247. *The Electronic Spectra of* N-*Heteroaromatic Systems. Part III.* The* $\pi \rightarrow \pi$ *Transitions of the Monocyclic Hydroxy-azines.*

By S. F. MASON

The ultraviolet absorption spectra of the enolic, cationic, anionic, and zwitterionic forms of the monocyclic hydroxy-azines have been measured in aqueous solution, and the spectra of the enols and zwitterions, fixed as the *O*- and the *N*-methyl derivatives, respectively, have been obtained in non-polar solvents. The first absorption band in the spectra of the different charged forms of a given compound lie at wavelengths in the sequence, zwitterion > anion > cation > enol, and the spectrum of the zwitterion shifts considerably towards the red region on changing from aqueous to non-polar solvents. The solvent effect is inconsistent with the valence-bond theory of the spectra, and a molecular-orbital theory is developed to account for the solvent shifts and the spectral differences between the compounds studied and their various charged forms.

THE hydroxy-derivatives of *N*-heteroaromatic systems can exist, in general, as any one of four different species, the neutral enol (*e.g.* I), the cation (*e.g.* II), the anion (*e.g.* III), and the zwitterion (*e.g.* IVa) or amide (*e.g.* IVb). In *N*-heteroaromatic hydroxy-compounds, the zwitterionic or amide form of a given compound usually absorbed[1] radiation at longer wavelengths than the enol, use being made of this property to determine the concentration

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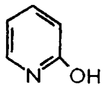

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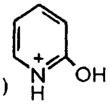

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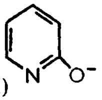

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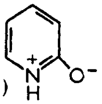

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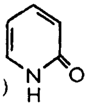

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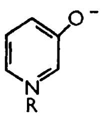

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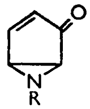

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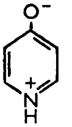

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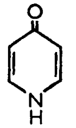

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* Part II, preceding paper.

[1] Mason, *J.*, 1957, 5010.

TABLE. 1. *The electronic absorption spectra of the enol (E), cation (C), anion (A), and zwitterion (Z) of some* N-*heteroaromatic hydroxy-compounds and their* O- *and* N-*methyl derivatives. The oscillator strength (f) of the* $\pi \longrightarrow \pi$ *absorption band of longest wavelength in the spectra of the enolic and zwitterionic forms. Values in italics refer to shoulders.*

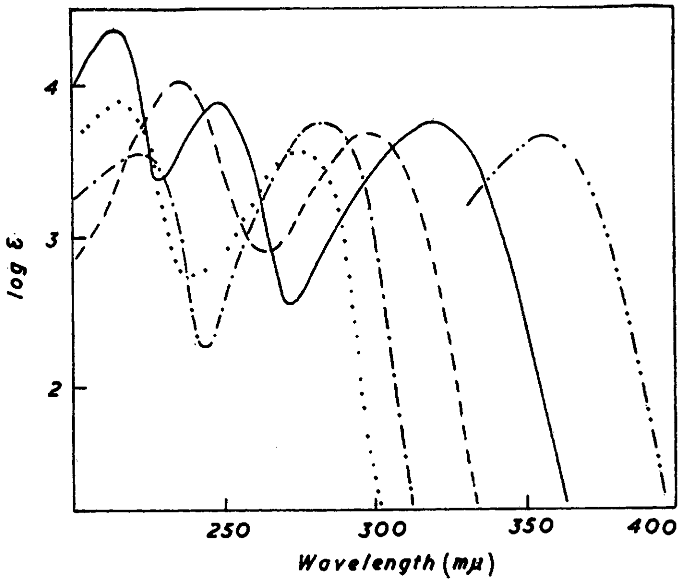
Compound	pK_a	Solvent	Species	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	*f*
2-Hydroxypyridine	0·75 [a]	pH 6	Z	293; 224 [e]	5890; 7230 [e]	0·117
	11·62 [a]	pH 13	A	291; 230	5070; 9000	
		10N-H_2SO_4	C	277; 209	6950; 3600	
2-Methoxypyridine	3·28 [a]	pH 7	E	269; $<$205 [e]	3230; $>$5300	0·065
		pH 1	C	279; 210	6920; 3550	
1-Methyl-2-pyridone	0·32 [a]	pH 5	Z	297; 226 [e]	5700; 6100 [e]	0·110
		10N-H_2SO_4	C	279; 210	6250; 3500	
3-Hydroxypyridine	4·86 [a]	pH 6·8	Z + E	315; 278; 246 [e]	3060; 2320; 5120 [e]	—
	8·72 [a]	pH 13	A	298; 236	4960; 11,000	
		pH 2	C	283; 222	5840; 3730	
3-Methoxypyridine	4·88 [a]	pH 7	E	276; 216 [e]	3960; 8320 [e]	0·052
		pH 2	C	284; 224	6240; 4290	
3-Hydroxypyridine 1-methochloride	4·96 [a]	pH 7	Z	320; 249 [e]	5810; 8120	0·088
		pH 2	C	288; 224	5900; 3790	
4-Hydroxypyridine	3·27 [a]	pH 7	Z	253	14,800	0·296
	11·09 [a]	pH 13	A	*260*; 239	*2200*; 14,150	
		pH 0	C	234	9800	
4-Methoxypyridine	6·62 [a]	pH 9	E	*235*; 222	*2000*; 9300	~0·05
		pH 4	C	235	9500	
1-Methyl-4-pyridone	3·33 [a]	pH 7	Z	260	18,900	0·328
		pH 1	C	239	11,800	
2-Hydroxypyrazine	−0·1 [a]	pH 5	Z	317; 221	5520; 8820	0·128
	8·23 [a]	pH 10·5	A	316; 227	5640; 11,240	
		10N-H_2SO_4	C	342; 222	6220; 10,400	
2-Methoxypyrazine	0·75 [a]	C_6H_{12} [d]	E	277; 210	5760; 11,500	—
		pH 7	E	290; 209 [e]	5240; 9600 [e]	0·108
		5N-H_2SO_4	C	304; 218	6900; 9220	
1-Methyl-2-pyrazone	−0·04 [a]	pH 7	Z	321; 224 [e]	5830; 9100 [e]	0·129
		10N-H_2SO_4	C	345; 225	6410; 10,900	
3-Hydroxypyridazine	−1·8 [a]	pH 6	Z	281; 220 [e]	2790; 3160 [e]	0·069
	10·46 [a]	pH 13	A	295; 227	2850; 5910	
		15N-H_2SO_4	C	265; 215	2560; 2750	
3-Methoxypyridazine	2·52 [a]	pH 6	E	265; $<$210	2330; $>$3000	0·058
		C_6H_{12} [d]	E	272; 214	1990; 3140	
		pH 0	C	269; 217	2010; 2490	
4-Hydroxypyridazine	1·07 [a]	pH 4·8	Z	262 [e]	12,740 [e]	0·287
	8·68 [a]	pH 13	A	270; 245	4650; 12,840	
		5N-H_2SO_4	C	244	8400	
4-Methoxypyridazine	3·70 [a]	pH 7	E	254; 224 [e]	2570; 8240	0·06
		C_6H_{12} [d]	E	259; 216	1560; 5970	
		pH 1	C	247	10,320	
2-Hydroxypyrimidine	2·24 [b]	pH 6·0	Z	298; 212	4750; 10,820	0·091
	9·17 [b]	pH 13	A	292; 220	4600; 11,700	
		pH 0	C	309; $<$210	5700; $>$10,000	
2-Methoxypyrimidine	~1	pH 7	E	264; $<$210	4660; $>$6000	0·072
		C_6H_{12} [d]	E	264; $<$210	4180; $>$7500	
		5N-H_2SO_4	C	273; $<$210	5020; $>$9000	
4-Hydroxypyrimidine	1·69 [b]	pH 6·2	Z	*260*; 223 [b]	*3740*; 7320 [b]	~0·09
	8·60 [b]	pH 13	A	263; 227 [b]	3280; 11,100 [b]	
		5N-H_2SO_4	C	251; 224 [b]	2970; 9840 [b]	
4-Methoxypyrimidine	2·5 [b]	pH 7	E	248; $<$215	3370; $>$6500	0·066
		C_6H_{12} [d]	E	248; $<$215	3100; $>$6000	
		pH 0	C	*240*; 227	6700; 7750	
1-Methyl-4-pyrimidone	2·02 [c]	pH 6	Z	240	14,600	0·315
		pH 0	C	*250*; 229	*2650*; 10,200	
3-Methyl-4-pyrimidone	1·84 [b]	pH 5	Z	269; 221 [b]	3900; 6810 [b]	0·095
		2·5N-HCl	C	258; 226 [b]	2940; 9080 [b]	
5-Hydroxypyrimidine	1·87 [c]	pH 4·32	Z + E	*325*; 271; 214 [e]	*107*; 4750; 9720 [e]	—
	6·78 [b]	pH 9·5	A	304; 238	4450; 11,240	
		2N-H_2SO_4	C	285; 223	4700; 6950	
		EtOH	E	276; 218 [e]	5330; 9970 [e]	0·098

[a] Quoted from ref. 3. [b] Quoted from ref. 5. [c] Quoted from ref. 4. [d] *cyclo*Hexane solution; only the $\pi \longrightarrow \pi$ bands are listed. [e] Quoted from ref. 1.

of the tautomers at equilibrium.[1] To study further the effect of ionisation on the light absorption of these compounds, the ultraviolet spectra of the anionic and cationic species of a number of *N*-heteroaromatic hydroxy-compounds have now been measured in aqueous solution, and, to throw light on the nature of the electronic transitions involved, the effect of change of solvent upon the spectra of the enolic and zwitterionic forms, fixed as the *O*- and *N*-methyl derivative of the compounds, respectively, has been investigated. The results obtained are recorded in the Tables and the Figures.

In general, it is found (Table 1; Figs. 1 and 2) that the long-wave absorption bands in the spectra of the different charged species of a given *N*-heteroaromatic hydroxy-compound lie at wavelengths in the order: zwitterion > anion > cation > enol, provided that bands of corresponding intensity are compared. In the 4-hydroxy-derivatives of pyridine and pyridazine low-intensity bands or shoulders appear in the spectra of the enol and the anion on the long-wave side of the main high-intensity bands (Table 1; Fig. 2). The main bands are comparable in intensity to the single measurable absorption bands of the cation and zwitterion forms, and their positions follow the general sequence given above (Fig. 2). The various charged species of the 4-hydroxy-derivatives of pyridine and pyridazine absorb at shorter wavelengths and with higher intensities than the corresponding species of the isomeric derivatives (Table 1; Figs. 1 and 2). A similar contrast between the spectra of 4-hydroxypyrimidine and those of its isomers is not observed, owing to structural and tautomeric complexities, which lead also, in the case of these and other hydroxy-diazines, to some deviations from the generally observed order in the positions of the long-wave band of charged species.

FIG. 1. *The ultraviolet absorption spectra of* . . . . . *3-methoxypyridine at* pH 7, —·—·— *the cation* (pH 2), *and* — — — *the anion* (pH 13) *of 3-hydroxypyridine, and* ——— *3-hydroxypyridine* 1-*metho-hydroxide* (i.e. V) *in water* (pH. 7), *and* —··—··— *in dioxan.*



The effect of changing from aqueous to non-polar solvents on the position of the long-wavelength band of the zwitterionic or amide form of the hydroxypyridines is profound (Table 2; Fig. 1). The absorption of 1-methyl-2- and -4-pyridone shifts 1000 cm.$^{-1}$ towards the red region on change from aqueous to *cyclo*hexane solution, whilst that of the 3-compound (V; R = Me) moves 3000 cm.$^{-1}$ towards the red region on changing from aqueous to dioxan solution, this zwitterion being insoluble in *cyclo*hexane. The absorption

TABLE 2. *The effect of solvents on the position of the first* $\pi \longrightarrow \pi$ *band in the spectra of the* N-*methyl derivatives of the hydroxypyridines* (*zwitterionic forms*).

Solvent		1-Methyl-2-pyridone	1-Methyl-3-pyridoxide ion	1-Methyl-4-pyridone
Dioxan–water	0%	297	320	260
	30%	298	323·5	261
	60%	300	328	262
	80%	302	332	263
	95%	304	340·5	264·5
	100%	307	356	265·5
Ethanol		300	328	262
*cyclo*Hexane		308·5	[a]	266·5

[a] Insoluble.

of the methoxy-derivatives of the azines, which have fixed enolic forms, undergoes only small blue or red shifts on changing from aqueous to *cyclo*hexane solution (Table 1; Fig. 3). The wavelength of the absorption maximum of the methoxy-azine can change considerably, owing to the appearance of vibrational fine structure in the spectrum measured in *cyclo*hexane, but the position of the band origin, in general, does not change greatly (Fig. 3).

The relative positions and intensities of the long wavelength bands in the spectra of 2- and 4-hydroxypyridine and their *N*-methyl derivatives have been interpreted by means of qualitative valence-bond theory.[2] If the amide structures (IVb) and (VIb) predominate in the ground states of 2- and 4-hydroxypyridine, respectively, and if the excited states are

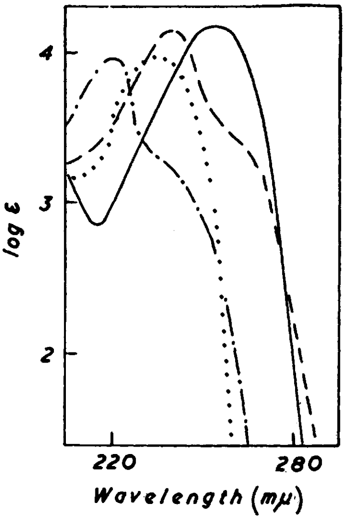


FIG. 2. *The ultraviolet absorption spectra of* —·—·— 4-*methoxypyridine at* pH 9, ... *the cation* N-*hydrochloric acid,* — — — — *the anion* (pH 13), *and* ——— *the zwitterion or amide form of* 4-*hydroxypyridine* (pH 7).

made up largely from the zwitterionic structures (IVa) and (VIa), respectively, the separation of charge during the electronic excitation is greater in 4- than in 2-hydroxypyridine. The greater the separation of charge, the larger is the energy difference between the ground and the excited state, so that 4-hydroxypyridine should absorb at shorter wavelengths than the 2-isomer, as observed.[2] The greater separation of charge should result also in a larger transition moment, and the ratio of the intensities of the long-wavelength band in the spectra of 4- and 2-hydroxypyridine should approximately equal the ratio of the squares of the distances between the charged centres in (VIa) and (IVa), respectively.[2] The ratio [2] of the squares of the distances between the charged centres is 2·86, whilst the ratio of the oscillator strengths of the long-wavelength transitions in the spectra of 4- and 2-hydroxypyridine is 2·53, and of the corresponding *N*-methyl derivatives is 2·98 (Table 1). For the analogous cases of 4- and 3-hydroxypyridazine, and 1- and 3-methyl-4-pyrimidone, the ratios of the oscillator strengths are 4·16 and 3·32, respectively (Table 1), in poorer

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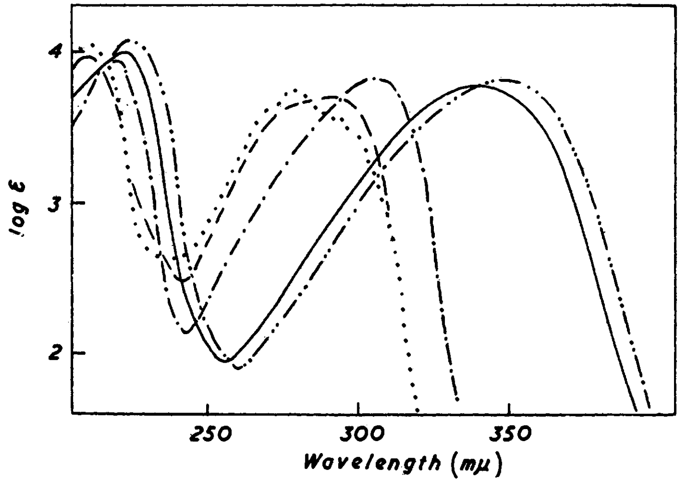
[2] Berson, *J. Amer. Chem. Soc.*, 1953, **75**, 3521.

agreement with the ratio of the squares of the distances between the charged centres.

The foregoing valence-bond interpretation of the relative intensities and positions of the first absorption band in the spectra of the zwitterionic or amide form of 2- and 4-hydroxypyridine requires that the excited state of the transitions should be more polar than the ground state. The red shift in the spectra of 1-methyl-2- and -4-pyridone observed on changing from aqueous to *cyclo*hexane solution suggests, on the contrary, that the ground state is more polar than the excited state. In aqueous solution the polar ground state is more stabilised by solvation than is the excited state, and the transition energy is increased relative to that measured in *cyclo*hexane where the solvation energy of a polar state is much smaller. Dipole-moment measurements also show that the ground state is highly polar, the moments [3] of 1-methyl-2- and -4-pyridone being 4·15 and 6·9 D, respectively. Moreover, the valence-bond treatment cannot be generalised to cover the 1 : 3-hydroxy-azines. The "*meta*-quinonoid" structure (Vb), analogous to (IVb) and (VIb), cannot predominate in the ground state of the 3-compound (V), which, in view of its salt-like character, is more adequately described by the zwitterion structure (Va).

FIG. 3. *The ultraviolet absorption spectra of* — — — *the neutral molecule of* 2-*methoxypyrazine in water* (pH 7), *and* . . . . . *in* cyclo*hexane,* —·—·— *the cation of* 2-*methoxypyrazine* (5N-*sulphuric acid*), ——— *the cation of* 2-*hydroxypyrazine* (10N-*sulphuric acid*), *and* —··—··— *the cation of* 1-*methyl*-2-*pyrazone* (10N-*sulphuric acid*).



Molecular-orbital theory offers a more general explanation of the relative positions and intensities of the absorption bands in the spectra of the 1 : 3- as well as of the 1 : 2- and 1 : 4-hydroxy-azines, and it accounts for the shifts of the bands observed on passing from one charged species to another. The hydroxy-group, and more particularly the negatively-charged oxy-group, conjugates with an azine nucleus, the lone-pair electrons of the oxygen atom being delocalised over the ring. The lone-pair electrons of oxygen enter a π-orbital which corresponds to the non-bonding molecular orbital in the analogous carbanion, the benzyl ion, and, being non-bonding electrons, they are loosely held and are readily promoted on absorption of light to an unoccupied π-orbital. The highest occupied and lowest unoccupied π-orbitals of a hydroxy-azine can be treated, respectively, as the non-bonding molecular orbital and the lowest unoccupied π-orbitals of the benzyl anion perturbed by the substitution of an oxygen atom at the exocyclic position and by aza-substitution in the ring. The charge distributions in the non-bonding molecular orbital (ψ_N) and the two lowest unoccupied π-orbitals (ψ_I and ψ_{II}) of the benzyl anion are given

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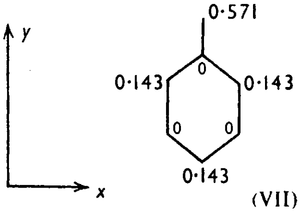
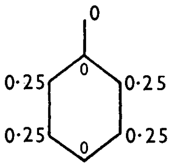
[3] Albert and Phillips, *J.*, 1956, 1294.

in (VII), (VIII), and (IX), respectively. The energies of the orbitals ψ_N, ψ_I, and ψ_{II} are



(VII)



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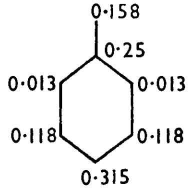

(IX)

0, β, and $1{\cdot}26\beta$ respectively, where β is the carbon–carbon resonance integral. Electronic transitions from ψ_N (VII) to ψ_I (VIII) and to ψ_{II} (IX) are allowed with transition energies of β and $1{\cdot}26\beta$, respectively, and with transition moments along the x and y axes of (VII), respectively. For absorption in the 300-mμ region, the theoretical oscillator strength of the first transition, $\psi_N \longrightarrow \psi_I$, is 0·15, and of the second transition, $\psi_N \longrightarrow \psi_{II}$, is 0·84, the ratio of the two oscillator strengths being 5·5.

On substitution of an oxygen atom at the exocyclic position and aza-substitution in the ring of the benzyl anion, the energies of the orbitals ψ_N, ψ_I, and ψ_{II} are changed, according to first-order perturbation theory, by an amount proportional to the fractional charges at the positions of substitution, given in (VII), (VIII), and (IX), respectively, and to the increment in the Coulomb integral of the substituent relative to carbon ($\Delta\alpha$). Thus, the energies of the first electronic transition, $\psi_N \longrightarrow \psi_I$, in the enol, cation, anion, and zwitterion form of 3-hydroxypyridine, E_{IE}, E_{IC}, E_{IA}, and E_{IZ} respectively, are

$$E_{IE} = \beta + 0{\cdot}571\Delta\alpha_{OH} - 0{\cdot}25\Delta\alpha_{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$E_{IC} = \beta + 0{\cdot}571\Delta\alpha_{OH} - 0{\cdot}25\Delta\alpha_{NH^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$E_{IA} = \beta + 0{\cdot}571\Delta\alpha_{O^-} - 0{\cdot}25\Delta\alpha_{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$E_{IZ} = \beta + 0{\cdot}571\Delta\alpha_{O^-} - 0{\cdot}25\Delta\alpha_{NH^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\Delta\alpha_{OH}$ and $\Delta\alpha_{O^-}$ are the increments in the Coulomb integrals of a neutral and a negatively-charged oxygen atom, respectively, relative to carbon, and $\Delta\alpha_N$ and $\Delta\alpha_{NH^+}$ are the corresponding increments of a neutral and a positively charged nitrogen atom, respectively. From the free energies of ionisation of the hydroxy-azines it has been found [4] that $\Delta\alpha_N = 0{\cdot}6\beta$ and $\Delta\alpha_{NH^+} = 2{\cdot}5\beta$, whilst it is probable that $\Delta\alpha_{OH} \simeq \beta$, and $\Delta\alpha_{O^-} \simeq 0$. The precise values are not very significant, but it is important that $\Delta\alpha_{NH^+} > \Delta\alpha_N$ and that $\Delta\alpha_{OH} > \Delta\alpha_{O^-}$. These inequalities show (equations 1—4) that the energies of the first electronic transition, $\psi_N \longrightarrow \psi_I$, in the charged species of 3-hydroxypyridine follow the order $E_{IE} > E_{IC} > E_{IA} > E_{IZ}$ (Fig. 4), as is found experimentally (Fig. 1; Table 1). The observed transition energies are not obtained quantitatively from eqns. (1)—(4) and the given Coulomb parameters, and, conversely, consistent values for the differences ($\Delta\alpha_{NH^+} - \Delta\alpha_N$) and $\Delta\alpha_{OH} - \Delta\alpha_{O^-}$) cannot be derived from the observed energies and eqns. (1)—(4), or the analogous equations for the other hydroxy-azines. Eqns. (1)—(4) and their analogues are ill-conditioned, owing to the very approximate nature of the theory employed, but they indicate correctly the qualitative order of the transition energies in the charged species of the various hydroxy-azines.

The energy of the second electronic transition, $\psi_N \longrightarrow \psi_{II}$, in a given charged form of 3-hydroxypyridine, E_{II}, is given by

$$E_{II} = 1{\cdot}26\beta + 0{\cdot}413\Delta\alpha_{o} - 0{\cdot}118\Delta\alpha_{n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $\Delta\alpha_o$ is either $\Delta\alpha_{OH}$ or $\Delta\alpha_{O^-}$, and $\Delta\alpha_n$ is either $\Delta\alpha_N$ or $\Delta\alpha_{NH^+}$, depending upon the charged species considered. Eqn. (5) indicates that the energies of the second transition

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[4] Mason, *J.*, 1958, 674.

in the charged forms of 3-hydroxypyridine should follow the same order as those of the first transition, though the differences in transition energy between one charged species and another should be smaller (Fig. 4), as is found (Fig. 1; Table 1).

In 2-hydroxypyridine the energies of the first, $\psi_N \longrightarrow \psi_I$, and the second, $\psi_N \longrightarrow \psi_{II}$, electronic transitions, E_I and E_{II}, respectively, are given by

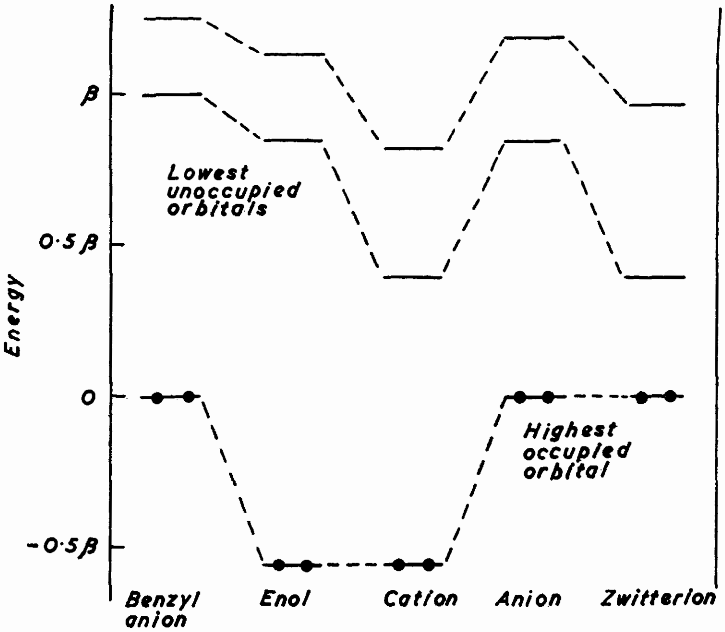
$$E_I = \beta + 0{\cdot}571\Delta\alpha_o - 0{\cdot}107\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$E_{II} = 1{\cdot}26\beta + 0{\cdot}413\Delta\alpha_o + 0{\cdot}130\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The charged species of 2-hydroxypyridine should have energies for the first transition, from eqn. (6), lying in the sequence $E_{IE} > E_{IC} > E_{IA} > E_{IZ}$, and for the second transition, from eqn. (7), in the order $E_{IIC} > E_{IIE} > E_{IIZ} > E_{IIA}$, whilst the spectrum of a given charged form should be displaced as a whole to shorter wavelengths relative to that of the corresponding charged species of 3-hydroxypyridine. The observed absorption bands follow these orders, though the enolic form, as represented by 2-methoxypyridine in neutral solution, may be anomalous since a second absorption maximum at short wavelengths could not be measured (Table 1).

FIG. 4. *The energies of the highest occupied and the lowest unoccupied orbitals of the enol, cation, anion, and zwitterion of* 3-*hydroxypyridine derived by the first-order perturbation of the corresponding orbitals of the benzyl anion.*



In 4-hydroxypyridine the energies E_I and E_{II} of the electronic transitions, $\psi_N \longrightarrow \psi_I$ and $\psi_N \longrightarrow \psi_{II}$ respectively, are given by

$$E_I = \beta + 0{\cdot}571\Delta\alpha_o + 0{\cdot}143\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

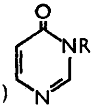
and

$$E_{II} = 1{\cdot}26\beta + 0{\cdot}413\Delta\alpha_o - 0{\cdot}172\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

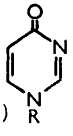
The energy of the second transition becomes less than that of the first if $\Delta\alpha_n > 0{\cdot}7\beta$ when the oxygen atom is negatively charged, since $\Delta\alpha_{O^-} \simeq 0$, and at a still smaller value of $\Delta\alpha_n$ when the oxygen atom is neutral. In the cationic and the zwitterionic form of 4-hydroxypyridine the nitrogen atom is positively charged, and as $\Delta\alpha_{NH^+} = 2{\cdot}5\beta$, the single high-intensity absorption band of these species is due to the second transition, $\psi_N \longrightarrow \psi_{II}$. The nitrogen atom is formally neutral in the enolic and anionic form, and since $\Delta\alpha_N = 0{\cdot}6\beta$, the energy of the first transition should be slightly less than that of the second, thus accounting for the low-intensity shoulders on the long-wavelength side of the main high-intensity band in the spectra of these species (Fig. 2; Table 1). The orders of the energies of these transitions, $E_{IE} > E_{IA}$ and $E_{IIE} > E_{IIC} > E_{IIA} > E_{IIZ}$, agree with the positions of the shoulders and of the main bands, respectively (Table 1). For a given charged form the shoulder should lie (eqns. 1—9) at a shorter wavelength and the main absorption band at a longer wavelength than the bands due to the first and the second transition respectively in the spectra of the corresponding charged species of either 2- or 3-hydroxypyridine, as is observed (Table 1).

In the electronic spectrum of the benzyl anion the intensity of the second transition, $\psi_N \longrightarrow \psi_{II}$, should be some 5·5 times greater than that of the first transition, $\psi_N \longrightarrow \psi_I$, and to a first approximation the intensity ratio should be the same in the spectra of the hydroxy-derivatives of the monocyclic azines. Apart from the cationic forms of 2- and 3-hydroxypyridine, the short wavelength absorption bands of the hydroxy-azines studied are more intense than the long wavelength bands, though the ratio of the intensities is generally less than the theoretical value of 5·5 (Table 1). Aza-substitution of a ring position in the benzyl anion has the effect of distorting the orbitals, ψ_N, ψ_I, and ψ_{II}. In particular charge is drawn to the position of the nitrogen atom in the orbital ψ_N from other positions. Thus, in 3-hydroxypyridine charge is drawn from the 2-, 4-, 6-, and exocyclic positions to, the nitrogen atom in orbital ψ_N, with the result that an electronic transition to orbital ψ_I is increased and to orbital ψ_{II} is decreased in intensity. A similar intensity change should occur in 2-hydroxypyridine, and the changes should be even more pronounced in the zwitterion and, more particularly, the cation form of these compounds where the nitrogen atoms are positively charged, as is observed (Table 1) With 4-hydroxypyridine the attraction of charge to the nitrogen atom in the ground state should have the contrary effect of diminishing the intensity of the first transition, $\psi_N \longrightarrow \psi_I$, and enhancing that of the second, $\psi_N \longrightarrow \psi_{II}$. Appearing as a shoulder in the spectrum, the first transition is of uncertain intensity, but the extinction coefficient at the point of inflection (Fig. 2) being taken as an approximate measure, which represents an upper value, it is found that the ratio of the intensities of the second to the first transition in 4-hydroxypyridine is the highest of those for all the hydroxy-azines studied, exceeding the theoretical value of 5·5 in the case of the anionic form (Table).

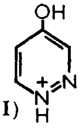
The interpretation of the electronic spectra of the hydroxy-diazines is complicated by the possible existence, in general, of two zwitterionic and two cationic forms of these compounds. There is a unique zwitterionic form of 2- and of 5-hydroxypyrimidine by symmetry, but the 4-isomer has the two zwitterionic or amide forms (X; R = H) and (XI; R = H) which co-exit in the ratio of about 2 : 1 in neutral aqueous solution.[4,5] In



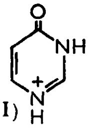
(X)



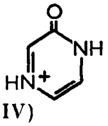
(XI)



(XII)



(XIII)



(XIV)

3- and 4-hydroxypyridazine and 2-hydroxypyrazine the predominant zwitterion or amide species is formed by the bonding of the tautomeric hydrogen atom to the ring nitrogen atom α or γ to it.[1] The cations of the hydroxypyridazines are formed by the protonation of the oxygen atom of the zwitterion [4] (*e.g.* XII), but in those of 2- and 4-hydroxypyrimidine a nitrogen and not the oxygen atom is protonated [5] (*e.g.* XIII). The cation of 2-hydroxypyrazine (XIV) resembles the latter type, since its spectrum resembles that of the *N*-methyl but not that of the *O*-methyl derivatives (Fig. 3).

[5] Brown, Hoerger, and Mason, *J.*, 1955, 211.

The energies E_{I} and E_{II}, of the first two transitions in the spectra of the anionic and enolic form of 2-hydroxypyrazine are given by

$$E_{\text{I}} = \beta + 0{\cdot}571\Delta\alpha_{o} - 0{\cdot}357\Delta\alpha_{\text{N}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$E_{\text{II}} = 1{\cdot}26\beta + 0{\cdot}413\Delta\alpha_{o} + 0{\cdot}012\Delta\alpha_{\text{N}} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

whilst for the zwitterion the corresponding expressions are

$$E_{\text{I}} = \beta + 0{\cdot}571\Delta\alpha_{\text{O}^-} - 0{\cdot}107\Delta\alpha_{\text{NH}^+} - 0{\cdot}25\Delta\alpha_{\text{N}} \quad . \quad . \quad . \quad . \quad (12)$$

and

$$E_{\text{II}} = 1{\cdot}26\beta + 0{\cdot}413\Delta\alpha_{\text{O}^-} + 0{\cdot}130\Delta\alpha_{\text{NH}^+} - 0{\cdot}118\Delta\alpha_{\text{N}} \quad . \quad . \quad . \quad (13)$$

and for the cation (XIV)

$$E_{\text{I}} = \beta + 0{\cdot}571\Delta\alpha_{\text{O}^-} - 0{\cdot}357\Delta\alpha_{\text{NH}^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$E_{\text{II}} = 1{\cdot}26\beta + 0{\cdot}413\Delta\alpha_{\text{O}^-} + 0{\cdot}012\Delta\alpha_{\text{NH}^+} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Eqns. (10)—(15) indicate that the energies of the first transition in the spectra of the charged species of 2-hydroxypyrazine should follow the sequence, $E_{\text{IE}} > E_{\text{IA}} > E_{\text{IZ}} > E_{\text{IC}}$, whilst the energies of the second transition should lie in the order $E_{\text{IIE}} > E_{\text{IIZ}} > E_{\text{IIC}} > E_{\text{IIA}}$, as is found experimentally (Table 1).

Similar expressions can be derived for the energies of the first two transitions in the spectra of the other hydroxy-diazines. For the case of 3-hydroxypyridazine the predicted sequences of transition energies are $E_{\text{IE}} > E_{\text{IC}} > E_{\text{IA}} > E_{\text{IZ}}$ and $E_{\text{IIC}} > E_{\text{IIE}} > E_{\text{IIZ}} > E_{\text{IIA}}$. These orders are observed, apart from the first absorption band of the zwitterion which lies at a shorter wavelength than that of the anion, and the second band of the enol, as represented by 3-methoxypyridazine in neutral solution, which was not measurable (Table 1). The patterns of the absorption bands in the spectra of the charged species of 4-hydroxypyridazine and 4-hydroxypyridine are very similar (Table 1). The equations for the transition energies in the case of the former compound are

$$E_{\text{I}} = \beta + 0{\cdot}571\Delta\alpha_{o} + 0{\cdot}143\Delta\alpha_{n} - 0{\cdot}25\Delta\alpha_{\text{N}} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and

$$E_{\text{II}} = 1{\cdot}26\beta + 0{\cdot}413\Delta\alpha_{o} - 0{\cdot}172\Delta\alpha_{n} - 0{\cdot}118\Delta\alpha_{\text{N}} \quad . \quad . \quad . \quad . \quad (17)$$

As in the case of 4-hydroxypyridine the first transition is perceptible only in the spectra of the enolic and anionic species of 4-hydroxypyridazine, but the additional nitrogen atom in the latter lowers the energy of the first transition more than that of the second (eqns. 8, 9, 16, 17), so that the absorption due to the first transition appears as a discrete band (Table 1), and not just as a shoulder on the side of the main absorption band (Fig. 2). The spectrum of a given charged form of 4-hydroxypyridazine should be displaced to longer wavelengths relative to that of the corresponding species of 4-hydroxypyridine (eqns. 8, 9, 16, 17), and the sequences of transition energies should be the same in both compounds, as is observed (Table 1).

The predicted orders of the transition energies in the case of 2-hydroxypyrimidine are $E_{\text{IE}} > E_{\text{IA}} > E_{\text{IZ}} > E_{\text{IC}}$ and $E_{\text{IIC}} > E_{\text{IIE}} > E_{\text{IIZ}} > E_{\text{IIA}}$. The absorption maxima due to the second transition in the enol and the cation could not be measured, but otherwise these orders are supported by the experimental data (Table 1). In neutral aqueous solution 4-hydroxypyrimidine exists in two zwitterionic or amide forms [4,5] which can be studied separately as the respective derivatives, 1- and 3-methyl-4-pyrimidone, (XI; R = Me) and (X; R = Me). The expected sequences of transition energies are $E_{\text{IE}} > E_{\text{I(XI)}} > E_{\text{IC}} > E_{\text{IA}} > E_{\text{I(X)}}$ and $E_{\text{IIE}} > E_{\text{II(X)}} > E_{\text{IIA}} > E_{\text{IIC}} > E_{\text{II(XI)}}$. The band due to the first transition in 1-methyl-4-pyrimidone (XI; R = Me) is overlaid by the high-intensity absorption due to the second transition,[5] but apart from this the first sequence is found experimentally (Table 1). However, the data show that the transition energies of the anion and the cation form lie in the order contrary to that expected from the second sequence, which is otherwise followed (Table 1). The spectrum of a given charged form of 5-hydroxypyrimidine should be displaced to longer wavelengths relative to that of the corresponding species of 3-hydroxypyridine, and the sequences of the transition energies should be the same in both compounds, as is found experimentally (Table 1).

The molecular-orbital theory of the light absorption of the hydroxy-azines is consistent with the wavelength shifts observed in the spectra of the zwitterionic and enolic forms of the compounds on changing from an aqueous to a non-polar solvent. In the ground state, according to the present approximation, the nitrogen atom of the zwitterion (V; R = Me) carries a unit positive charge, and the oxygen atom 0·571 of a negative charge, the remaining negative charge being distributed over the carbon atoms α and γ to the carbon carrying the oxygen atom (VII). In the first excited state the positive charge on the nitrogen atom is reduced to 0·75, and the oxygen atom is neutral, the 0·75 of a negative charge being shared between the carbon atoms α and β to that carrying the oxygen (VIII). The first excited state should be less polar than the ground state, therefore, in conformity with the large red shift (3000 cm.$^{-1}$) in the first absorption band of the species (V; R = Me) observed on passing from aqueous to dioxan solution (Table 2).

The ground state of 1-methyl-2-pyridone is less polar than that of the 3-isomer, the nitrogen atom carrying 0·857 of a positive charge, and the corresponding negative charge being distributed over the oxygen atom and the carbon atoms α and γ to the carbon atom carrying it (VII). However, the charge distributions in the first excited state of 1-methyl-2-pyridone and the 3-isomer are the same, namely, 0·75 of a positive charge on the nitrogen atom with the corresponding negative charge shared between the carbon atoms α and β to the carbon atoms carrying the oxygen atom (VIII). The decrease in polarity during the transition, $\psi_N \longrightarrow \psi_I$, should be smaller in 1-methyl-2-pyridone than in the 3-isomer, which is consistent with the smaller red shift (1000 cm.$^{-1}$) in the first absorption band of 1-methyl-2-pyridone found on changing from aqueous to *cyclo*hexane solution (Table 2). The decrease in the polarity of 1-methyl-4-pyridone during the transition $\psi_N \longrightarrow \psi_{II}$ involving a change in charge distribution from (VII) to (IX), should also be smaller than that of the 3-isomer during the transition $\psi_N \longrightarrow \psi_I$ in conformity with the smaller red shift of 1000 cm.$^{-1}$ (Table 2).

The enolic forms of the hydroxy-azines should be more polar in the excited state than in the ground state, and the absorption bands of this species might be expected to show blue shifts on changing from aqueous to non-polar solvents. The methoxy-azines, with fixed enolic forms, give only small shifts, which are both towards the red and the blue region, on passing from aqueous to *cyclo*hexane solution (Table 1; Fig. 3). In the methoxy-azines it is probable that the stabilisation of the polar excited state by solvation in aqueous solution is offset by the stabilisation of the ground state, owing to hydrogen-bonding with the water molecules. In the present view it is the lone-pair electrons of the oxygen atom which are active in the first two electronic transitions of the hydroxyazines, and the energy of these electrons, which readily engage in hydrogen-bonding, should be particularly sensitive to the nature of the solvent employed.

EXPERIMENTAL

Materials.—The pyridazine derivatives were kindly supplied by Drs. K. Eichenberger, R. Rometsch, and J. Druey,[6] and 5-hydroxypyrimidine by Dr. J. F. W. McOmie. 2- and 4-Hydroxypyrimidine and their *N*- and *O*-methyl derivatives were prepared as in Brown, Hoerger, and Mason,[5] and the remaining compounds as in Albert and Phillips.[3]

Spectra.—These were measured with Hilger Uvispek Quartz Spectrophotometers, the solvents listed in Tables 1 and 2 being used.

The author is indebted to the Australian National University for a Research Fellowship and to the Royal Society for the provision of a spectrophotometer.

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[6] Eichenberger, Rometsch, and Druey, *Helv. Chim. Acta*, 1954, **37**, 1298; 1956, **39**, 1755.