716. *The Electronic Spectra of Some Monosubstituted Pyridines and Pyridinium Ions.*

By E. Spinner.

The electronic spectra of the monomethyl-, monochloro-, monobromo-, and monocyano-pyridines and their cations in the range 208—300 mμ are reported and discussed. Some conclusions previously reached concerning the structures of certain pyridine ions are examined.

Complete near-ultraviolet spectra are available for pyridines and pyridinium ions containing the substituents NH_2,[1,2] O^-,[3] S^-,[4] SMe,[4] and OMe,[3] the first four of which exert large spectral effects, but for substituents exerting small or intermediate-sized spectral effects, such as alkyl,[5] halogen,[6-8] and cyano,[9] data are more limited and few extend as far as the *K*-[10] (*E*-,[11] *p*-,[12]) band.* It is known that spectral substituent effects in pyridine and the pyridinium ion do not always parallel those found in substituted benzenes, *e.g.*, the methyl group in 4-picoline and its cation shifts the *B*-[11] (α-[12]) band to shorter wavelengths.[5] For the 4-methoxypyridinium ion an unexpected cation structure has been inferred from the ultraviolet spectrum.[13] A fuller study of pyridinium ions containing substituents with intermediate spectral effects, and a closer comparison between the spectra of substituted benzene, pyridine, and pyridinium ions seemed indicated.

Experimental.—Materials. The methyl-, chloro-, bromo-, and cyano-pyridines were purified commercial specimens, the methyl, 4-chloro-,[14] and 4-bromo-derivatives [14] being purified both by fractional distillation (the last two compounds at 70°/40 mm. and 89°/30 mm., respectively) and fractional freezing. 4-Methoxypyridine had b. p. 107°/50 mm. and m. p. 4°.

4-Iodopyridine was obtained by a modification of the method of Haitinger and Lieben.[15] Heating of 4-chloropyridine (2 g.) and hydriodic acid (*d* 1·94) (10 ml.) in a sealed tube at 145° for 18 hr., followed by extraction of the precipitate obtained with boiling water (25 ml.) containing some sulphur dioxide, gave, on cooling of the extract to −5°, pure 4-iodopyridine hydriodide (1·2 g., 20%). To this, in water (10 ml.) at 60°, were added sodium hydrogen carbonate (0·4 g.) and sodium sulphite (0·1 g.) in water (2 ml.). The (steam-volatile) precipitate of 4-iodopyridine was recrystallised from water at 60° containing some sodium hydrogen carbonate and sodium sulphite. The compound is stable for several weeks if kept beneath this recrystallisation liquor in a refrigerator, and for several days in the dark when dry. It had m. p. 93° (decomp.) (Found: C, 29·1; H, 1·8; N, 6·6. Calc. for C_5H_4IN: C, 29·3; H, 1·9; N, 6·8%).

Spectral examination. The substances were examined in aqueous solutions buffered at the appropriate pH values; all were stable under the conditions used. 4-Chloro-, 4-bromo-, and 4-iodo-pyridine were found (by spectroscopy) to have ionisation constants, in pK_a values, of 3·88 ± 0·04, 3·82 ± 0·04, and 4·06 ± 0·03, respectively (the author thanks Dr. D. D. Perrin

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* Several [10-12] band nomenclatures are in common use.

[1] Steck and Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397.
[2] Mason, *J.*, 1960, 219.
[3] Mason, *J.*, 1959, 1253.
[4] Albert and Barlin, *J.*, 1959, 2384.
[5] Andon, Cox, and Herington, *Trans. Faraday Soc.*, 1954, **50**, 918.
[6] Stephenson, *J. Chem. Phys.*, 1954, **22**, 1077.
[7] Brown and McDaniel, *J. Amer. Chem. Soc.*, 1955, **77**, 3752.
[8] Tsubomura, *J. Chem. Soc. Japan*, 1957, **78**, 293.
[9] Mason, *J.*, 1959, 1247.
[10] Burawoy, *J.*, 1939, 1177.
[11] Braude, *Ann. Reports*, 1945, **42**, 105.
[12] Clar, "Aromatische Kohlenwasserstoffe," Springer, Berlin, 2nd edn., 1952, p. 186; Mason, *Quart. Rev.*, 1961, **15**, 287.
[13] Tsubomura, *J. Chem. Phys.*, 1958, **28**, 355.
[14] Wibaut and Broekman, *Rec. Trav. chim.*, 1939, **58**, 885.
[15] Haitinger and Lieben, *Monatsh.*, 1885, **6**, 320.

and Mr. H. Satrapa for these determinations). The ionisation constants of the other compounds examined are known.[7,8,16] Spectra were determined with a Perkin-Elmer Spectracord model 4000 A, and peak intensities were checked with an Optica CF4 manual spectrophotometer. The wavelength at which the Spectracord slit width was 1 mm. (206—208 mμ) was taken to be the limit of the accessible spectrum.

DISCUSSION

All the substances examined show the *B*-band, which usually exhibits fine structure here even in aqueous solution, and most of them show the (one) *K*-band in the accessible spectral region (see Table). As is normally the case for disubstituted benzenes, there is no correlation between *B*- and *K*-band shifts. *meta*- and *ortho*-Disubstituted benzenes frequently show two[17] *K*-bands; if 3- and 2-substituted pyridines do give rise to a second *K*-band (which seems unlikely) it is below 210 mμ. Some generalisations that also embrace previous data[1-4] for saturated substituents with large effects follow.

K-*Bands*.—All substituents, in any position, seem to displace the *K*-band of pyridine and the pyridinium ion to longer wavelengths. For saturated substituents, $\lambda_{max.}$ increases in the order 2-X·C_5H_4N (by up to 5 mμ) < X·C_6H_5 < 3-X·C_5H_4N < 4-X·C_5H_4N, but for the electron-withdrawing unsaturated substituents CN and CHO[18] in the order 4-X·C_5H_4N < 3-X·C_5H_4N < 2-X·C_5H_4N < X·C_6H_5. Cation formation always displaces the band to longer wavelengths, only slightly so in 2-substitued pyridines, but much more strongly if there is a saturated substituent in the 3- and even more in the 4-position; in the last-mentioned case the shift on ionisation is roughly correlated with the bathochromic effect of X in neutral 4-X·C_5H_4N.

B-*Bands*.—In the 2- and 3-positions of pyridine and the pyridinium ion all substituents seem to displace the *B*-band to longer wavelengths. In the 4-position methyl and, even more so, methoxyl displace the band to shorter wavelengths (the latter, however, not by as much as a previous spectrum[3] at lower resolution seemed to indicate); halogen, NH_2,[2] and perhaps also O^-,[3] displace the band to slightly longer, and electron-withdrawing unsaturated substituents (CN, CHO,[18] NO_2[19]) to much longer wavelengths. For saturated substituents in pyridines and pyridinium ions, $\lambda_{max.}$ increases in the order[2,8] 4-X·C_5H_4N < X·C_6H_5 < 2-X·C_5H_4N $\leqslant$ 3-X·C_5H_4N, but for electron-withdrawing unsaturated substitutents the order is exactly the reverse. Cation formation in pyridines containing saturated substituents generally displaces the *B*-band to longer wavelengths in the 2- and, even more so, in the 3-position, whereas in 4-substituted pyridines, and also in 2- and 3-picoline, it results in small short-wavelength shifts. In the cyanopyridines, cation formation produces hardly any displacements.

Theoretical Explanations.—Several molecular-orbital treatments of the electronic spectra of pyridines containing saturated substituents have appeared. Mason's treatment,[2,3] in which the substituted pyridine is regarded as a perturbed benzyl anion, yields the correct sequence of transition energies between 2-, 3-, and 4-substituted compounds (unlike Murrell's charge-transfer model[20] which predicts[2] the reverse sequence for the *B*-band), but it does not seem able to predict the substituent effects on the *B*-band in 4-substituted pyridines. Chandra and Basu's calculations for the *B*-band in picolines[21] by perturbation theory give the result that in 4-, but not in 2- or 3-picoline, the inductive effect outweighs the hyperconjugation effect; this explanation of the hypsochromic effect of 4-methyl does not, however, account for the precisely analogous (though larger) hypsochromic effect of 4-methoxyl on the *B*-band. Favini and Simonetta's Pariser–Parr

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[16] Albert, "Heterocyclic Chemistry," Athlone Press, London, 1959, pp. 343—344.

[17] Forbes, *Canad. J. Chem.*, 1958, **36**, 1350; Dearden and Forbes, *ibid.*, p. 1362; Forbes and Leckie, *ibid.*, p. 1371.

[18] Nakamoto and Martell, *J. Amer. Chem. Soc.*, 1959, **81**, 5857.

[19] Gruber, *Canad. J. Chem.*, 1953, **31**, 1020.

[20] Murrell, *J.*, 1959, 296.

[21] Chandra and Basu, *J.*, 1959, 1623.

Ultraviolet absorption spectra (in water).

	$\lambda_{\text{max.}}$ * (mμ)							log ε						
X	*K*-Band			*B*-Band				*K*-Band			*B*-Band			
Substituted pyridines ($X\text{-}C_5H_4N$)														
H	198 †		*240*	*246*	251	257	263	3·9 †		*3·05*	*3·22*	3·37	3·42	3·25
2-Me	$<$206				*257*	262	268	$>$3·64				*3·48*	3·54	3·41
2-Cl	209				*258*	264	270	3·74				*3·43*	3·49	3·33
2-Br	212				*260*	265	*272*	3·78				*3·48*	3·55	*3·40*
2-CN	*212*	217						*3·89*	3·96					
	220	*224*		*253*	260	265	272	3·96	*3·86*		*3·40*	3·56	3·63	3·51
3-Me	$<$208			*251*	257	263	269	$>$3·60			*3·23*	3·39	3·45	3·30
3-Cl	211			*254*	261	267	274	3·77			*3·19*	3·37	3·46	3·29
3-Br	216				*262*	268	*274*	3·76				*3·35*	3·43	*3·31*
3-CN	*213*	217						*3·95*	4·00					
	221	226		*252*	259	265	272	*3·95*	3·84		*3·22*	3·36	3·42	3·30
4-Me	$<$207			*244*	*251*	255	262	$>$3·3			*3·08*	*3·23*	3·30	3·20
4-Cl	210		*240*	*246*	252	258	265	3·87		*2·94*	*3·10*	3·25	3·34	3·22
4-Br	219		*240*	*246*	252	258	265	3·60		*3·02*	*3·13*	3·27	3·36	3·20
4-I ‡	239				*255*	262	269	3·88				*3·62*	3·55	3·36
4-CN	208	211						3·95	4·05					
	216	220			*270*	276	*284*	3·98	4·01			*3·47*	3·50	*3·39*
4-MeO ‡	218			*240*	245	*250*	*258*	3·91			*3·00*	2·96	*2·86*	*2·30*
Substituted pyridinium ions ($X\text{-}C_5H_4NH^+$)														
H	200·5 §				*251*	256	*261*					*3·63*	3·70	*3·53*
2-Me	$<$206					262	*270*	$>$3·49					3·80	*3·61*
2-Cl	211					271		3·61					3·80	
2-Br	212					275		3·76					3·76	
2-CN	222				*261*	267	*273*	3·64				*3·81*	3·91	*3·83*
3-Me	209				*258*	262	*269*	3·50				*3·67*	3·70	*3·55*
3-Cl	215					270	*277*	3·60					3·68	*3·53*
3-Br	*221*					274		*3·68*					3·68	
3-CN	217	221	226		*259*	265	*271*	3·75	3·75	3·65		*3·59*	3·67	*3·56*
4-Me	217					252	*258*	3·71					3·65	*3·53*
4-Cl	230				*252*	257	*263*	3·96				*3·58*	3·68	*3·59*
4-Br ¶	244				*250*	*257*	*264*	4·03				*3·98*	*3·89*	*3·66*
4-I ‡¶	*279*			*249*	*256*	262	268	*3·79*			*3·75*	*3·87*	3·94	3·90
4-CN	222	*228*			*269*	276	*282*	3·92	*3·87*			*3·62*	3·70	*3·63*
4-MeO ‡	236				*240*	*245*	*251*	4·043				*4·04*	*3·93*	*3·65*
Substituted benzenes ($X\text{-}C_6H_5$) ‖														
H	203·5					254		3·87					2·31	
Me	206·5					261		3·85					2·35	
	209·5					263·5		3·87					2·28	
Br	210					261		3·90					2·28	
I **	227	232		*246*	251	256	261	4·10	4·08		*2·77*	2·83	2·85	2·79
CN	224					271		4·11					3·00	
MeO	217					269		3·81					3·17	

* Inflexions in italics. † Picket, Corning, McPherson, Wieder, and Semenow, reported in Weissberger, " The Technique of Organic Chemistry," Vol. IX, Interscience, Publ., Inc., New York, 1956, p. 666. ‡ For complete spectra of 2- and 3-methoxy- and -iodo-pyridine and their cations, see refs. 3 and 7. § Schubert, Craven, Minton, and Murphy, *Tetrahedron*, 1959, **5**, 194. ¶ The *B*-band is telescoped on top of the *K*-band. ‖ Data from Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714, except for iodobenzene which is quoted from Dearden and Forbes, *Canad. J. Chem.*, 1959, **37**, 1305. ** Solvent cyclohexane.

calculations for the *B*-band in the chloropyridine[22] spectra did not yield the correct sequence of shifts. No molecular-orbital treatment covering the whole range of substituents satisfactorily has been produced.

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[22] Favini and Simonetta, *Gazzetta*, 1960, **90**, 363.

The model in which co-ordination of oscillations by localised π-electrons is assumed,[23] which is favoured by the author, at present permits no predictions regarding the B-band and only a few (qualitative ones) regarding the K-band. The decrease in inductomeric polarisabilities in the order $C{=}C > C{=}N > C{=}NH^+$ should lead to displacements to shorter wavelengths from benzene to pyridine to pyridinium ion, but the increase in polarising power in the same order may often lead to long-wavelength displacements in this order. In unsymmetrical systems the $(N \longrightarrow V)$ transition, which gives rise to the K-band, is generally accompanied by some overall migration of electrons; [23] this is largely analogous to that postulated by the valence-bond resonance picture [24] and is often the most important factor to be considered.

Either theory would predict that this migration towards the CN group in benzonitrile [see (I)] would be rendered more difficult, that the K-band would be displaced to shorter wavelengths when a CH is replaced by the more electronegative N, and that this effect would be especially pronounced for 4-cyanopyridine. Even greater effects might be predicted for the cyanopyridinium ions. The prediction is borne out for the neutral cyanopyridines, but not for the ions. In the latter there is presumably no overall electron migration towards CN on excitation.

In pyridines and pyridinium ions containing saturated substituents the direction of the electron migration is undoubtedly towards the ring-nitrogen atom or NH^+ group, respectively [see (II) and (III)]. Here the bathochromic effect of a substituent (especially in the 4-position), on the K-band, should be determined by its mesomeric effect according to the valence-bond model, and by its inductomeric polarisability according to the author's model.

In this connection the strong bathochromic effects of the higher halogens in the pyridine series are noteworthy, bromine being equal to methoxyl, and iodine almost equal to amino in the neutral species, while 4-bromine actually has a greater effect than 4-methoxyl in the cations. A comparison between the ionisation constants of 4-bromo- (pK_a 3·8) and 4-iodo- (4·1) with those [16] of 4-methoxy- (6·6) and 4-amino-pyridine (9·2) rules out the equalities in mesomeric effects Br = MeO and I = NH_2.

By contrast, in *para*-substituted nitrobenzenes the bathochromic effects, on the K-bands, of all halogens,[25] including iodine (34 mμ), are smaller than that of methoxyl [26] (45 mμ) and much smaller than that of amino [27] (113 mμ). For *para*-disubstituted benzenes the facility of the overall electron migration which accompanies the $N \longrightarrow V$ transition, and hence (in highly polar systems) the shift of the K-band, is paralleled by the " interaction dipole moment " (deviation from additivity) in the ground state. (This correlation is demanded equally by the valence-bond and the author's [23] theory.) In accord with this parallelism, the interaction moment [28] is considerably greater in 4-methoxy- (0·32 D) than in 4-chloro- (0·19 D) or 4-bromo-nitrobenzene (0·21 D), but is about the same (0·12—0·15 D) in 4-chloro-, 4-bromo-, and 4-methoxy-pyridine. These results illustrate the danger of attempts to establish a constant scale of electronic or spectral effect of substituents for apparently similar series of compounds.

Application to Some Structural Problems.—The electronic spectrum of the 4-methoxypyridinium ion now obtained shows the B-band which a previous spectrum under lower resolution [3] had not shown. This finding destroys the basis of the electronic-spectral argument by which Tsubomura [13] had deduced that the structure of this ion is represented mainly by the canonical form (IIIb) in the ground state. A normal pyridinium ion structure [*i.e.*, essentially (IIIa)] is thus indicated here (see also Spinner and White [29]).

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[23] Spinner, *Spectrochim. Acta*, 1961, **17**, 545; Spinner and Burawoy, *ibid.*, p. 558.

[24] Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 273.

[25] Burawoy and Thompson, *J.*, 1956, 4314.

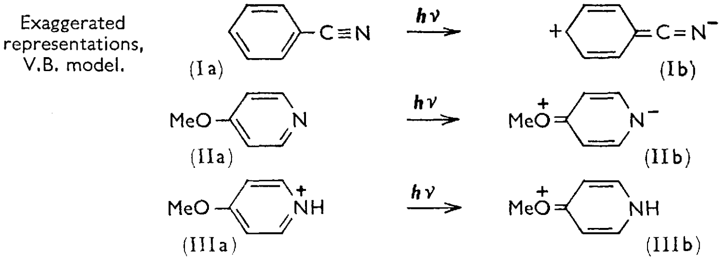
[26] Burawoy and Chamberlain, *J.*, 1952, 2310.

[27] Burawoy and Critchley, *Tetrahedron*, 1959, **5**, 340.

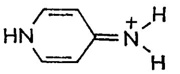
[28] Sharpe and Walker, *J.*, 1961, 4522.

[29] Spinner and White, *J.*, 1962, 3115.

In connection with the controversy about the structure of the cation of 4-pyridone[30,31] it seemed desirable to look for signs of a *B*-band in its cation spectrum (none had been reported previously[3]). Inflexions at 239, 244, and (very faintly) at 251 mμ have, in fact, now been found, as required for a 4-hydroxypyridinium structure (III; HO in place of MeO) for this ion. (However, while the spectrum of the 4-methoxypyridinium ion is merely displaced to slightly longer wavelengths in very strong sulphuric acid, that of the 4-pyridone cation is displaced to slightly shorter wavelengths, and two more inflexions, at 246 and 248 mμ, appear.)



The vibration spectra of 2- and 4-aminopyridine, unlike those of other 2- and 4-substituted pyridines,[29,32] change considerably on cation formation,[33] and the only really intense bands in the infrared spectra of the former two ions are those due to vibrations involving the exocyclic nitrogen atom. From this and other evidence it was concluded[33] that the positive charge there resides essentially on that atom [*i.e.*, the structure of the 4-substituted ion is essentially (IV)]. The electronic spectrum of the 2-aminopyridine cation[1,2] is equally compatible with this type and the normal pyridinium type of structure for this ion. On the other hand, in the light of the knowledge now obtained, the shift of the *K*-band on cation formation by 4-aminopyridine (22 mμ) seems unexpectedly small in terms of a normal pyridinium ion structure (cf. the corresponding shifts of 35 mμ for 4-methylthio-,[4] 40 mμ for 4-iodo-, and 18 mμ for 4-methoxy-pyridine). In agreement with this view, Essery and Schofield[34] report long-wavelength shifts not greater than 25 mμ on cation formation by substituted 4-aminopyridines in which there is essentially no steric hindrance, while there is a shift of at least * 30 mμ in the case of 4-amino-*N*,*N*,3,5-tetramethylpyridine, the cation of which should have a normal pyridinium ion structure because here the coplanarity required for (IV) is not sterically possible.



(IV)

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Department of Medical Chemistry, Institute of Advanced Studies,
The Australian National University,
Canberra, A.C.T., Australia.

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* The neutral species shows a double peak; the shift of the main peak is 50 mμ, but this figure is presumably misleading.

[30] Sensi and Gallo, *Ann. Chim. appl.* (*Italy*), 1954, **44**, 232; Spinner, *J.*, 1960, 1226.

[31] Jones, Katritzky, and Lagowski, *Chem. and Ind.*, 1960, 870; Katritzky and Jones, *Proc. Chem. Soc.*, 1960, 313.

[32] Spinner, following paper.

[33] Spinner, *J.*, 1962, 3119.

[34] Essery and Schofield, *J.*, 1961, 3939.