THE STRUCTURE OF SOME BENZYLIDENEAMINO-PYRIDINIUM IODIDES*

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The UV, IR, and PMR spectra of a number of m- and p-substituted N-(benzylideneamino)-pyridinium iodides confirm the structure of hydrazonium compounds proposed for them previously. On the basis of physicochemical data, a hypothesis has been put forward of the participation of the pyridinium ring in an intramolecular interaction of the conjugation type. Charge-transfer bands are observed in the UV spectra of some of these compounds.

The products of the condensation of carbonyl compounds with N-aminopyridinium iodide are representatives of a little-studied hydrazonium series. They were first described as recently as 1967 [2, 3].

We have investigated the IR, UV, and PMR spectra of a number of benzylideneaminopyridinium iodides (Table 1), and a description of their spectral characteristics is given below.

PMR Spectra. In the PMR spectra (solutions in DMSO) the doublet of the α protons of the pyridine ring and the signal of a proton on a C=N, not infrequently superposed on this doublet, are found in weak fields (Table 2). The triplets of the γ proton and the β protons of the pyridine ring and, particularly, of the phenyl radical are located in a stronger field.

The centers of the triplets of the γ proton (8.70 ppm) and of the β protons (8.30 ppm), as compared with those of substituted pyridines, are shifted downfield because of salt formation. The signal of the azomethine proton is shifted downfield on the introduction of electron-accepting substituents into the benzene ring, while the pyridine protons experience this effect feebly.

We have performed a rough correlation of the chemical shifts of the α, β, and γ protons of the pyridine ring and of the proton on the azomethine bond with Hammett's polar σ constants of the m and p substituents in the benzene part of the molecule. From the values of ρ it may be considered that a substituent in the benzene ring exerts the greatest influence on the screening of the azomethine proton (ρ = 0.36), while, as was to be expected, the protons of the pyridine ring are insensitive (ρ = 0.14, 0.08, and 0.17 for the α, β, and γ protons, respectively). However, apparently, the ring nitrogen atom, which bears a positive charge, is nevertheless capable to some extent of transmitting the electronic effect of a substituent.

IR Spectra. For each of the benzylidene derivatives, four bands are observed in the ~1600 cm^{-1} and 1587-1565 cm^{-1} regions, and a shoulder at ~1450 cm^{-1} on the 1480-1470 cm^{-1} band that is characteristic for the pyridinium cation. A band with a frequency of 1620 cm^{-1} was assigned to the $\nu_{C=N}$ vibrations. In this region, N-aminopyridinium iodide has a broad absorption band (1610-1630 cm^{-1}) of the deformation vibrations of an NH_2 group. In this case, the characteristic band of the pyridinium ion again appears clearly in the 1375-1380 cm^{-1} region. The somewhat low $\nu_{C=N}$ frequency, as compared with the azomethines, can be explained by the accepting influence of the quaternary nitrogen atom.

The IR spectrum of each of the benzylidene derivatives has a medium-intensity band of an "aldehyde" CH group in the 1310-1290 cm^{-1} region. So far as concerns the vibrations of the $N-\overset{+}{N}$ bond, these may be expected to be more characteristic than those for an N–N bond. A medium-intensity band at 1152-1145 cm^{-1} possibly belongs to these.

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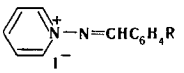
TABLE 1



Compound	R	mp, °C	Literature data, mp, °C[a]
I	H	162—163	159—160[4]
II	*p*-CH_3	139—140 [b]	—
III	*m*-CH_3	110—111,5 [c]	—
IV	*p*-$(CH_3)_2CH$	157—158,5	138—139[4]
V	*p*-$(CH_3)_2N$	216	206—207[4], 216[2]
VI	*p*-Br	204—204,5	197—198[4]
VII	*m*-Cl	173—174 [d]	—
VIII	*m*-HO	152—153	99—100[4]
IX	*p*-NO_2	242	213—214[4], 242[2]
X	*m*-NO_2	197—198,5	188—189[3], 191—193[2]
XI	*p*-CH_3O	184—185 [e]	—
XII	*m*-CH_3O	139—141 [f]	

[a]Apparently, the low values of the melting points given in the literature [3, 4] are due to the presence of impurities difficult to separate. [b]Found, %: C 48.2; H 4.0; N 8.6. $C_{13}H_{13}IN_2$. Calculated, %: C 48.2; H 4.0; N 8.6. [c]Found, %: C 48.2; H 4.0; N 8.7. $C_{13}H_{13}IN_2$. Calculated, %: C 48.2; H 4.0; N 8.6. [d]Found,%: C 41.8; H 2.9; N 8.1. $C_{12}H_{10}ClIN_2$. Calculated, %: C 41.8; H 2.9; N 8.1. [e]Found, %: C 45.8; H 3.8; N 8.3. $C_{12}H_{13}IN_2O$. Calculated, %: C 45.9; H 3.8; N 8.2. [f]Found, %: C 45.8; H 3.8; N 8.3. $C_{13}H_{13}IN_2O$. Calculated,%: C 45.9; H 3.8; N 8.2.

TABLE 2. Chemical Shifts (δ, ppm)

Comp.	Doublet of α protons	Triplet of γ protons	Triplet of β protons	Phenyl protons
I	9.30 9.37 9.26	8.88 8.70 8.65	8.55 8.37 8.25	8.02 7.95 7.93 7.70 7.58
II	9.40 9.45 9.37	8.90 8.70 8.55	8.40 8.25 8.15	7.93 7.82 7.84 7.35
III	9.33 9.43 9.30	8.85 8.70 8.60	8.42 8.30 8.15	7.82 7.75 7.56 7.47
IV	9.45 9.52 9.42	8.90 8.80 8.65	8.48 8.35 8.25	8.11 7.95 7.62 7.47
V	8.92 9.30 9.20	9.70 8.60 8.45	8.30 8.20 8.07	7.87 7.73 6.93 6.79
VI	9.35 9.40 9.32	8.82 8.72 8.60	8.40 8.30 8.20	8.08 7.92 7.89 7.74
VII	9.46 9.35 9.46	8.86 8.72 8.58	8.40 8.30 8.15	7.98 (center) 7.74 (center)
VIII	9.30 9.92 9.40	8.85 8.72 8.60	8.40 8.30 8.18	7.48 7.39 7.16 (center)
IX	9.62 9.62 9.49	8.90 8.80	8.70 8.60	8.70 8.58 8.48 8.37
X	9.62 9.47 9.40	8.86 (center)	8.66 (center)	8.42 8.32 8.20 8.03 7.92 7.75
XI	9.38 9.43 9.32	8.83 8.70 8.58	8.40 8.30	8.07 7.92 7.26 7.10
XII	9.40 9.45 9.37	8.85 8.70 8.57	8.36 8.27 8.15	7.60 7.52 7.35 (center)
XIII	— 9.80 9.65	8.76 (center)	8.52 8.40 8.20	

UV Spectra. Many investigations have been devoted to the UV spectra of N-aminopyridinium iodides, since they are a convenient subject for the study of charge-transfer complexes. We have found that the majority of the N-(benzylideneamino)pyridinium iodides studied are characterized in ethanolic solution by two bands (215-220 and 255-305 nm) but they sometimes have another long-wave band of low intensity which may be assigned to charge transfer [for example, at 345 nm in (VIII)] (Table 3).

Generally [5], bands at 300-400 nm in alkylpyridinium iodides are explained by the formation of charge-transfer complexes, but Tandon et al. [6] have ascribed to it preferentially the shortest-wave band at 220 nm, although this conclusion appears doubtful. For compounds of this type, the appearance of two charge-transfer bands may be expected, although the short-wave part is masked by other bands. Absorption in the long-wave UV region of the spectrum does not always appear, either [7]. The two charge-transfer bands were initially [5] ascribed to the formation of an iodine atom in the $2P_{1/2}$ or $2P_{3/2}$ state in the excitation of pyridinium iodide $Py^+I^- \rightarrow Py \cdot I \cdot$, but later this fact was explained by the presence of two adjacent molecular orbitals in the pyridinium ion [8, 9].

Bands characteristic for the UV spectra of pyridine (251 and 270 nm) are present in all the derivatives that we studied. They can hardly be assigned to two different chromophores (the heterocycle and the C=N bond) as was done previously [7]. They are, rather, due to the molecule as a whole, with an admixture of the absorption caused by charge transfer. Sometimes they are resolved, and the spectrum acquires a more complex form. The bathochromic shift of the band at 255 nm in the N-(benzylideneamino)pyridinium

TABLE 3. UV Spectra of N-Benzylideneiminopyridinium Iodides (concentration $2.5 \cdot 10^{-5}$ M)

Comp.	Solvent	λ_{max}, nm (log ε)
I	100% ethanol (z=79,6)	215 (4,43), 283 (4,22)
	Acetone (z=71,3)	247 (4,19), 298 (3,90)
	Acetonitrile (z=71,3)	247 (4,34), 280 (4,24)
	DMSO (z=71,1)	241,5 (4,17), 278 (4,24), 438 (2,15), 570 (2,58)
	CH_3COOH (z=79,2)	222 (4,05), 286 (4,32), 363 (3,38)
	H_2SO_4	263 (3,66), 298 (4,29), 352 (3,36)
II	Ethanol	213 (4,43), 275 (4,09), 302 (4,28)
	DMSO	240 (4,18), 285 (4,24)
	CH_3COOH	290 (4,30), 360 (3,35)
III	Ethanol	207 (4,54), 290 (4,22)
	Acetonitrile	247,5 (4,29), 298 (4,36)
	DMSO	299 (4,32)
IV	Ethanol	214,5 (4,46), 302 (4,30)
V	Ethanol	219 (4,38), 255 (4,01), 301 (3,82), 406 (4,04)
	Acetone	216 (4,02), 251 (3,93), 320 (3,42), 402 (4,02)
	Acetonitrile	246,5 (4,45), 295 (3,90), 402 (4,35)
	DMSO	258 (4,04), 290 (3,88), 401 (4,22)
	H_2SO_4	255 (4,12)
VI	Ethanol	212,5 (4,42), 261 (4,21), 290 (3,97)
	Acetone	260 (4,62), 290 (4,64)
	Acetonitrile	247 (4,29), 298 (4,40)
	DMSO	296 (4,35), 420 (0,84)
	CH_3COOH	297,5 (4,35)
	H_2SO_4	219 (4,00), 256 (3,84), 330 (4,41), 278 (4,25)
VII	Ethanol	208 (4,59), 275 (4,10)
VIII	Ethanol	290 (4,33), 345 (shoulder) (3,83)
IX	Ethanol	216 (4,42), 269 (4,30)
	Acetone	258 (4,43), 280 (4,37)
	Acetonitrile	247,5 (4,31), 285 (4,42)
	CH_3COOH	287 (4,47), 362 (3,72)
X	Ethanol	220 (4,32), 255 (4,08)
XI	Ethanol	218,5 (4,46), 265 (3,93), 320 (4,39)
XII	Ethanol	270 (4,56), 290 (4,16)
XIII	Ethanol	211 (4,28), 255 (3,90)
	Acetone	240 (4,22)
	Acetonitrile	247 (4,29)
	DMSO	241 (4,17), 260 (3,91)
	CH_3COOH	245 (3,86), 290 (3,41)
	H_2SO_4	255 (3,93)

iodides and the increase in its intensity as compared with the unsubstituted pyridinium cation are obviously connected with a lengthening of the chain of conjugation.

For the compounds that we have studied, the long-wave charge-transfer band is less sensitive to the polarity of the solvent than for compounds with a substituent immediately adjacent to the pyridine nitrogen. It is extremely difficult to estimate the degree of charge transfer in complexes of this type.

We have found the clear appearance of charge-transfer bands in the compounds with the strongest acceptor and donor substituents – (V, VI, and IX). The high sensitivity of the charge-transfer bands to the influence of substituents likewise confirms that the electronic transitions in the molecules of this type can actually be represented as charge transfers (see Table 3). However, it is not possible to trace a clear relationship, which again indicates that the bands have a complex nature.

For (V), a band is found at 410 nm which is almost independent of the polarity of the solvent and is apparently due to the dimethylamino group. (Such a phenomenon is also known for other compounds not forming similar complexes but having a substituent with an unshared pair of electrons [10].)

EXPERIMENTAL

The PMR spectra (Table 1) were taken on a Varian instrument (60 MHz) in DMSO (concentration 8 mole %); the IR spectra were obtained using mulls in paraffin oil and tablets with KBr on a UR-20 instrument; and the UV spectra were obtained on an SFD-2 spectrometer. The PMR spectra were recorded by R. G. Gainullina, the IR spectra by Z. S. Titova, and the UV spectra by G. M. Dorozhkina, for which we express our deep gratitude to them.

The compounds given in Table 1 were obtained by boiling equimolecular amounts of N-aminopyridinium iodide (XIII) [11] (mp 163-164°C) and benzaldehydes in absolute ethanol with the addition of 2-3 drops of hydriodic acid. On cooling, the solutions deposited crystals in various shades of yellow. They were purified by recrystallization from absolute ethanol (to constant melting point).

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