**259.** *The Electronic Spectra of* N-*Heteroaromatic Systems. Part VII.* Analogues of the Cinnamoyl Anion.*

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The ultraviolet absorption spectra have been measured for the anionic, cationic, and neutral forms of the pyridine-aldoximes and of the zwitterionic form of the 1-methochloride derivatives in aqueous solutions. The results and spectroscopic data for the various ionic species of the acetamidopyridines are interpreted in terms of a cinnamoyl anion model. The limitations of the model indicate that conjugation between the substituent and the pyridine nucleus is restricted in the ground state.

THE electronic spectra of ionic species of monocyclic N-heteroaromatic amines, and hydroxy- and mercapto-compounds which possess a p-orbital on the exocyclic atom conjugated with the nucleus have been interpreted in terms of a perturbed benzyl anion model.[1] In order to examine the generality of the method of interpretation, the electronic spectra of the four charged species of the pyridine-aldoximes, *e.g.*, the neutral oxime (I), the cation (II), the anion (III), and the zwitterionic form (IV), in aqueous solution have been
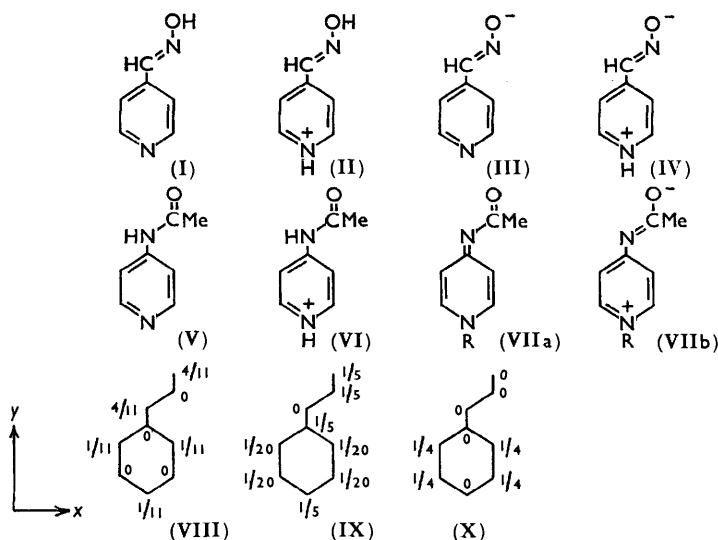
measured, these compounds being analogues of the cinnamoyl anion with an exocyclic group of three conjugated atoms. The results are recorded in the Figures and in the Table, together with spectroscopic data [2] for the three accessible ionic species of the isoconjugate acetamidopyridines, *e.g.*, the neutral amide (V), the cation (VI), and the acetylimine (VIIa) or its zwitterionic form (VIIb).

As in the case of the pyridine derivatives with a monatomic conjugated substituent,[1] the long-wave bands in the spectra lie at wavelengths in the general order, zwitterion > anion > cation > neutral form; and a similar order holds for the second absorption band with the exception of the neutral and cationic forms of the 2-substituted compounds. Further, for a particular charged species and a given position of substitution, the pyridinealdoximes absorb at a longer wavelength than the corresponding acetamidopyridines, the

* Part VI, *J.*, 1960, 219.

[1] Mason, *J.*, 1959, 1253; 1960, 219.

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

same generalisation holding for the second absorption band in the spectra of the 2- and the 3-substituted compounds (Table). For a given substituent in a particular ionic form, the wavelength maxima of the absorption bands depend less on the position of the substituent in the pyridine nucleus in the aldoxime and acetamido-series (Table) than in the pyridine derivatives with conjugated monatomic substituents,[1] the variation of band position with position of substitution being relatively small and irregular. However, there are trends in the aldoxime and acetamido-series, the wavelength of maximum absorption depending upon the position of the substituent in the general order 2- ⩾ 3- > 4-pyridine, for the long-wave absorption band, and 3- > 2- > 4-pyridine for the second band.

The electronic absorption spectra in aqueous solution of the neutral (N), *cationic* (C), *anionic* (A), *and zwitterionic* (Z) *forms of the pyridine-aldoximes and acetamidopyridines.* (Values in italics refer to shoulders.)

Compound	pK_a [b]	Solvent	Species	$\lambda_{max.}$ (mμ) [b]	$\varepsilon_{max.}$ [b]
Pyridine-2-aldoxime	3·63	pH 7	N	277; 239	7,550; 10,500
	10·14	pH 1	C	294; 238; 206	11,600; 8,100; 12,300
		pH 13	A	289; *270*	15,300; *12,000*
-1-methochloride	8·00	pH 11	Z	335; *285*; 220	18,400; *5,300*; 5,100
Pyridine-3-aldoxime	4·10	pH 7	N	*275*; 243	*4,700*; 11,600
	10·36	pH 2	C	*285*; 250; 220	*4,600*; 8,800; 11,900
		pH 13	A	*295*; 274	6,500; 14,000
-2-methochloride	9·22	pH 12	Z	*335*; 288; 242	4,200; 14,700; 12,900
Pyridine-4-aldoxime	4·77	pH 7	N	246; <200	12,600; >14,000
	9·99	pH 2	C	275; <200	15,500; >10,000
		pH 13	A	289; 225	18,000; 5,900
-1-methochloride	8·57	pH 11	Z	336; 239	22,000; 6,000
2-Acetamidopyridine [a]	4·09	pH 9·7	N	273; 231	7,000; 10,000
		pH 0	C	291; 229	11,800; 12,200
2-Acetylimino-1,2-dihydro-1-methylpyridine [a]	7·12	pH 14	Z	311; 265	7,400; 5,400
3-Acetamidopyridine [a]	4·46	pH 9·7	N	271; 236	3,100; 9,800
		pH 0	C	287; 247; 212	5,300; 11,000; 19,000
Anhydro-3-acetamido-1-methyl-pyridinium hydroxide [a]	11	pH 14	Z	*312*; 273	*3,500*; 8,900
4-Acetamidopyridine [a]	5·87	pH 9·7	N	244	17,700
		pH 0	C	266; 206	20,000; 12,300
4-Acetylimino-1,4-dihydro-1-methyl-pyridine [a]	11·03	pH 14	Z	312; 269	18,000; 5,800

[a] Data quoted from Jones and Katritzky, *J.*, 1959, 1317. [b] The ionization constants and spectra of the neutral and zwitterionic forms of the aldoximes are quoted from Mason, *J.*, 1960, 22.

Some of the general features may be explained on the assumption that the π-electron system of these compounds is similar to that of the cinnamoyl anion. In the ground state the lone-pair electrons of the exocyclic nitrogen atom in the acetamido-pyridines or one of the lone-pairs of the oxygen atom in the aldoximes occupy an orbital derived from the non-bonding molecular orbital of the cinnamoyl anion, ψ_N, which has the one-electron charge distribution (VIII). On the absorption of light, one of the delocalised lone-pair electrons is promoted to a similarly derived unoccupied molecular orbital. The two lowest unoccupied molecular orbitals of the cinnamoyl anion are a degenerate pair, with an energy equal to that of the carbon–carbon resonance integral, β, above the zero energy of the non-bonding molecular orbital. Having the same energy and symmetry (A' in C_s), the configurations arising from the promotion of an electron from the non-bonding molecular orbital to the two lowest unoccupied orbitals interact strongly. However, the configuration interaction is minimal if the two lowest unoccupied orbitals, ψ_I and ψ_{II}, are given the forms represented by the one-electron charge distributions (IX) and (X) respectively, these forms approximating to different symmetries (B_2 and A_2, respectively, in C_{2v}), which would obtain exactly if the exocyclic atoms had a linear conformation. These forms of the lowest unoccupied orbitals of the cinnamoyl anion may be adopted for discussion with neglect of configuration interaction, with the additional justification that

the degeneracy of the orbitals is removed by hetero-substitution in the acetamido-pyridines and pyridine-aldoximes. For the *trans*-conformation of the cinnamoyl anion, corresponding to the stable *syn*-form of the aldoximes, the transition $\psi_N \longrightarrow \psi_I$ has a theoretical dipole length of 2·05 Å orientated nearly along the *y*-axis of (VIII) (the *y*-component has a length of 2·00 Å), and the transition $\psi_N \longrightarrow \psi_{II}$ has a dipole exactly along the *x*-axis of (VIII) with a length of 0·517 Å.

In the acetamidopyridines and pyridine-aldoximes the energies of the orbitals, ψ_N, ψ_I, and ψ_{II}, are lowered in the first order of perturbation theory by an amount equal to the

FIG. 1. *Ultraviolet absorption spectra of the* ——— *neutral,* . . . . . *cationic, and* ——— *anionic forms of pyridine-2-aldoxime, and of the* —·—·— *zwitterionic species of the 1-methochloride.*
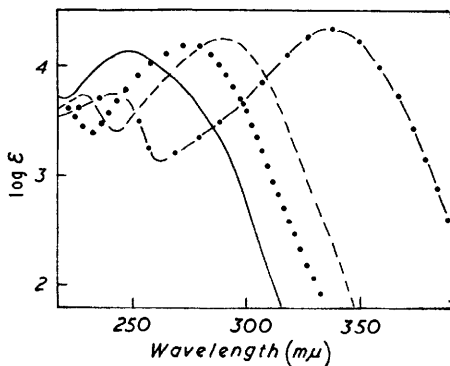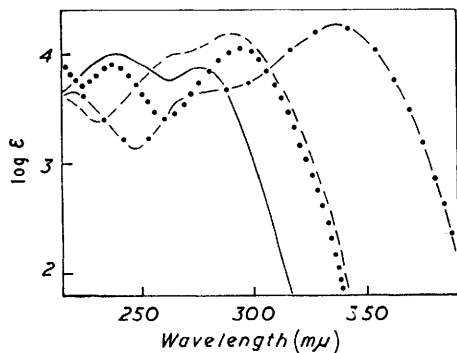
FIG. 2. *Ultraviolet absorption spectra of the* ——— *neutral,* . . . . . *cationic, and* ——— *anionic forms of pyridine-3-aldoxime, and of the* —·—·— *zwitterionic species of the 1-methochloride.*
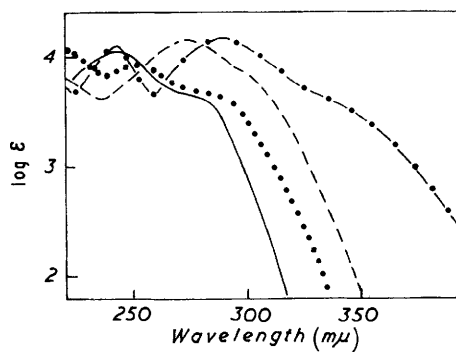
FIG. 3. *Ultraviolet absorption spectra of the* ——— *neutral,* . . . . . *cationic, and* ——— *anionic forms of pyridine-4-aldoxime, and of the* —·—·— *zwitterionic species of the 1-methochloride.*

product of the Coulomb integral increment of each hetero-atom relative to carbon, $\Delta\alpha$, and the charge density at the position of substitution in (VIII), (IX), and (X) respectively. Equations may be written for the energies of the transitions, $\psi_N \longrightarrow \psi_I$ and $\psi_N \longrightarrow \psi_{II}$, E_I and E_{II} respectively; *e.g.*, for the case of pyridine-4-aldoxime

$$E_I = \beta - 0 \cdot 20\Delta\alpha_N + 0 \cdot 16\Delta\alpha_O - 0 \cdot 10\Delta\alpha_n \quad . \quad . \quad . \quad . \quad (1)$$

$$E_{II} = \beta + 0 \cdot 36\Delta\alpha_O + 0 \cdot 09\Delta\alpha_n \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $\Delta\alpha_O$ and $\Delta\alpha_n$ refer to the Coulomb integral increments of either neutral ($\Delta\alpha_O$) or negatively charged oxygen ($\Delta\alpha_{O^-}$), and of neutral ($\Delta\alpha_N$) or positively charged nitrogen ($\Delta\alpha_{N^+}$), respectively, depending on the particular ionic species of the compound. From

ground-state phenomena it has been found [3] for the trigonal nitrogen atom that $\Delta\alpha_N = 0.6\beta$ and $\Delta\alpha_{N^+} = 2.5\beta$, whilst for oxygen it is probable [1] that $\Delta\alpha_O \simeq \beta$ and $\Delta\alpha_{O^-} \simeq 0$.

Equations (1) and (2) and their analogues indicate that for a particular ionic species and a given position of substitution the transition energies of an acetamidopyridine, E_I and E_{II}, should be larger than those of the corresponding pyridine-aldoxime by $0.56\Delta\alpha_N$ and $0.36\Delta\alpha_N$ respectively. In the aldoximes the exocyclic nitrogen atom is placed at an uncharged position in the non-bonding molecular orbital of the cinnamoyl anion (VIII), whilst the corresponding nitrogen atom in the acetamidopyridines occupies a position carrying a considerable charge. The highest occupied orbital thus lies at a lower energy in the acetamidopyridines than in the pyridine-aldoximes, and transitions from that orbital should, in general, require a larger energy, resulting in absorption at shorter wavelengths in the former than in the latter compounds. Experimentally the acetamido-pyridines are found to absorb generally at shorter wavelengths than the corresponding aldoximes: of the eighteen pairs of comparable bands, only the shorter-wavelength band of the cationic and zwitterionic forms of the 4-subsituted compounds are exceptional (Table).

The theoretical transition dipole lengths for the cinnamoyl anion suggest that in the spectra of the acetamidopyridines and pyridine-aldoximes the more intense of the first two absorption bands should be due to the transition, $\psi_N \longrightarrow \psi_I$, and the weaker to the transition, $\psi_N \longrightarrow \psi_{II}$. With these assignments, equation (1) and its analogues suggest that for a given compound the wavelengths of maximum absorption should follow the order zwitterion > anion, and cation > neutral form, for the long-wave band of the 3- and 4-substituted derivatives, and the cationic and neutral species of the 2-isomers; also for the short-wave band of the 3-substituted derivatives, and the anion and zwitterion forms of the 2-isomers. Such orders are observed experimentally without exception (Table). Similarly, equation (2) and its analogues indicate the converse wavelength orders anion > zwitterion, and neutral form > cation, the former for the long-wave band and the latter for the short-wave band of the 2-substituted compounds, and both for the short-wave band of the 4-isomers. Only one of these orders is observed experimentally, *i.e.*, there is a hypsochromic shift of the short-wave band in the spectra of 2-acetamido-pyridine and pyridine-2-aldoxime on cation formation (Table, Fig. 1).

The general lack of experimental support for equation (2) and its analogues points to a particular shortcoming of the cinnamoyl anion model for the electronic properties of the acetamido-pyridines and pyridine-aldoximes, that is, the assumption of complete conjugation between the substituent and the pyridine nucleus in the ground state. The protonation of the nuclear nitrogen atom in a pyridine derivative brings about a hypso-chromic shift of an absorption band only if the charge density at the position of the nitrogen atom is larger in the ground- than in the excited-state orbital. The charge densities at nuclear positions in the ground-state orbital of the acetamidopyridines and pyridine-aldoximes, analogous to (VIII), are due to the delocalisation of lone-pair electrons from an exocyclic atom, and if conjugation between the nucleus and substituent is restricted, the nuclear charge densities are correspondingly reduced. Comparison of the ionisation and tautomeric equilibrium constants of the acetamido-pyridines [2] and the pyridine-aldoximes [4] with those of the pyridine amines and hydroxy-compounds, respectively, has shown [2,4] that conjugation between the nucleus and the substituent is less complete in the former than in the latter series, and that the cinnamoyl anion is a less apposite model than the benzyl anion for the interpretation of the ground-state properties of the corresponding hetero-analogues. In the absence of conjugation between the nucleus and the substituent, the highest occupied orbitals in the acetamidopyridines or in the pyridine-aldoximes should have approximately the same energy, and corresponding transitions from those orbitals should show only small variations in energy. The spectral shifts observed on changing the position of the substituent in the acetamidopyridines or

[3] Mason, *J.*, 1958, 674.
[4] Mason, *J.*, 1960, 22.

pyridine-aldoximes are generally smaller (1—30 mμ) than those found in the spectra of the corresponding amino- and hydroxy-pyridines[1] (5—60 mμ), though smaller shifts would be expected, complete conjugation being assumed between the nucleus and the substituent, owing to the different π-electron systems of the corresponding carbanions. For corresponding orbitals, the one-electron charge densities, in general, vary from one position to another less in the cinnamoyl than in the benzyl anion, so that the energies required for the transition of an electron from one orbital to another should show generally a smaller variation with the position of the substituent in the hetero-analogues of the cinnamoyl than in those of the benzyl anion.

Experimental.—Absorption spectra were measured with a Hilger Uvispek Quartz Spectrophotometer, aqueous solutions being used with the pH values listed in the Table. Materials were as in ref. 4.

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