EFFECT OF SUBSTITUENTS ON THE PROPERTIES OF 2-(o-HYDROXYSTYRYL) BENZIMIDAZOLIUM SALTS

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The results of a calculation of the benzimidazolium cation and its 5(6)-substituted derivatives by the Hückel MO method show that the ±I effects of substituents have a considerably lesser influence on the magnitude of the charge on the $C_{(2)}$ atom than ±M effects. Replacement of $C_{(5)}$ by a positively charged nitrogen atom (imidazo[4,5-c]pyridinium dication) increases the charge on $C_{(2)}$ to the same extent as the introduction of a substituent with a vacant p_z orbital into the 5 position. In accordance with this, the methyl group in the 2 position of the 1,2,3,5-tetramethylimidazolio[4,5-c]pyridinium ion condenses with salicylaldehyde, but the merocyanine cannot be isolated from the 1,3,5-trimethyl-2-(o-hydroxystyryl)imidazolio[4,5-c]pyridinium diperchlorate because of the irreversible degradation of the latter.

As demonstrated in previous communications, the anhydro bases of 2-(o-hydroxystyryl)-1,3-dimethylbenzimidazolium ion, which exist only in the open form [1], are capable of being converted to spiropyrans when two (or at least one) NO_2 groups are present in the benzene ring of the benzimidazole portion of the molecule [2]. In order to establish to what extent the magnitude of the positive charge on $C_{(2)}$ and the associated possibility of intramolecular cyclization depend on the nature of the substituents, we used the Hückel MO (HMO) method to calculate the benzimidazolium cation (I) and its model structures – the 5(6)-derivatives (II–V), in which the real substituents were replaced by hypothetical substituents that have only inductive (±I, II, III; $\alpha_{C_{(5)}} \pm 0.1h_X$; h_X 3) or only mesomeric effects (±M, IV, V). The latter was considered as an inclusion in the overall π system of the additional filled or vacant (depending on the sign of the effect) p_z orbital (CH_2^-, CH_2^+) [3]. Since the nitrogen atoms in the imidazolium ring are equivalent, we adopted the same parameters for them by averaging the values recommended by Streitwieser [4] (h_{N^+} 1.75, k_{CN^+} 0.9).

The results of the calculation (Table 1) demonstrate that the inductive effect from the 5 position has little influence on the magnitude of the charge on $C_{(2)}$ and the $C_{(2)}$–N bond orders. However, these values depend markedly on the mesomeric effect. These results are in complete agreement with the above-men-

TABLE 1. Charges (q) on $C_{(2)}$ and Bond Orders (p_{CN}) in 5(6)-X-Benzimidazolium Ions (I–V) and in the 5-Azolium Analog (VI)

Structure	X	q	$p_{CN_{(1)}}$	$p_{CN_{(3)}}$
I	H	0,4429	1,5829	1,5829
II	$-I$	0,4481	1,5853	1,5801
III	$+I$	0,4374	1,5856	1,5803
IV	CH_2^-	0,3995	1,5608	1,5921
V	CH_2^+	0,4705	1,5639	1,5910
VI	—	0,4702	1,5612	1,5936

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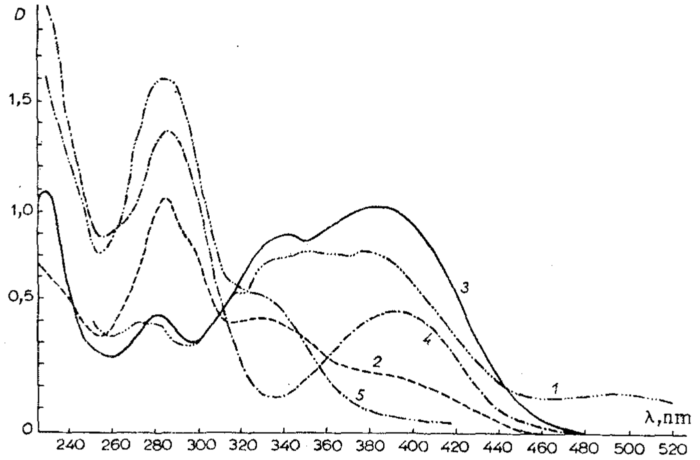


Fig. 1. Absorption spectra of alkaline solutions of 1,3,5-trimethyl-2-(o-hydroxystyryl)imidazolio[4,5-c]pyridinium ion (XI, c $0.5 \cdot 10^{-4}$ M): 1) freshly prepared aqueous solution of XI; 2) the same solution after 7 days; 3) solution of XI in 0.01 N HCl; 4) solution of XI after alkalization to pH 11; 5) alkaline solution after the addition of HCl to pH 1-2.

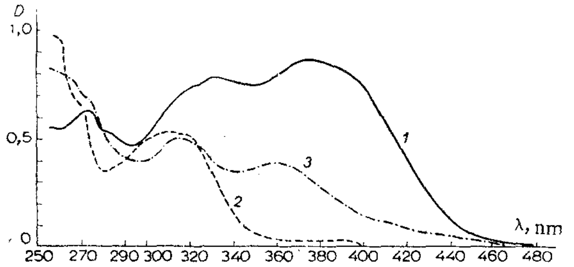
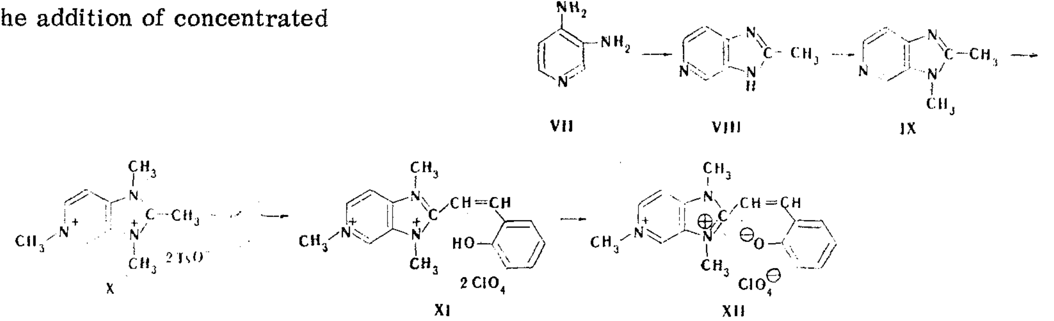


Fig. 2. Absorption spectra of solutions of XI in acetonitrile (c $0.5 \cdot 10^{-4}$ M): 1) freshly prepared solution; 2) solution of XI with an added equimolecular amount of triethylamine; 3) solution (2) after the addition of concentrated HCl to pH 1-2.

tioned fact of the production of spiropyrans from 5-nitro- and 5,6-dinitrobenzimidazoles. At the same time, the calculation showed that the 5-azolium analog of the benzimidazolium ion (VI) has the same positive charge on $C_{(2)}$ as when a hypothetical substituent of the CH_2^+ type (V) is present in the 5 position. On the basis of this, it might have been expected that the anhydro base of the 2-(o-hydroxystyryl)imidazoliopyridinium ion would be capable of intramolecular cyclization. For experimental verification of this conclusion, we synthesized 1,3,5-trimethyl-2-(o-hydroxystyryl)imidazolio-[4,5-c]pyridinium diperchlorate (XI) via the following scheme.



Compound XI is obtained as light-yellow crystals that are soluble in water. The spectra of aqueous solutions have weak absorption at 480-500 nm, which is absent in acidic solutions (Fig. 1). Alkalization of a solution of XI with triethylamine leads to the appearance of a deep-red color, which disappears rapidly, and the solution becomes yellow. A compound with a spectrum that differs markedly from that of XI is formed on reacidification. The same transformations occur, although considerably more slowly, with XI when neutral aqueous solutions of it are allowed to stand. Acid solutions of XI are more stable. When equimolecular amounts of triethylamine are added to a solution of XI in anhydrous acetonitrile, the solution becomes blue instantaneously and is then rapidly decolorized (Fig. 2), but in this case also the transformations are irreversible. The products of the transformations could not be isolated in pure form.

We explain the above transformations by the fact that a proton is initially split out from the OH group by the action of the bases, and merocyanine XII, which has negative solvatochromism (a solution of XI in water is red, while a solution in acetonitrile is blue), is formed. The partial formation of XII is apparently observed also in neutral aqueous solutions of XI because of the increased acidity of the phenol group, which also leads to the appearance of weak absorption at 480-500 nm. The disappearance of this absorption in acidic media is due to the suppression of the ionization of the OH group in XI. However, XII, being positively charged, can interact with nucleophiles at either $C_{(2)}$ or $C_{(4)}$, which also leads to irreversible transformations caused by opening of either the imidazolium or pyridinium rings.

Thus, although the 2-(o-hydroxystyryl)imidazolio[4,5-c]pyridinium ion proved to be a completely accessible product, the instability of its anhydro base does not make it possible to reliably estimate the capacity of the latter for intramolecular cyclization.

EXPERIMENTAL

3,4-Diaminopyridine (VII). This compound was obtained by reduction of 3-nitro-4-aminopyridine [5] with sodium sulfide [6].

2-Methylimidazo[4,5-c]pyridine (VIII). This compound was obtained in 40-45% yield by condensation of VII with acetic anhydride via the method in [7] and had mp 143°. Crystallization from 25% aqueous acetone (1 : 120) and prolonged drying at 120° gave a product with mp 166-168° (170° [7]). The dihydrate of VIII had mp 135° and R_f 0.82 [alcohol—chloroform (1 : 2), dark spot on illumination with UV light].*

N-Monomethyl Derivatives of 2-Methylimidazo[4,5-c]pyridine (IX). A 0.4 ml (4 mmole) sample of dimethyl sulfate was added with stirring at 50° to a solution of 0.34 g (2 mmole) of the dihydrate of VIII in 7 ml of 0.4 M KOH. At the end of the reaction (~15-20 min), the pH fell to 5-6. A total of 2-3 ml of a 0.4 M solution of potassium hydroxide was then added, and the reaction products were extracted with 60-80 ml of butanol. The solvent was removed by vacuum distillation to give an almost quantitative yield of IX. The mixture obtained was used for the subsequent alkylation. The mixture of IX was extracted with benzene (five 20-ml portions for 0.4 g of the mixture), the extract was evaporated to one third of its original volume, and petroleum ether was added to precipitate ~0.06 g of 1,2-dimethyl-1H-imidazo[4,5-c]pyridine with mp 174° [8] and R_f 0.82 [chloroform—alcohol (1 : 2), blue luminescence on illumination with UV light].

1,2,3,5-Tetramethyl-1H-imidazolio[4,5-c]pyridinium Ditosylate (X). A 0.15 g (1 mmole) sample of IX and 0.56 g (3 mmole) of methyl p-toluenesulfonate were heated at 140° for 30-40 min. The end of the reaction was determined by thin-layer chromatography by the disappearance of the starting compounds. The resulting resinous mass was washed several times with boiling dry benzene and allowed to stand for crystallization for 10-12 h under petroleum ether. The yield was quantitative. Compound X was obtained as yellowish, very hygroscopic crystals with R_f 0.45 [alcohol—chloroform (2 : 1)].

1,3,5-Trimethyl-2-(o-hydroxystyryl)imidazolio[4,5-c]pyridinium Diperchlorate (XI). A mixture of 2.6 g (5 mmole) of X and 0.53 ml (5 mmole) of salicylaldehyde was refluxed in 8 ml of acetic anhydride for 5 h. The mixture was cooled and diluted with 5 ml of water, 1 ml of 60% perchloric acid was added, and the mixture was treated with charcoal. It was then cooled, and XI was salted out with magnesium perchlorate and crystallized from water (1 : 25) acidified with perchloric acid (pH 2) to give 15-20% of a product with mp 287°. IR spectrum (in KBr): 1655, 1600, 1500, 1220, 1100, 1040 cm^{-1}. The UV spectra were recorded with an SF-8 spectrometer. Found: C 43.2; H 4.1; Cl 14.2; N 9.1%. $C_{17}H_{19}Cl_2N_3O_9$. Calculated: C 42.5; H 4.0; Cl 14.8; N 8.8%.

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*Here and elsewhere, the R_f values presented are for chromatography on activity II Al_2O_3.