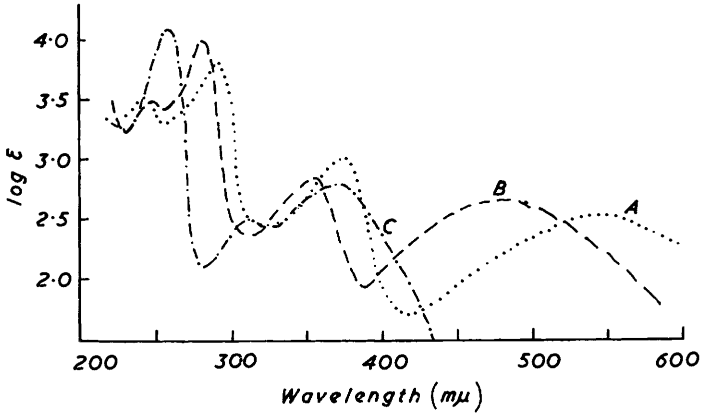
304. *Anhydro-salts. Part II.* The Absorption Spectra of Phenol-betaines.*

By J. P. SAXENA, (the late) W. H. STAFFORD, and WINIFRED L. STAFFORD.

A series of phenol-betaines has been prepared and their absorption spectra have been recorded. A marked relation between the capacity of the solvent for hydrogen-bonding and the absorption spectrum in that solvent is discussed.

THE dipolar structure of the anhydro-salt (I; R = Me) from 8-hydroxy-1-methylquinolinium hydroxide[1,2] has been confirmed by spectroscopic measurements at several pH values.[3] Its unusual colour—red as a solid, violet in non-polar solvents—merited some explanation; accordingly the betaine was prepared both by the original unusual method of treating 8-hydroxyquinoline with diazomethane, and by the action of potassium carbonate on the methiodide of 8-hydroxyquinoline. The products were spectroscopically similar although analytically different owing to solvation. The observation that the compound was red in aqueous solution and purple in chloroform prompted an investigation of the influence of hydrogen-bonding on the absorption spectrum of anhydro-salts in general.

FIG. 1. *8-Hydroxy-*1*-methylquinolinium anhydro-salt, (A) in chloroform, (B) in ethanol, (C) in acidic ethanol.*



In Fig. 1, the absorption spectra of the compound (I) in chloroform, ethanol, and acid solutions are recorded. The apparent differences are attributed to the existence of the three states (I), (II), and (III) individually in the respective solvents. Comparison

---

* Part I, *J.*, 1952, 580.

[1] Caronna and Sansone, *Gazzetta*, 1939, **69**, 24.

[2] Schenkel-Rudin, *Helv. Chim. Acta*, 1944, **27**, 1456.

[3] Phillips and Keown, *J. Amer. Chem. Soc.*, 1951, **73**, 5483.

of the absorption of light by the cation (III; R = Me) and by 8-hydroxyquinoline hydrochloride (cf. III; R = H) shows the expected similarity consonant with hybrid structures in which one electron pair of the phenolic group is merged with the π-electron system of the quinoline ring. In chloroform, the contributing forms (Ia, b, c, etc.) of the betaine lead to an analogous hybrid in which the structural difference that there is no sharing of an electron pair of the oxygen atom with a hydrogen atom must be responsible for the marked difference in light absorption. Coulson [4] attributes it to the fact that the bonded molecule when excited does not have enough overlap in the bonding n-orbital to hold it together, with the result that the excited state is of much the same energy as an unbonded molecule, whereas the energy of the ground state is lowered by that of the hydrogen bond.

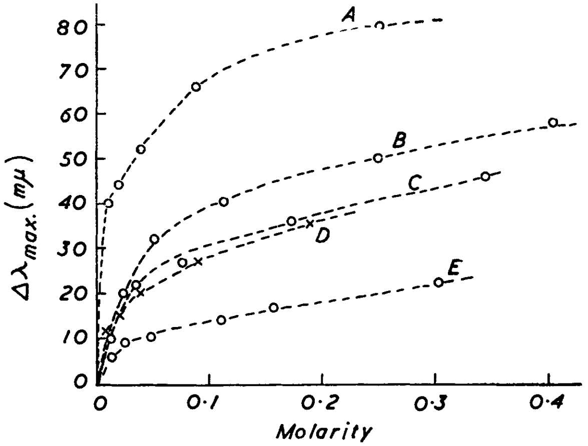
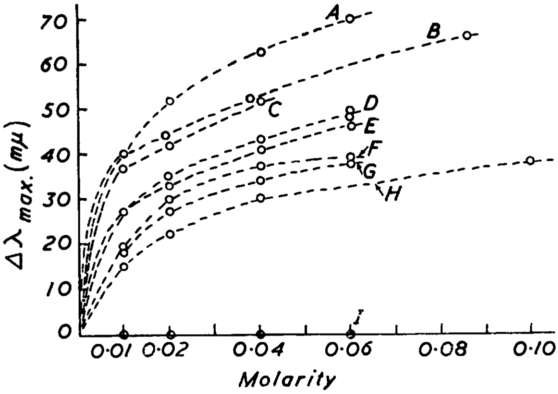


FIG. 2. *8-Hydroxy-1-methylquinolinium anhydro-salt in chloroform containing (A) 2-hydroxybiphenyl, (B) methanol, (C) ethanol, (D) borneol, (E) t-butyl alcohol.*

G. 3. *8-Hydroxy-1-methylquinolinium anhydro-salt in chloroform containing (A)* p-*nitrophenol, (B) 2-hydroxybiphenyl, (C)* m-*nitrophenol, (D)* m-*bromophenol,* p-*bromophenol, or methyl* p-*hydroxybenzoate, (E)* m-*fluorophenol, (F)* p-*fluorophenol, (G) methyl* m-*hydroxybenzoate, (H) phenol, (I)* o-*nitrophenol.*



The state (II) of the substance in ethanol (R′ = Et) represents an intermediate state in which an electron pair is partly shared in the hydrogen bond, mirrored in an intermediate absorption type. This large effect may be considered as due to a change in the polarisation of the molecular orbital of the quinoline ring resulting because the conjugated electron pair of the oxygen atom is progressively shared and ultimately captured by a hydrogen atom. Thus there is a displacement of the electrons in the molecular orbital resulting in the electrons' being more closely bound to the oxygen atom. In the cation (III) the forms (b), etc., contribute minimally, but in (II) and (I) they are much more important. The conclusion was reached that the deep colour of anhydro-salts of this type may be attributed to the existence of a dipolar structure in which the negative character is

---

[4] Coulson, *Research*, 1957, **10**, 149.

associated in part with carbon atoms of an aromatic nucleus.[5] This conclusion has been extended to explain the colour of azulene and its derivatives.[6]

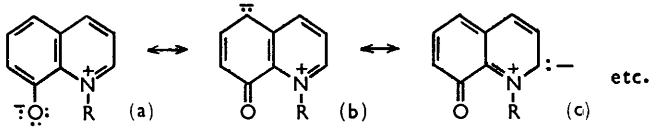
As with merocyanines, a high dielectric constant of the solvent caused hypsochromic displacements in the visible absorption maximum, shown in Table 1. The presence of a hydroxyl group produces a larger shift, as shown by comparing the effect of t-butyl alcohol (ε 10·9), which gives $\lambda_{max.}$ 502 mμ, with the value 535 mμ for acetone (ε 20·7). The pronounced effects of *o*-nitrotoluene and nitromethane may be attributed to their acidity, and thus also to their ability to form hydrogen bonds with the betaine.

TABLE 1. *Dependence of the position of the visible absorption maximum of compound* (I) *on the dielectric constant* (ε) *of the solvent.*

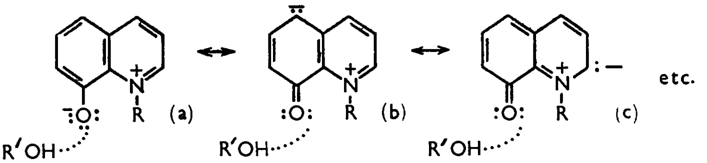
Solvent	$\lambda_{max.}$ (mean)	ε at 25°	Solvent	$\lambda_{max.}$ (mean)	ε at 25°
C_6H_6	568	2·28	Bu^tOH	502	10·9
$CHCl_3$	554	4·81	EtOH	484	24·3
EtOAc	539	6·02	H_2O	443	78·5
$COMe_2$	535	20·7	$MeNO_2$	388	20·8 (or 39·4 Remick)
$PhNO_2$	530	34·8	PhOH (satd. soln. in $CHCl_3$)	443	9·68 at 60°
MeCN	512	38·8			
o-$C_6H_4Me{\cdot}NO_2$	508	24·7			

A detailed examination of the effect of hydroxylic solvents confirmed the essence of the above hypothesis, but introduced a new problem. Figs. 2 and 3 summarise a series of experiments in which the effectiveness of a number of compounds as hydrogen-bonding agents were compared (*i.e.*, R′ varied in state II). The concentration of the betaine was kept constant and the change in the visible absorption measured for different concentrations of the various hydroxylic materials. Grossly, the internally chelated *o*-nitrophenol had no effect, whereas the others had a pronounced effect, supporting the responsibility of hydrogen-bonding. Unexpectedly the visible absorption band moved progressively as a unit hypsochromically with no marked changes in the value of the extinction coefficient. The expectation is that an equilibrium between the two states (I) and (II) displaced by an increase in hydroxylic-solvent concentration should cause the progressive disappearance of the band corresponding to (I) and the appropriate appearance of a band corresponding to (II). In fact the maximum was translated ($\Delta\lambda_{max.}$ plotted) as the concentration of the hydroxylic solvent was increased through all intermediate positions, with no indications of an equilibrium. Figs. 2 and 3 show that the substances differ in their effect in the expected order, but the shape of the $\Delta\lambda_{max.}$–concentration

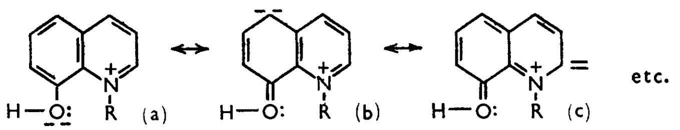
(I)



(II)



(III)

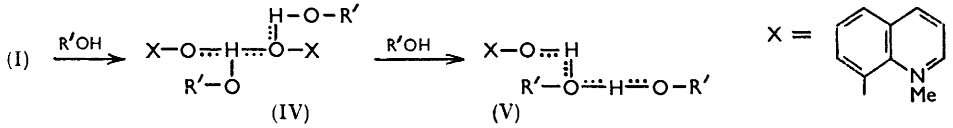


---

[5] Part I, Stafford, *J.*, 1952, 580.

[6] Stafford and Reid, *Chem. and Ind.*, 1954, 277.

curves is unusual. The only apparent explanation is that the first stage of the bonding is complete at the end of the sharp rise, and the subsequent slow rise is due to formation of polymeric hydrogen-bonds as in states (IV) and (V).



The translation with maintenance of the value of the extinction coefficient was not found with acetic acid. Here the normal translation occurred, but the height of the maximum diminished and the typical salt absorption appeared.

In an attempt to show the existence of hydrogen bonding between the betaine and hydroxylic solvents, Lund's work[7] on anionic systems was extended by determination of the infrared absorption spectra of solutions of the betaine in chloroform containing varying proportions of ethanol, phenol, and *p*-nitrophenol. The positions of the bands due to hydroxyl are listed in Tables 2, 3, and 4. The concentration of the betaine was constant at 0·005M while that of the hydroxylic compounds was increased over a wide range from 0·004M. The ability of these compounds to form inter-hydrogen bonds made interpretation of the spectra rather difficult but the following observations can be made.

TABLE 2. *Infrared absorption maxima in the hydroxyl region of ethanol–chloroform solutions in presence and in absence of compound* (I).

Molarity of EtOH ...	0·0041	0·0068	0·034	0·068	0·204	1·36	0·0041	1·36
Ratio, (I): EtOH ...	1 : 0·8	1 : 1·36	1 : 6·8	1 : 13·6	1 : 40·8	1 : 252	—	—
Band 1	3600s	3600s	3600s	3600ms	3590m	3580w	3630s	3620s
„ 2	3460w	3460w	3440w	3430w	3420m	3440—3260s	3460s	3480—3300s

TABLE 3. *Infrared absorption maxima in the hydroxyl region of* p-*nitrophenol–chloroform solutions in presence and in absence of substance* (I).

Molarity of p-NO_2·C_6H_4·OH ...	0·004	0·04	0·096	0·004	0·04	0·096
Ratio, (I): p-NO_2·C_6H_4·OH ...	1 : 0·8	1 : 8	1 : 19	—	—	—
Band 1	3650w	3618s	3610s	3640m	3615s	3610s
„ 2	—	3380m	3370s	—	3410m	3390s
„ 3	—	3200s	3200s	—	3207s	3220s

TABLE 4. *Infrared absorption maxima in the hydroxyl region of phenol–chloroform solutions in presence and in absence of substance* (I).

Molarity of PhOH	0·0056	0·016	0·04	0·192	0·46	0·0056	0·016	0·04	0·192	0·46
Ratio, (I): PhOH	1 : 1·1	1 : 3·2	1 : 8	1 : 38·4	1 : 92	—	—	—	—	—
Ratio, $CHCl_3$: PhOH	50 : 1	20 : 1	7·5 : 1	2 : 1	1 : 1·5	50 : 1	20 : 1	7·5 : 1	2 : 1	1 : 1·5
Band 1	3616s	3630s	3630s	3605s	3620s	3616s	3630s	3628s	3605s	3620s
„ 2	3275vw	3303w	3360 3300 }w	3325w	3570—3360s	3275vw	3303w	3400 3355 }w 3320	3330w	3570—3360s

Both bands of ethanol solutions in chloroform are shifted to lower frequency by amounts varying from 25 to 40 cm.$^{-1}$ when the betaine is present. In addition the intensity of band 1 falls and of band 2 rises with increased ethanol concentration, indicating that the betaine reduces the concentration of free hydroxyl and increases that of bonded hydroxyl. It is noteworthy that the bathochromic shifts occur even at low betaine : ethanol ratios, suggesting that the effect is not a general one of an increasingly polar environment.

With *p*-nitrophenol, evidence again appears (Table 3) for the formation of hydrogen bonds with the betaine. The intensity of band 3 rises from that observed for the solvent, on addition of the phenol if the betaine is present, indicating that a small reduction in the

---

[7] Lund, *Acta Chem. Scand.*, 1958, **12**, 298.

concentration of free hydroxyl and an increase in the concentration of bonded hydroxyl occur. Also band 2, due to bonded hydroxyl, is shifted to lower frequency, showing that the betaine has introduced bonds of greater strength than those present in a solvent mixture of the same proportions.

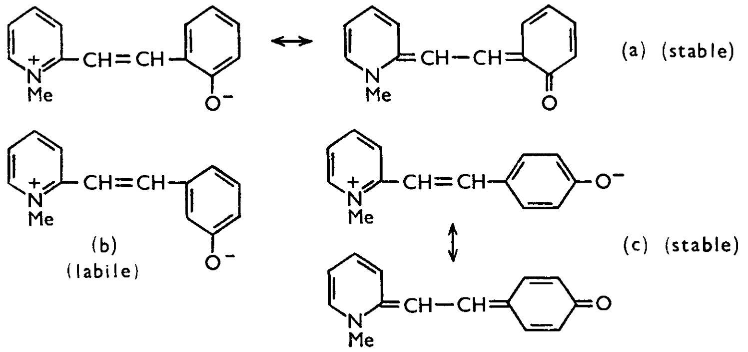
However, when phenol is used, the infrared absorption spectrum remains almost unchanged in presence or absence of the betaine. The fact that the bonded-hydroxyl band moves to higher frequency with increase of phenol concentration in contrast to the situation with the other two hydroxy-compounds examined is probably significant. The gradual shift (Table 4) from 3275 up to 3325 cm.$^{-1}$ is followed by a sharp change to a broad maximum at 3465 cm.$^{-1}$ between the chloroform : phenol ratios 2 : 1 and 1 : 1·5. This is of the same order as the findings of Bellamy, Hallam, and Williams [8] for the dilution of an acetone or acetonitrile solution of phenol with an inert solvent. Thus the complexity of the phenol–chloroform association may be preventing or masking a bonding effect to the betaine.

In Fig. 2, the curve representing the change in visible absorption maximum with concentration of ethanol shows a break from a sharp to a slow rise at about 0·04M, which, since the betaine concentration is 0·00055M, corresponds to a betaine : ethanol ratio of 1 : 70. The infrared absorption spectrum changes considerably in the bonded-hydroxyl region for solution and solvents at about this betaine : ethanol ratio, indicating the association of hydroxyl molecules as formulated for example by (V). Similarly for phenol, the change in the visible absorption curve (Fig. 3) for which a 0·001M-betaine solution was employed occurs at a betaine : phenol ratio of 1 : 10 which also corresponds to a change in the bonded-hydroxyl absorption (Table 4). In addition, the three solutions containing *p*-nitrophenol have widely different absorption in the hydroxyl region, all corresponding to different parts of the visible absorption curve. It is noteworthy that the change from a chloroform : phenol ratio of 2 : 1 to 1 : 1·5 which is strongly marked in the infrared absorption spectrum has little effect on the colour of the solution.

Since the curves showing the effect of different solvents on chloroform solutions of the betaine are almost parallel at high concentration of added material, where association of solvent molecules occurs, the influence on the visible absorption maximum of the betaine is primarily one of simple hydrogen-bonding, with the result that a convenient method is available for placing several compounds in their correct order of capacity to form external hydrogen-bonds.

The absorption spectra of anhydro-salts whose cationic and anionic centres are separated by a more extended conjugated system were examined. *o*-, *m*-, and *p*-Hydroxyphenylstilbazoles were prepared by condensing α-picoline with hydroxybenzaldehydes, and the methiodides were formed in the usual manner. Addition of aqueous potassium carbonate solution to those of the *ortho*- and the *para*-isomer gave orange betaines, (VIa and c), which were extracted into chloroform as violet solutions. Only compound (VIa)

(VI)



---

[8] Bellamy, Hallam, and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120.

was obtained crystalline. It was necessary to employ 2N-sodium hydroxide to obtain a betaine from the methiodide of the *meta*-isomer. This orange material could only sparingly be extracted into chloroform. Its lower stability is probably due to the absence of a pyridone quinone form of (VIb).

The absorption maxima of *o*-, *m*-, and *p*-hydroxyphenylstilbazolium methiodide in ethanol and alkaline ethanol solution are listed in Table 5, and the spectra of the betaine (VIa) in ethanol, chloroform, and benzene are recorded in Fig. 4.

TABLE 5. *Absorption maxima of* o-, m-, *and* p-*hydroxyphenylstilbazolium methiodides.*

Isomer	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε
o, in EtOH	—	—	358—360	3·98	295—299	3·96
o, in alkaline EtOH ...	494	4·36	348	4·23	250	4·12
m, in EtOH	—	—	345	4·25	276	3·84
m, in alkaline EtOH ...	425—440 (infl.)	3·6	360—362	4·22	268	3·98
p, in EtOH	—	—	372	4·16	286	4·01
p, in alkaline EtOH ...	494—496	4·44	—	—	285—286	3·84

The spectra of the betaines (VIa and c) are analogous to those of the 8-hydroxyquinolinium betaine, but with the first band bathochromically shifted and of higher extinction value, as expected for a more extended conjugated system. That of the *meta*-isomer (VIb) has a point of inflexion in place of the first peak, with extinction value comparable to that of the 8-hydroxyquinolinium anhydro-salt (Fig. 1). The hydroxyphenylstilbazolium betaines were found to be thermochromic. Thus a solution of compound (VIa) in chloroform at room temperature is purple, changing to blue at the boiling point, and to orange-red at —80°. Increase in temperature is considered to decrease the polar association of the solvent molecules with the betaine, resulting in a change analogous to state (II) ⟶ state (I).

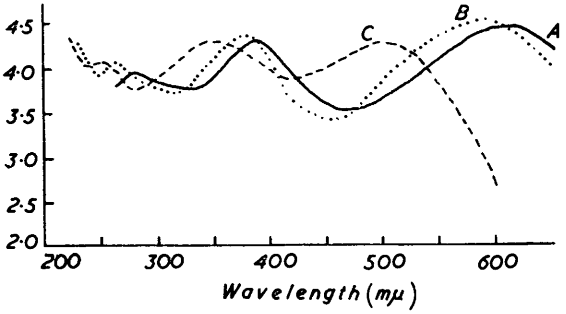


FIG. 4. (o-*Hydroxyphenyl*)-1-*methylstilbazolium anhydro-salt* (*A*) *in benzene*, (*B*) *in chloroform*, (*C*) *in ethanol*.

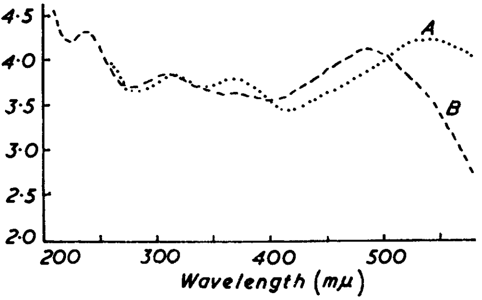


FIG. 5. 2-p-*Hydroxyphenyl*-1-*methylquinolinium anhydro-salt* (*A*) *in chloroform*, (*B*) *in ethanol*.

2-*o*-, *m*-, and *p*-Hydroxyphenylquinoline were prepared by condensing *o*-aminobenzaldehyde with *o*-, *m*-, and *p*-hydroxyacetophenone, and the methiodides formed. 2-*o*-Hydroxyphenylquinolinium iodide gave no colour with alkali, probably owing to pseudo-base formation. The other two isomers yielded coloured betaines (VIIb and c), but only that from the *para*-isomer could be isolated crystalline. The absorption maxima of the methiodides of *m*- and *p*-hydroxyphenylquinoline in ethanol and alkaline ethanol solution are given in Table 6, and the spectra of the betaine (VIIc) in ethanol and chloroform are recorded in Fig. 5. It is apparent that the relation between solvent and spectrum derived from the study of 8-hydroxyquinolinium anhydro-salt applies also to those with a more extended dipolar system.

(VII)

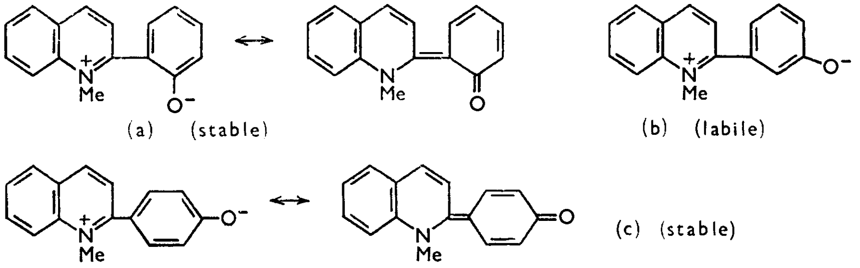


TABLE 6. *Absorption maxima of* m- *and* p-*hydroxyphenylquinolinium iodide.*

Isomer	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε
m, in EtOH	—	—	328—330	4·1	266—268	3·85
m, in alkaline EtOH ...	450	2·66	328—332 (infl.)	3·79	308	3·84
p, in EtOH	—	—	335—337	4·01	270	4·2
p, in alkaline EtOH ...	478—480	4·04	373	4·02	315, 282	4·11, 4·02

FIG. 6. 3-*Hydroxy*-1-*methylpyridinium iodide* (*A*) *in ethanol,* (*B*) *in acidic ethanol,* (*C*) *in alkaline ethanol.*

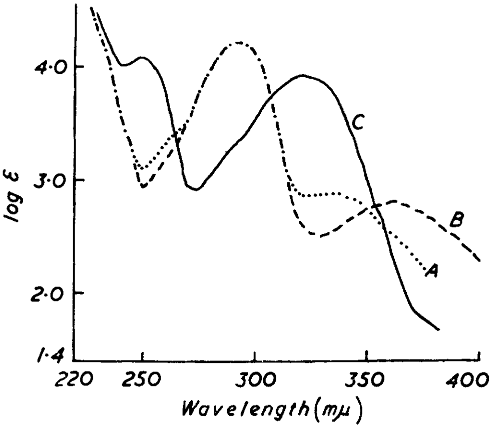
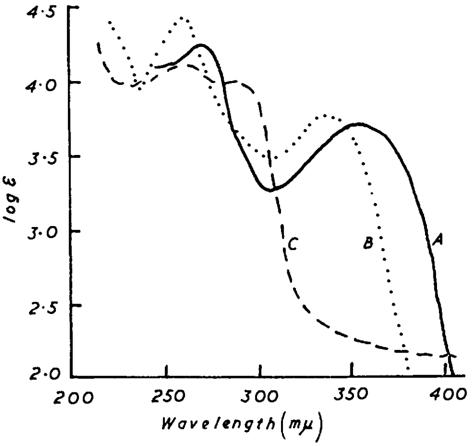
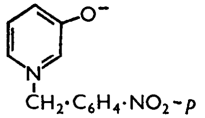


FIG. 7. 3-*Hydroxy*-1-p-*nitrobenzylpyridinium anhydro-salt* (*A*) *in chloroform,* (*B*) *in ethanol,* (*C*) *in acidic ethanol.*



Finally, anhydro-salts from 1-alkyl-3-hydroxypyridinium hydroxides were examined to discover if the relation also holds good for those whose cationic and anionic centres are associated with a monocyclic system, and therefore whose absorption falls entirely in the ultraviolet region.[6] 3-Hydroxy-1-methylpyridinium iodide did not yield an isolable betaine on treatment with potassium carbonate solution, but its absorption spectrum was measured in acidic, ethanol, and alkaline ethanol solutions, and recorded in Fig. 6. The betaine (VIII) from 3-hydroxy-1-*p*-nitrobenzylpyridinium bromide was however obtained as a crystalline hydrate. The substance may be regarded as a pseudo-base. It yielded a picrate identical with that derived directly from the bromide. The absorption spectra in ethanol and chloroform solutions are recorded in Fig. 7. Thus the capacity of change of solvent to change the electronic state and therefore the absorption spectrum also applies to simple monocyclic anhydro-salts.



(VIII)

EXPERIMENTAL.

Methiodides and Derivation of Betaines.—General methods. A solution of 8-hydroxyquinoline in " AnalaR " acetone was boiled with methyl iodide for 2—3 hr., until the quaternary salt separated. The acetone and excess of methyl iodide were removed and the residue after being washed with ether was recrystallised from ethanol–ether. The methiodide was then treated with aqueous 2N-potassium carbonate, and the resulting betaine extracted into chloroform. The extract was dried (K_2CO_3) and concentrated under reduced pressure.

8-Hydroxy-1-methylquinolinium iodide had m. p. 143° (decomp.) (Found: N, 5·0; I, 44·0. Calc. for $C_{10}H_{10}ONI$: N, 4·9; I, 44·3%).

8-*Hydroxy*-1-*methylquinolinium Anhydro-salt.*—The betaine was obtained as orange crystals from the violet chloroform solution by addition of ligroin. These were converted by drying under a vacuum into violet-red needles, m. p. 115° (decomp.) (Found: C, 68·4; H, 6·16; N, 7·5. Calc. for $C_{10}H_9ON,H_2O$: C, 67·8; H, 6·2; N, 7·9%). The compound when prepared by the method of Caronna and Sansone [1] was obtained without water of crystallisation.

Preparation of Hydroxyphenylstilbazoles.—α-Picoline (10 g.), *o*- or *p*-hydroxybenzaldehyde (13 g.), and water (7 g.), in a Carius tube, were kept in an autoclave for 8 hr. at 140°. The unchanged materials were removed in steam, and the oily residue was extracted with ether. The extract was dried and evaporated. The residue was treated in ethanol solution with charcoal, and the product crystallised from ligroin, giving the *o*-, m. p. 132°, and the *p*-hydroxy-isomer, m. p. 217°. *m*-Hydroxyphenylstilbazole was not formed from *m*-hydroxybenzaldehyde under these conditions. Chiang and Hartung's method [9] gave the compound obtained as colourless needles, m. p. 136°. These gave: o-*hydroxyphenyl*-1-*methylstilbazolium iodide*, m. p. 240° (Found: C, 49·0; H, 3·9; N, 3·8; I, 37·0. $C_{15}H_{14}ONI$ requires C, 49·6; H, 4·1; N, 4·1; I, 37·5%) [*picrate* (Found: N, 13·6. $C_{21}H_{16}O_8N_4$ requires N, 13·6%)]; m-*hydroxy*-1-*methylphenylstilbazolium iodide*, m. p. 205—207° (Found: C, 49·0; H, 4·4; N, 4·25; I, 37·5%); and the para-*isomer*, m. p. 257° (Found: C, 49·5; H, 4·3; N, 4·5; I, 37·0%), all yellow needles.

o-*Hydroxyphenyl*-1-*methylstilbazolium anhydro-salt* formed violet needles (from chloroform–benzene), m. p. 154° (decomp.) (Found: C, 67·0; H, 6·45; N, 5·35. $C_{14}H_{13}ON,2H_2O$ requires C, 67·9; H, 6·1; N, 5·7%).

2-o-, -m-, and -p-*Hydroxyphenylquinolines.*—*o*-Aminobenzaldehyde (1 g.) in ethanol (20 ml.) was added to the hydroxyacetophenone (1 g.) in ethanol (10 ml.), followed by 10% ethanolic sodium ethoxide (10 ml.). The mixture was warmed slightly and left at room temperature overnight. After removal of the solvent the solid residue was added to sufficient dilute hydrochloric acid to acidify the suspension, which was then extracted with ether to remove unchanged material. Subsequent neutralisation of the aqueous solution with sodium hydrogen carbonate precipitated the required compound. Thus were obtained: 2-o-*Hydroxyphenylquinoline*, yellow needles (from ethanol) (1·2 g.), m. p. 115—117° (Found: C, 81·3; H, 4·85; N, 6·65. $C_{15}H_{11}ON$ requires C, 81·5; H, 5·0; N, 6·3%) [*methiodide*, formed only in boiling methanol (4 hr.), yellow needles, m. p. 180° (decomp.) (Found: I, 34·7. $C_{16}H_{14}ONI$ requires I, 35·0%)].

2-m-*Hydroxyphenylquinoline*, colourless needles (from aqueous ethanol) (1 g.), m. p. 156—157° (Found: C, 81·3; H, 4·8; N, 6·4%) [*methiodide*, yellow needles, m. p. 194—195° (Found: I, 34·9%)].

2-p-*Hydroxyphenylquinoline*, colourless needles (from ligroin–benzene) (1·4 g.), m. p. 237—238° (Found: C, 81·5; H, 5·05; N, 6·5%) [*methiodide*, yellow needles, m. p. 209° (Found: I, 34·8%)], giving *betaine*, orange needles (from chloroform–benzene), m. p. 85·5° (Found: N, 5·6. $C_{16}H_{13}ON$ requires N, 5·96%).

3-*Hydroxy*-1-*methylpyridinium Iodide.*—This was obtained by boiling 3-hydroxypyridine in acetone under reflux with methyl iodide for 1 hr., as colourless prisms, m. p. 120·5° (Found: C, 28·2; H, 3·9; N, 5·5; I, 49·8. Calc. for C_6H_8ONI,H_2O: C, 28·4; H, 4·0; N, 5·5; I, 49·5%).

3-*Hydroxy*-1-p-*nitrobenzylpyridinium Bromide.*—A colourless solid was formed on boiling 3-hydroxypyridine in acetone with *p*-nitrobenzyl bromide for 1 hr., and recrystallised from ethanol (m. p. 216—217°) (Found: N, 8·15; Br, 23·8. Calc. for $C_{12}H_{11}O_3N_2Br$: N, 8·5; Br, 24·3%) [picrate, m. p. 177° (Found: N, 15·8. Calc. for $C_{18}H_{13}O_{10}N_5$: N, 15·3%); *betaine*, colourless (from chloroform–benzene), m. p. 177° (Found: C, 56·1; H, 4·0; N, 11·4. $C_{12}H_{10}O_3N_2,H_2O$ requires C, 56·7; H, 4·7; N, 11·3%).

---

[9] Chiang and Hartung, *J. Org. Chem.*, 1945, **10**, 21.

Spectra.—A Unicam quartz spectrophotometer SP.500 was used in the determination of the visible absorption spectra. The values for the absorption maxima of 8-hydroxy-1-methylquinolinium anhydro-salt (Table 1) were obtained for solutions prepared by diluting 1 ml. of a 0·00646M-solution in chloroform (washed with water and dried over potassium carbonate) to 25 ml. with the appropriate solvent. The infrared spectra were determined by using a Hilger spectrophotometer H 800 with a lithium fluoride prism. The phenol and *p*-nitrophenol were of " AnalaR " quality, and the ethanol was distilled off sodium.

The authors thank Dr. D. M. W. Anderson for determination of the infrared spectra and for helpful discussion.

THE UNIVERSITY, EDINBURGH, 9.

[*Received, September* 8*th*, 1958.]