EXPERIMENTAL

The x-ray experiment was carried out on an automatic Hilger Watts diffractometer (1781 independent reflections with F^2 σ, λ_{Cu-K_α}, graphite monochromator, ω-scanning, θ_{max} 57°). Monoclinic crystals: a = 11.254(2), b = 19.199(2), c = 7.4762(5) Å, β = 98.21(1)°, V = 1598.9(6) Å^3, Z = 4, $C_{18}H_{18}N_4O$. Space group $P2_1/n$.

Calculations were carried out on an Eclipse 200/S computer by a modified EXTL program.* IR absorption spectra were recorded on a UR-20 spectrometer. Integrated intensities of absorption bands were measured by the Ramsey method [12].

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*Modifications by A. I. Yanovski and R. G. Gerr at the Institute of Heteroorganic Compounds, Academy of Sciences of the USSR.

STRUCTURE AND COLOR OF PROTONATED BENZIMIDAZOLYL FORMAZANS

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UDC 547.556.9'785.5:541.651

Benzimidazolyl formazans were titrated spectrophotometrically and their base constants were determined. On the basis of quantum mechanical calculations of electron spectra a hypothesis concerning the chelate structure of the unsymmetrical benzimidazolyl formazans is proposed.

In a study of the photolysis of both sym- and unsym-benzimidazolyl formazans in the presence of tetrahalomethanes, the formation of intensely colored salts was observed [1]. Contrary to expectation, the unsymmetrical formazan hydrohalides obtained either photochemically or chemically are significantly more intensely colored (by 50-100 nm) in nonpolar solvents than the sym-formazan salts. The exceptions are the ortho-phenyl-substituted formazans (IIf, etc.), protonation of which is accompanied by a hypsochromic shift of the long-wave absorption band.

In order to determine the structure and interpret the chromaticity of the protonated forms, we studied the behavior of the sym- (Ia-d) and the unsym- (IIa-f) benzimidazolyl formazans in acid media. In solution the formazans exist as the open imino tautomers I and II [2].

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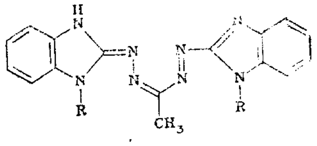
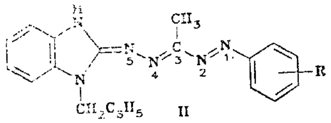


I

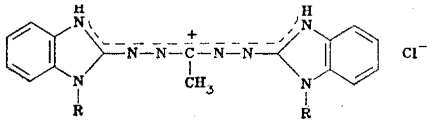


II

I, II a R=H; I b R=CH_3; c R=C_2H_5; d R=$CH_2C_6H_5$; II b R=p-NO_2; c R=p-Cl; d R=p-CH_3; e R=m-Cl; f R=o-CH_3

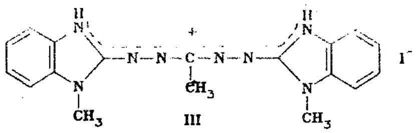
Spectrophotometric titration with hydrochloric (or hydrobromic) acid or formazan solutions in 50% alcohol demonstrated the formation of successively mono- and diprotonated forms of sym-formazans I and monoprotonated forms of unsym-formazans II (Fig. 1).

The spectral picture of sym-formazan titration as exemplified by Ib is characterized by three groups of curves (1-6, 7-10, 11-15, Fig. 1,a). Spectra 1-6 correspond to the addition of the first proton (pH 3.80-7) to the pyridinium nitrogen of the imidazole ring; the resulting hydrochloride is a symmetrical azacyanine in which the charge is delocalized:



Specifically such a structure can explain the intense color of the salt, which is exactly the same as the color of azacyanine (III). Similar data were previously obtained in the titration of sym-benzimidazolyl formazan bases in acetone [3].

Further titration forms the next group of spectral curves 7-10 (pH 1.2-3.8), which is characterized only by the increase in absorption intensity at 570-605 nm, without the appearance of a new isobestic point. In this pH range cis-trans isomerization of the azacyanine chain of the monoprotonated salt probably takes place [4]. A similar spectral picture appears in the hydrochloric acid titration (pH 2-7) of 1,5-di(1,3-dimethylbenzimidazolyl-2)-3-methyltetraazapentamethinecyaninium iodide (III).



III

Upon further titration of compounds Ib and III (pH < 2) the absorption at 550-620 nm disappears and an absorption maximum appears at 440-460 nm. At 490 nm an isobestic point appears. At this point the second proton adds to one of the four nitrogens of the formazan chain (more probably at $N_{(2)}$ or $N_{(4)}$). The pk_a value is <1, and it cannot be determined accurately by titration in aqueous alcohol. The picture is similar for the titration of formazans Ia,c,d. The sym-formazan dictations are extremely unstable and decompose quickly.

The color of the unsym-formazan hydrohalides depends on the kind of solvent. In nonpolar solvents (benzene, toluene), λ_{max} occurs at 615-680 nm, whereas in ethanol it is at 500-540 nm. The quite low pk_a values of IIa-e (Table 1) account for the instability of their hydrohalides, which has already been noted in a photolysis study [1] and in acid hydrolysis [5].

As was to be expected, in IIb,c the electron donor substituents at the phenyl radical at $N_{(1)}$ of the formazan chain cause a decrease in basicity (Table 1). The correlation between pk_a of formazans IIa,c,d and the Hammett σ_{pair} constants has a reaction constant $\rho = -1.2$ and a correlation coefficient $r = 0.995$. The calculation was carried out by a standard procedure [6].

In order to avoid hydrohalide hydrolysis in the determination of the basicity constants, formazans Ib and IIb,d were titrated potentiometrically with hydrochloric acid in anhydrous acetonitrile. The results confirm that unsym-benzimidazolyl formazans can form only the monoprotonated forms (for IIb and d, pk_a is 11.45 and 12.2 respectively), whereas sym-benzimidazolyl formazans form both mono- and di-protonated forms. For Ib, pk_a for the addition of the first proton is 14.14, for the second proton it is 6.02.

The unusually large bathochromic shift when the salts of unsym-benzimidazolyl formazans form cannot be explained simply by protonation of the open formazan structure. A more powerful chromophore must appear in the structure, which for such compounds can be the quasi-

TABLE 1. Spectral and Acid—Base Properties of Benzimidazolyl Formazans

Compound	λ_{max}*, nm			pK_{a_1}
	bases in 1:1 ethanol—water	hydrohalides		
		in 1:1 ethanol—water	in benzene	
Ia	512	565, 595	565, 595	4,34±0,10
Ib	535	575, 607	575, 607	4,54±0,09
Ic	535	575, 607	575, 607	5,20±0,09
Id	530	575, 607	575, 607	4,30±0,10
IIa	456	360, 530	380, 625, 670	3,03±0,10
IIb	510	517	350, 615, 660	2,60±0,10
IIc	472	365, 530	375, 635, 680	2,76±0,10
IId	460	370, 530	380, 625, 670	3,19±0,06
IIe	473	370, 535	375, 635, 680	2,85±0,06
IIf	452	370	390	3,16±0,05

*Due to low solubility the molar absorption coefficients cannot be calculated.

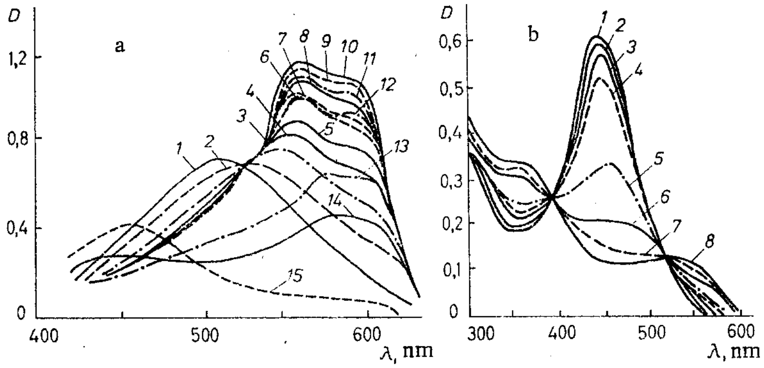
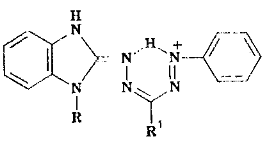
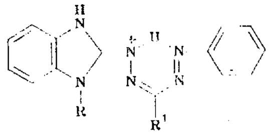


Fig. 1. Electron spectra of spectrophotometric titration (in 1:1 ethanol—water). a) methylformazan Ib (0.1 N HCl), pH values: 1) 6; 2) 4.77; 3) 4.50; 4) 4.30; 5) 4.05; 6) 3.80; 7) 3.50; 8) 3.23; 9) 2.50; 10) 2.14; 11) 1.20; 12) 0.90; 13) 0.56; 14) 0.25; 15) <0.25. b) formazan IIa (HCl solution), pH values: 1) 5.03; 2) 4.42; 3) 4.11; 4) 3.6; 5) 2.98; 6) 2.52; 7) 2.05; 8) 1.44.

aromatic formazan ring. From resonance considerations of the structure of IIa it is evident that the protonation center can be either $N_{(1)}$, which is the end of a quasiaromatic iminobenzimidazoline structure, or $N_{(5)}$ (corresponding to forms IV and V). We assumed the existence of a quasiaromatic ring in the protonation of formazan IIa of known open structure (anti-s-trans-trans configuration). Our assumption was verified by calculation of the electron absorption spectra by the Pariser—Parr—Pople method. Such calculations were previously carried out in a one-configuration approximation [7]. In the present study, configuration interaction (CI) was included in the parameters and geometry [7, 8] in the calculation of the IIa structure; nine once-excited configurations were taken into account. The extremely close coincidence of the energies of the very long wave transitions for IIa $\lambda^{exp}_{\pi_1 \to \pi_1^*} = 450$ nm, $\lambda^{theor}_{\pi_1 \to \pi_1^*} = 456$ nm) is evidence that the inclusion of CI was fruitful.



IV



V

The long wave absorption maximum of IIa hydrochloride is located at 635 nm, with an inflection at 670 nm (in CCl_4). By calculation, λ_{max} for IV with the quasiaromatic ring is 642 nm. This wavelength is due entirely to the $\pi_1 \to \pi^*_1$ transition, and is related to the intense π-electron transfer from the phenyl ring to the quasiaromatic ring. An estimate of π-bonding energies indicates a possible easy transition of chelate IV to another chelate V

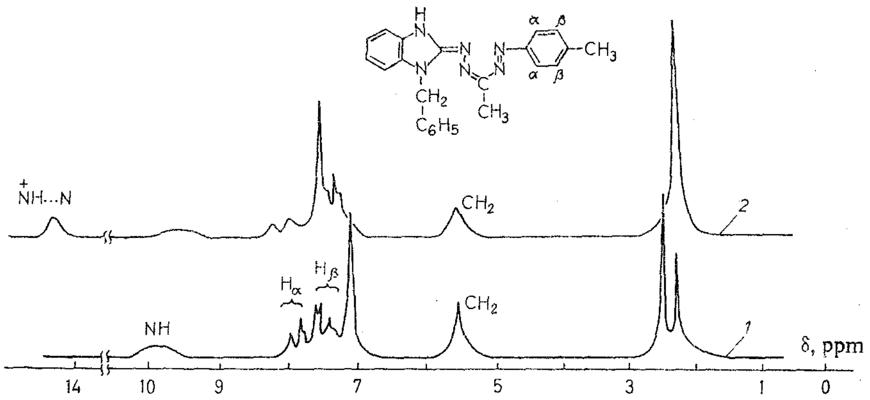


Fig. 2. PMR spectra of 1-p-tolyl-3-methyl-5-(1-benzylbenzimidazolyl-2) formazan, IId, in $CDCl_3$. 1) base; 2) after passage of gaseous HCl for 4 sec.

($\Delta E = 5.6$ kcal/mole). Obviously ortho substituents in the phenyl radical at $N_{(1)}$ prevent proton exchange between $N_{(1)}$ and $N_{(5)}$, and the structure of the highly colored ortho-phenyl-substituted formazan salt (IIf) corresponds to V, in the calculated spectrum of which the very long wave transition lies at 353 nm ($\pi_1 \rightarrow \pi^*_1$).

Chelate formation when IIa-e are protonated is confirmed by the PMR data (in $CDCl_3$) as exemplified by IId. The chemical shift of the NH proton at 9.95 ppm is strongly broadened and corresponds to the heterocyclic (Fig. 2, spectrum 1). After passage of the gaseous HCl through the formazan solution in the PMR spectrum, the signal once again appears at 14.6 ppm ($\overset{+}{N}H\cdots N$) [9] (Fig. 2, spectrum 2). In the aromatic protons (Fig. 2, spectrum 1) of IId, two doublets can be distinguished at 7.50 and 8.00 ppm that belong to the α- and β-protons of the phenyl substituent at $N_{(1)}$ (A_2B_2 system, $J_{H_\alpha H_\beta} = 9.1$ Hz). At 5.50 ppm there is a singlet of methylene protons, and in the stronger field, singlets at 2.46 (CH_3 attached to $-N{=}C{-}N{=}$) and 2.35 ppm (CH_3 of the phenyl substituent). After the passage of gaseous HCl through a solution of IId (Fig. 2, spectrum 2), the signal of the α-proton in the phenyl substituent shifts 0,2 ppm downfield; this confirms the formation of a chelate when protonation occurs. The downfield shift of the methylene proton signal (0.14 ppm) is the result of charge redistribution in heterocycle and formazan chain and a change in conformation; when this happens, the hetrocycle basicity is reduced, which is in agreement with out quantum mechanical calculations.

Thus the excessive π-character of the benzimidazole fragment insures the chelate structure of the formazan salt.

EXPERIMENTAL

Electron spectra of formazan solutions were obtained on Specord UV-Vis and Beckman Acta-6 and Acta 7 instruments ($l = 1$ cm). Ionization constants were determined by spectrophotometric titration of formazan solutions in 50% aqueous ethanol with hydrochloric acid; concentration of the latter varied from 0.1 N to concentrated, depending on the medium acidity required. Working concentrations of formazan solutions were $1.5 \cdot 10^{-5}$-$5 \cdot 10^{-5}$ M.

Ionization constants of the conjugate acids of Ib,d and IIb were determined by potentiometric titration of formazans in anhydrous acetonitrile containing 0.002 M $(C_2H_5)_4ClO_4$ buffer at 25 ± 0.1°. The titrant was 0.1 M perchloric acid in anhydrous nitromethane. Measurements were made with a pH-340 potentiometer by the procedure of [10].

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EPR AND POLAROGRAPHY OF NITROAZOLES.

5.* FIRST STEP IN THE ELECTROCHEMICAL REDUCTION OF 2-SUBSTITUTED 5(6)-NITROBENZIMIDAZOLE USING A ROTATING PLATINUM RING-DISK ELECTRODE

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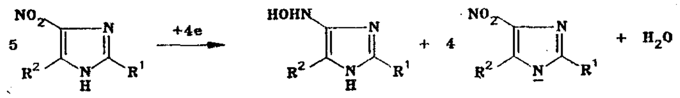
UDC 543.253:547.785.5+311.16

Using a rotating platinum ring-disk electrode, the electrochemical reduction of 2-substituted 5(6)-nitrobenzimidazoles at the platinum disk in acetonitrile and the oxidation of their radical anions at the ring were studied. During the reduction molecular hydrogen forms by a bimolecular reaction of two primary radical anions. The correlating of electrochemical quantities with the σ_I, σ_R, and σ^* substituent constants are evidence that $E^d_{1/2}$ depends on substituent resonance and induction effects to about the same extent, whereas i^d_{lim}, n, and $E^r_{1/2}$ depend predominantly on the resonance effect.

We have previously reported [2-4] on the electrochemical reduction of a number of nitroazole derivatives in acetonitrile. It was presumed that at the potentials of the first wave, nitroazoles not substituted at nitrogen gave unstable radical anions (RA) that decomposed with the elimination of hydrogen. The resulting nitroazole anions were reduced further at second-wave potentials to radical dianions (RDA) that were detected by EPR.

A somewhat different scheme of electrochemical reduction of nitroimidazoles in dimethylformamide was proposed by Kargin and co-workers [5]. In their opinion, only one-fifth of the starting molecule undergoes an electrochemical conversion at the first-wave potentials:

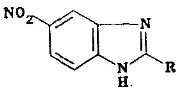


(1)

At second-wave potentials the deprotonated nitroimidazole molecule is reduced to an RDA.

When this scheme is realized, no hydrogen ought to form in the first step of the reaction.

Thus, in order to define more accurately and study in more detail the processes occurring at first-wave potentials, we undertook an electrochemical study of some 2-substituted 5(6)-nitrobenzimidazoles (I-VII) using a rotating platinum ring-disk electrode [6]



I–VII

I $R=N(CH_3)_2$, II $R=OC_2H_5$, III $R=OCH_3$, IV $R=H$, V $R=COOH_3$, VI $R=CF_3$, VII $R=CN$

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*For Communication 4, see [1].

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 6640-3. All-Union Scientific-Research and Design Institute for Monomers, Tula 300026. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 827-832, June, 1985. Original article submitted April 7, 1983; revision submitted March 7, 1984.