl anion model,¹ and an alternative charge-transfer model has been put forward to account for the neutral and cationic forms of *N*-heteroaromatic amines.² In order to examine the scope of application of these models, the electronic spectra of the three accessible ionic species of the monocyclic *N*-heteroaromatic amines, namely, the neutral amine (*e.g.*, I), the cation (*e.g.*, II), and the imine (*e.g.*, IIIa) or zwitterion form (*e.g.*, IIIb), have been measured in



aqueous solution, and the spectra of the amine and the imine forms have been obtained in less polar solvents. The results are recorded in Tables 1 and 2 and in the Figures. For a further examination of the theoretical models, the spectra^{3,4} of the four ionic species of the monocyclic *N*-heteroaromatic mercapto-compounds, namely, the neutral mercapto- (*e.g.*, IV), the cation (*e.g.*, V), the anion (*e.g.*, VI), and the thione (*e.g.*, VIIa) or zwitterion form (*e.g.*, VIIb), are given in Table 3.



Two generalisations emerge from the spectroscopic data for the pyridine derivatives (ref. 1, Tables I and 3). First, the long-wave absorption bands in the spectra of the various charged species of a given pyridine amine or hydroxy- or mercapto-compound lie at wavelengths in the order, zwitterion > anion > cation > neutral form, provided that bands of similar intensity are compared. In the spectrum of 4-aminopyridine a low-intensity shoulder appears on the long-wave side of the main high-intensity band, which is comparable in intensity to the single measurable absorption band of the cation and the imine form, the high-intensity bands following the general sequence given above (Table 1,

* Part V, *J.*, 1959, 1269.

¹ Mason, *J.*, 1959, 1253.

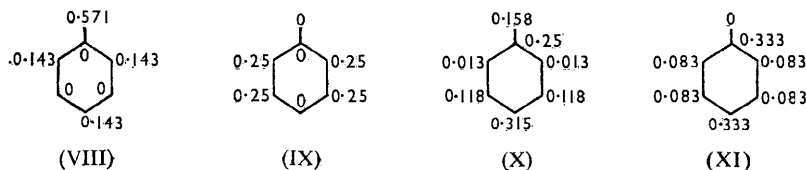
² Murrell, *J.*, 1959, 296.

³ Albert and Barlin, *J.*, 1959, 2384.

⁴ Marshall and Walker, *J.*, 1951, 1004; Boarland and McOmie, *J.*, 1952, 3716.

Fig. 2). Secondly, for a particular species of a given pyridine derivative the long-wave absorption bands lie at wavelengths dependent upon the position of substitution, in the order, 3- > 2- > 4-pyridine. The first generalisation is explained by both of the theoretical models, but the second is not compatible with the charge-transfer model.

In the benzyl anion model, it is assumed¹ that the lone-pair electrons of the amino-, hydroxy-, or mercapto-group are delocalised over the pyridine nucleus in the ground state, entering a π -orbital which corresponds to the non-bonding molecular orbital of the benzyl anion. Being loosely held, one of the delocalised lone-pair electrons is readily promoted on the absorption of light to an unoccupied π -orbital, which may be treated as an unoccupied orbital of the benzyl anion perturbed by hetero-substitution at the exocyclic position and in the nucleus. The one-electron charge distributions in the non-bonding molecular orbital (ψ_N) and the two lowest unoccupied π -orbitals (ψ_I and ψ_{II}) are given in (VIII), (IX), and (X) respectively, the energies of these orbitals being 0, β , and 1.26β



respectively, where β is the carbon-carbon resonance integral. In the charge-transfer model, it is assumed² that the lone-pair electrons of the exocyclic group are not appreciably delocalised over the nucleus in the ground state, and that on the absorption of light one of these electrons is transferred to a benzene-like orbital (ψ_I or ψ_{II}) confined to the nucleus. The orbital ψ_{II} has the one-electron charge distribution (XI), and like the orbital ψ_I it has an energy β .

For a given substituent in a particular ionic form the energy of the lone-pair electrons in the ground state is independent of the position of substitution in the pyridine nucleus according to the charge-transfer model. In the first excited state the energy of the promoted

TABLE 1. *The electronic absorption spectra in aqueous solution of the amine (A), cation (C), and imine (I) forms of some monocyclic N-heteroaromatic amines. Values in italics refer to shoulders.*

Compound	pK_a	Solvent	Species	λ_{max} . (m μ)	ϵ
2-Aminopyridine	6.86 ^c	pH 9.5	A	287; 229	3800; 9400
			C	300; 229	5700; 8900
1-methochloride	12.2 ^e	pH 14	I	317; 251	4100; 11,700
3-Aminopyridine	5.98 ^e	pH 9	A	288; 231	3000; 8200
			C	315; 250	3600; 7600
4-Aminopyridine	9.17 ^e	pH 12	A	265; 241	2400; 14,000
			C	263	16,500
1-methochloride	12.5 ^d	pH 14	I	268	16,500
2-Aminopyrimidine ^a	3.54	pH 7	A	292; 224	3200; 13,000
			C	302; 221	4000; 14,800
1-methochloride ^a	10.75	pH 13	I	345; 236	2900; 15,500
4-Aminopyrimidine ^a	5.71	pH 13	A	268; 233	5200; 18,200
			C	246	18,600
1-methochloride ^a	12.22	pH 13	I	315; 253	620; 16,200
5-Aminopyrimidine ^b	2.60	pH 7	A	298; 236	3100; 11,000
			C	332; 253	3700; 14,400
3-Amino-6-methylpyridazine ...	5.32 \pm 0.05	pH 8	A	295; 231	2070; 8800
			C	293; 228	2850; 5600
2-methochloride	11.8 \pm 0.2	pH 14	I	326; 244	1700; 7800
4-Aminopyridazine	6.69 ^e	pH 9	A	280; 249	3700; 11,800
			C	272	13,100
2-Aminopyrazine	3.14 ^e	pH 7	A	316; 230	4960; 10,500
			C	326; 229	5800; 10,700

^a Brown, Hoerger, and Mason, *J.*, 1955, 4035. ^b Whittaker, *J.*, 1951, 1565. ^c Albert, Goldacre, and Phillips, *J.*, 1948, 2240. ^d Angyal and Angyal, *J.*, 1952, 1461. ^e Albert, *Chem. Soc. Special Publ.* No. 3, 1955, p. 132.

electron is equal in corresponding 2- and 3-substituted pyridines, where the transition takes place to the orbital ψ_I , and is smaller in the 4-isomer, where ψ_{III} is the lowest unoccupied orbital, since the charge densities at the *ortho*- and *meta*-positions of ψ_I (IX) are equal and smaller than that at the *para*-position of ψ_{III} (XI). The long-wave absorption bands of corresponding pyridine derivatives should, therefore, lie at wavelengths in the

TABLE 2. *The effect of solvents on the positions [λ_{\max} . (m μ)] of the ultraviolet absorption bands of some N-heteroaromatic amines and imines.*

	λ_{\max} . in water	λ_{\max} . in ethanol	λ_{\max} . in cyclohexane
2-Aminopyridine	287; 229	296; 230	288; 231
1-Methyl-2-pyridone imine	317; 251		362; 255
3-Aminopyridine	288; 231	295; 235	292; 232
4-Aminopyridine	265; 241	270; 246	260; 233
1-Methyl-4-pyridone imine	268		272
2-Aminopyrimidine	292; 224	296; 226	283; 223
1-Methyl-2-pyrimidone imine	345; 236		373; 236
4-Aminopyrimidine	268; 233	274; 236	263; 228
1-Methyl-4-pyrimidone imine	315; 253		340; 283
3-Amino-6-methylpyridazine	295; 231	310; 234	290; 229
2,6-Dimethyl-3-pyridazone imine	326; 244		360; 250
2-Aminopyrazine	316; 230	322; 233	310; 228

TABLE 3. *The electronic absorption spectra in aqueous solution of the neutral thiol (N), cation (C), anion (A), and zwitterion or thione (Z) forms of some N-heteroaromatic mercapto-compounds. Values in italics refer to shoulders.*

Compound	Species	λ_{\max} . (m μ)	ϵ
2-Methylthiopyridine ^a	N	292; 247	4200; 8700
	C	317; 250	8000; 7000
2-Mercaptopyridine ^a	C	302; 238	8700; 6200
	A	310; 264	4700; 12,500
	Z	345; 273	7400; 10,700
	N	294; 253	2500; 8700
3-Methylthiopyridine ^a	C	327; 268; 288	2800; 8700; 10,000
	C	310; 255; 221	3200; 7800; 11,000
	A	313; 268; 219	2600; 13,500; 9800
	Z	361; 290; 232	2300; 12,000; 14,000
4-Methylthiopyridine ^a	N	263; 214	12,500; 9500
	C	299; 229	19,000; 8700
	C	282; 222	17,000; 7900
4-Mercaptopyridine ^a	A	286; 222	15,000; 11,000
	Z	327; 275; 231	22,000; 1300; 10,500
	N	280; 250	2500; 14,000
4-Methyl-2-methylthiopyrimidine ^b	C	304; 253; 215	4600; 14,000; 6000
	C	366; 285; 221	1400; 25,000; 8000
	A	300; 269	2500; 17,000
	Z	338; 277; 215	3300; 19,000; 10,000
6-Methyl-4-methylthiopyrimidine ^b	N	277; 213	10,000; 7000
	C	300; 223	20,000; 6600
4-Mercapto-6-methylpyrimidine ^b	C	312;	18,000;
	A	292;	16,000;
	Z	322; 288	11,000; 10,000

^a Albert and Barlin, *J.*, 1959, 2384. ^b Marshall and Walker, *J.*, 1951, 1004.

order: 4- > 3- = 2-pyridine, according to the charge-transfer model, contrary to the observed order.

In the benzyl anion model the energies of the transitions $\psi_N \rightarrow \psi_I$ and $\psi_N \rightarrow \psi_{II}$, E_I and E_{II} respectively, are given for 2-substituted pyridines by:

$$E_I = \beta + 0.571\Delta\alpha_x - 0.107\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$E_{II} = 1.26\beta + 0.413\Delta\alpha_x + 0.130\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for 3-substituted pyridines by:

$$E_I = \beta + 0.571\Delta\alpha_x - 0.25\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$E_{II} = 1.26\beta + 0.413\Delta\alpha_x - 0.118\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and for 4-substituted pyridines by:

$$E_I = \beta + 0.571\Delta\alpha_x + 0.143\Delta\alpha_n \quad \dots \quad (5)$$

$$E_{II} = 1.26\beta + 0.413\Delta\alpha_x - 0.172\Delta\alpha_n \quad \dots \quad (6)$$

where $\Delta\alpha_x$ and $\Delta\alpha_n$ are the increments in the Coulomb integrals of the exocyclic substituent and the nuclear nitrogen atom respectively. From ground-state phenomena it has been found⁵ for neutral and positively charged nitrogen that $\Delta\alpha_N = 0.6\beta$ and $\Delta\alpha_{NH^+} = 2.5\beta$, whilst it is probable that $\Delta\alpha_{OH} \simeq \beta$, and $\Delta\alpha_{SH}, \Delta\alpha_{O^-} \simeq 0$, negatively charged nitrogen and sulphur having small negative values with $\Delta\alpha_{N^-} > \Delta\alpha_{S^-}$. For present purposes only the inequalities in the values of the Coulomb parameters are important.

From equations (1), (3), and (5) it is apparent that irrespective of the nature and of the charge of the exocyclic substituent the absorption maximum due to the transition $\psi_N \rightarrow \psi_I$ should lie at wavelengths dependent upon the position of the substituent, in the experimentally observed order, 3- > 2- > 4-pyridine. In certain 4-substituted

FIG. 1. Ultraviolet absorption spectra of 2-aminopyridine, (A) at pH 9.5 (neutral molecule), and (B) at pH 1 (cation), and of 1-methyl-2-pyridone imine (C) in aqueous solution (pH 14), and (D) in cyclohexane solution.

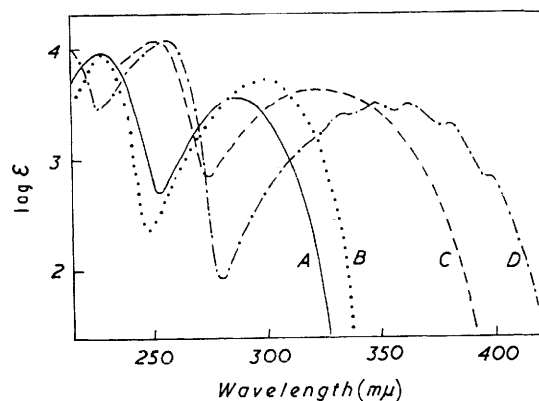
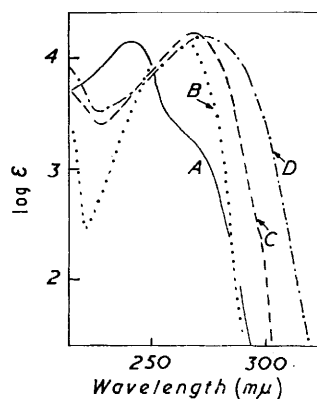


FIG. 2. Ultraviolet absorption spectra of 4-aminopyridine, (A) at pH 12 (neutral molecule), and (B) at pH 1 (cation), and of 1-methyl-4-pyridone imine (C) in aqueous solution (pH 14), and (D) in cyclohexane solution.



pyridines it is probable that the energy of the transition $\psi_N \rightarrow \psi_{II}$ is smaller than that of the transition $\psi_N \rightarrow \psi_I$, since, from equations (5) and (6), E_{II} becomes less than E_I if $\Delta\alpha_n > 0.7\beta$ when $\Delta\alpha_x \simeq 0$, and at a still smaller value of $\Delta\alpha_n$ when the exocyclic atom is more electronegative than carbon, *i.e.*, when $\Delta\alpha_x$ is positive. Thus, only when the nuclear nitrogen atom is neutral and when the exocyclic substituent is not too electropositive does a low-intensity shoulder, due to the transition $\psi_N \rightarrow \psi_I$, appear upon the long-wavelength side of the main high-intensity band, due to the transition $\psi_N \rightarrow \psi_{II}$, in the spectra of the 4-substituted pyridines, namely, the neutral species of 4-amino- (Table 1, Fig. 2) and 4-methoxy- and the anion of 4-hydroxy-pyridine.¹ In the spectrum of the zwitterionic form of 4-mercaptopyridine, where the exocyclic atom is the most electropositive of the substituents studied (negatively charged sulphur) and the nuclear nitrogen atom is positively charged, the low-intensity shoulder appears on the short-wavelength side of the long-wave high-intensity band (Table 3). The weak band is probably overlaid in the spectra of other 4-substituted pyridine species, as only high-intensity bands are observed (Tables 1 and 3, Fig. 2). With reasonable values for the Coulomb parameters, the transition $\psi_N \rightarrow \psi_{II}$ in the 4-substituted pyridines (eqn. 6) should give rise to absorption at shorter wavelengths than the transition $\psi_N \rightarrow \psi_I$ in the corresponding 2- and 3-substituted pyridines (eqns. 1 and 3), as is observed.

For the benzyl anion the theoretical oscillator strengths of the transitions $\psi_N \rightarrow \psi_I$

and $\psi_N \longrightarrow \psi_{II}$ are 0.15 and 0.84 respectively,¹ and of the two bands generally observed in the spectra of the hetero-analogues that due to the latter transition should be the more intense. In the spectra of the 4-substituted pyridines the band assigned on energy grounds to the transition $\psi_N \longrightarrow \psi_{II}$ has a much greater intensity than that ascribed to the transition $\psi_N \longrightarrow \psi_I$, and in the 2- and 3-substituted pyridines the band at short wavelengths is generally more intense than the long-wavelength band (Tables 1 and 3), both the energies and the intensities suggesting that these bands are due to the transitions $\psi_N \longrightarrow \psi_{II}$ and $\psi_N \longrightarrow \psi_I$ respectively.

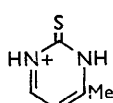
Equations (2), (4), and (6) indicate that for a particular ionic species of a given substituent the high-intensity band due to the transition $\psi_N \longrightarrow \psi_{II}$ should lie at wavelengths, dependent upon the position of the substituent, in the order, 4- > 3- > 2-pyridine, as is found (Tables 1 and 3). As a function of the charged species for a given substituted pyridine the wavelength order for the band due to the transition $\psi_N \longrightarrow \psi_{II}$ should be zwitterion > anion > cation > neutral form, only for 3- and 4-substitution, and for the 2-substituted pyridines hypsochromic shifts should result from the change of a neutral form into the cation, or of an anion into the zwitterionic form. The theoretical order is observed experimentally in the 3- and 4-substituted pyridines, but not in the charged species of 2-mercapto- and 2-methylthio-pyridine. However, the short-wave band in the spectrum of 2-aminopyridine undergoes no shift on cation formation, and the corresponding band in the cases of the related compounds, 2-amino-pyrimidine and -pyrazine and 3-aminopyridazine, undergoes a hypsochromic shift (see Tables 1 and 3), as required by the equations: for 2-aminopyrimidine,

$$E_{II} = 1.26\beta + 0.543\Delta\alpha_N + 0.130\Delta\alpha_n \dots \dots \dots (7)$$

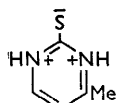
and for 2-aminopyrazine and 3-aminopyridazine,

$$E_{II} = 1.26\beta + 0.295\Delta\alpha_N + 0.130\Delta\alpha_n \dots \dots \dots (8)$$

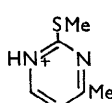
In general, the spectra of the substituted diazines resemble those of the corresponding pyridines, though there are new features due to the existence of additional ionic and tautomeric species. The cation of 2-mercapto-4-methylpyrimidine absorbs at a longer wavelength than any other charged species of this compound, though the long-wave band of the cation of 4-methyl-2-methylthiopyrimidine lies at a wavelength intermediate between that of the neutral molecule and that of the anion of the mercapto-compound, in conformity with the order generally observed for the charged species of a given substituted azine. Thus the cation of 2-mercapto-4-methylpyrimidine probably has the structure (XII), which should absorb at longer wavelengths than any other charged species of this compound, whilst the cation of 4-methyl-2-methylthiopyrimidine probably has the normal structure (XIII), analogous to that of 2-mercapto- and 2-methylthio-pyridine. Further, the zwitterion or thione form of 4-mercapto-6-methylpyrimidine gives two absorption bands whose intensities are lower than that of the single absorption band of the other charged species of the compound. The two bands are probably due to the two isomeric



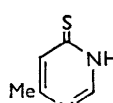
(XII a)



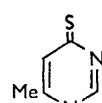
(XII b)



(XIII)



(XIV)



(XV)

4-thiopyrimidone species (XIV) and (XV), the former giving rise to the long-wave and the latter to the short-wave band, since the corresponding 4-pyrimidone species co-exist in the ratio of about 2 : 1 in neutral aqueous solution, and 3-methyl-4-pyrimidone absorbs at longer wavelengths than 1-methyl-4-pyrimidone,^{1,5} in conformity with the present theory.

During the transitions $\psi_N \longrightarrow \psi_{II}$ and, more particularly, $\psi_N \longrightarrow \psi_I$ there is a charge

⁵ Mason, J., 1958, 674.

migration from the exocyclic atom into the nucleus of the substituted azines. The zwitterionic species of the substituted azines are, therefore, less polar in the excited state than in the ground state, both the negative charge on the exocyclic atom and the positive charge on the nuclear nitrogen atom being reduced during these transitions. Conversely, the neutral species become more polar on excitation, the electronic migration conferring a positive charge on the exocyclic atom and a negative charge on the nuclear nitrogen atom. The wavelength shifts observed in the spectra of the zwitterionic imino- and neutral amino-forms of the amino-azines (Table 2, Figs. 1 and 2) provide some support for the magnitude and direction of these electronic migrations. In aqueous solution the imino-species is stabilised by solvation in the ground state, and the solvation shell, which cannot reorientate during the transition, is strained when the less polar excited state is formed. In cyclohexane solution the ground state is stabilised by solvation to a smaller degree, and the neighbouring solvent molecules are less subject to orientational strain during the transition, so that the excitation energy is reduced. Thus the bands due to the transition $\psi_N \rightarrow \psi_I$ in the spectra of the imine species undergo large red shifts when the solvent is changed from water to cyclohexane, and the bands due to the transition $\psi_N \rightarrow \psi_{II}$, in which the electronic migration into the azine nucleus is smaller, undergo smaller bathochromic shifts (Table 2, Figs. 1 and 2).

In the amine species the small polarity of the ground state, due to the delocalisation of the lone-pair electrons of the exocyclic atom over the nucleus, is considerably enhanced in the excited state. Although the solvent molecules cannot reorientate during the electronic transition, the solvation shell of a polar solvent formed in the ground state should stabilise the excited state more effectively than the corresponding shell of a non-polar solvent. However, the effect of change of solvent upon the spectra of the amine species should be small, since the ground state is also stabilised more by polar than non-polar solvents, and there is additional stabilisation of the ground state in hydroxylic solvents due to hydrogen-bonding. In particular, any hydrogen-bonding which involves the lone-pair electrons of the amino-group should increase the transition energy. The observed shifts in the spectra of the amino-species due to change of solvent are, in general, small. The bathochromic shifts found on changing from aqueous to alcoholic solution may be ascribed to the greater hydrogen-bonding capacity of water, and the hypsochromic shifts observed in the majority of the amines studied on changing from aqueous to cyclohexane solution (Table 2) are probably due to the differential stabilisation of the excited state in water, this effect outweighing in most cases, notably the aminodiazines, the stabilisation of the ground state due to hydrogen-bonding. In the aminodiazines the lone-pair electrons of the amino-group are more conjugated with the nucleus and are less available for hydrogen-bonding than in the aminopyridines, since the σ -bonds of the amino-group are more nearly trigonal and the π -electron charge density on the nitrogen atom of the amino-group, including that of the lone-pair electrons, is smaller in the former than in the latter compounds.⁶

Experimental.—3-Amino-6-methyl- and 4-amino-pyridazine were kindly supplied by Dr. J. Druey, and 2-aminopyrazine and 2- and 4-aminopyrimidine by Dr. D. J. Brown. The aminopyridines were commercial specimens. The methiodides were prepared according to the directions of Brown, Hoerger, and Mason.⁷

Ionisation constants were determined for M/100-aqueous solution by potentiometric titration, a Cambridge pH meter with glass and calomel electrodes being used.

Spectra were measured with a Hilger Uvispek quartz spectrophotometer, and the solvents listed in Tables 1 and 2.

The author is indebted to Professor A. Albert for the provision of data before their publication, and to the Royal Society for the loan of a spectrophotometer.

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[Received, July 17th, 1959.]

⁶ Mason, *J.*, 1958, 3619.

⁷ Brown, Hoerger, and Mason, *J.*, 1955, 4035.