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RESEARCHES ON BENZ- AND NAPHTHAZOLES

XV. Amphoteric Properties of Benzimidazole Formazans*

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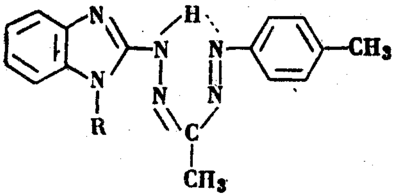
Visible region absorption spectra of unsymmetric and symmetric benzimidazole formazans in neutral, acid, and alkaline ethanol solution are discussed. Unsymmetric 1-benzimidazolyl-5-arylformazans are stable in alkaline solution, but decompose in an acid one. Symmetric 1,5-dibenzimidazolylformazans are amphoteric, giving crystalline monohydrogen halide salts, and monosodium salts. It is concluded that these salts have an azacyanine structure.

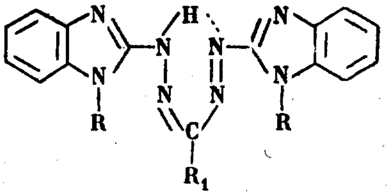
Previously preparation of 1, 5-dibenzimidazolylformazans by autoxidation of 1-alkyl-2-hydrazinobenzimidazoles in solution in primary alcohols [1], and of unsymmetric 1-benzimidazolyl-5-arylformazans by coupling of aryl diazonium salts with 2-hydrazinobenzimidazole hydrazones [2] has been described. Their properties and ability to form complexes have been studied [3].

IR spectroscopy was used to investigate the structure of the formazans of these two types. It was established that symmetric formazans, such as triarylformazans [5, 6], have a chelate structure, with a stable formazan ring. On the other hand, the formazan ring in unsymmetric formazans is unstable or open; this is evidenced by, for example, appearance of an NH group band (3400-2900 cm^{-1}) in the IR spectrum.

In the present work the abilities of some unsymmetric (I, II) and symmetric (III-VIII) benzimidazole formazans to form salts (with hydrogen halides and with sodium) were investigated.



I $R=CH_2C_6H_5$;
II $R=CH_3$;



III $R=CH_2C_6H_5$; $R_1=CH_3$;
IV $R=CH_2C_6H_5$; $R_1=H$;
V $R=CH_2C_6H_5$; $R_1=n\text{-}C_3H_7$;
VI $R=CH_3$; $R_1=CH_3$;
VII $R=C_2H_5$; $R_1=CH_3$;
VIII $R=H$; $R_1=CH_3$.

The unsymmetric formazans I, II are soluble in ethanolic alkali with deepening of color (Table 1), but their sodium salts are easily hydrolyzed, and hence were not obtained crystalline. These formazans are unstable to acids, and on acidifying an ethanol solution, are decomposed in a few minutes, with decolorization.

The symmetric 1,5-dibenzimidazolylformazans III-VII are amphoteric and quite stable both in acid and alkaline solutions. They behave as monacid bases (forming monohydrochlorides) and monobasic acids (forming monosodium salts). Their salts with hydrogen halides and with sodium can be obtained crystalline.

Hydrochlorides and hydrobromides of 1,5-dibenzimidazolylformazans are prepared crystaline by adding the hydrogen halide acid to an acetone solution of the formazan. Crystalline sodium salts are prepared by making ethanol solutions of the formazans alkaline. Alkylation of 1,5-dibenzimidazolylformazan VIII unsubstituted at the imidazole ring with the theoretical amount of alkyl halide in ethanolic alkali, led to separation of the crystalline sodium salts of 1, 5-di(1'-alkyl) benzimidazolylformazans.

Comparing the visible spectra of formazans III-VII in neutral, acid, and alkaline solutions, it is seen (see Table 1), that on passing from formazan to hydrochloride or sodium salt there is a bathochromic shift, and the absorption peak is doubled. The spectra of the hydrochloride and sodium salt resemble one another with regard to curve

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*For Part XIV see [3].

character and positions of peaks. Formazan VIII is an exception, having only one peak.

Table 1

Spectral Characteristics of Benzimidazole Formazans at various pH Values of the Ethanol Solutions

Compound number	Name	λ_{max}, mμ ($\varepsilon \cdot 10^{-4}$), in ethanol		
		Neutral solution	Acid solution, HCl, pH 1–2	Alkaline solution, NaOH, pH 11–12
I	1-(1'-Benzylbenzimidazolyl-2')-3-methyl-5-p-tolylformazan	452(3.47)	Irreversible decolorization	525(5.15)
II	1-(1'-Methylbenzimidazolyl-2')-3-methyl-5-p-tolylformazan	452(4.03)		520(4.01)
III	1, 5-Di(1'-benzylbenzimidazolyl-2')-3-methylformazan	536(5.53)	575(7.28) 590(7.01) 610(7.69)	568(7.49) 592(6.31) 604(6.43)
IV	1, 5-Di(1'-benzylbenzimidazolyl-2')-formazan	538(6.67)	586(8.31) 603(7.96) 618(8.14)	574(7.96) 600(7.01) 614(6.65)
V	1, 5-Di(1'-benzylbenzimidazolyl-2')-3-n-propylformazan	542(5.02)	582(7.33) 596(7.17) 616(8.03)	572(7.86) 596(6.63) 608(6.88)
VI	1, 5-Di(1'-methylbenzimidazolyl-2')-3-methylformazan	530(5.74)	570(7.73) 586(7.41) 604(7.94)	565(7.98) 590(6.67) 598(6.67)
VII	1, 5-Di(1'-ethylbenzimidazolyl-2')-3-methylformazan	536(5.89)	576(7.41) 590(6.96) 610(7.78)	567(7.84) 590(6.89) 603(7.01)
VIII	1, 5-Dibenzimizolyl-3-methyl-formazan	514(3.86)	560(3.92) 576(3.83) 592(3.99)	548(5.46)

Note: In the cases of formazans III-VII, values λ_{max_1}, λ_{min}, λ_{max_2} are given for acid in alkaline solutions.

Table 2

Hydrogen Halide Salts of 1, 5-Dibenzimidazolylformazans

Compound number	Salt	mp, ° C (decomp)	Formula	Found, %		Calculated, %	
				Halogen	N	Halogen	N
III	Hydrochloride	193—194	$C_{30}H_{27}N_8 \cdot HCl$	6.67	20.72	6.65	21.00
	Hydrochloride	185	$C_{30}H_{27}N_8 \cdot HBr$	18.03	—	17.79	—
IV	Hydrochloride	203—204	$C_{29}H_{24}N_8 \cdot HCl$	6.86	20.85	6.83	21.59
	Hydrochloride	180—181	$C_{29}H_{24}N_8 \cdot HBr$	14.32	—	14.13	—
VI	Hydrochloride	200—203	$C_{18}H_{18}N_8 \cdot HCl \cdot 2H_2O$	8.47	26.26	8.46	26.75
VII	Hydrochloride	175—176	$C_{20}H_{22}N_8 \cdot HCl$	8.54	—	8.62	—

The resemblance between the visible spectra of the hydrochlorides and sodium salts indicates a common structure. Obviously formation of salts of symmetric formazans involves opening of the chelate ring, and equalization of electron density in the cation or anion of the dye along all the conjugated chain, including the imidazole ring. Cation and anion structures correspond to the limiting structures A and B respectively.*

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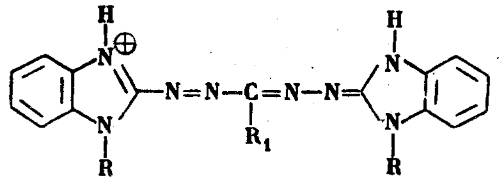
* The same structure is ascribed [7] to the hydrochloride and sodium salt of tetraazpentamethine benzothiazole dye.

This conclusion is supported by IR spectrum data: the >NH group band, absent with formazan III, appears in the hydrochloride (3354 cm^{-1})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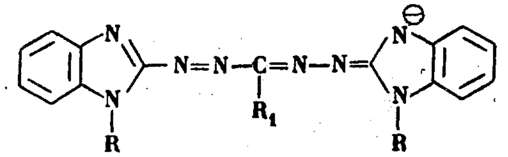
B

Thus the hydrochloride and sodium salts of symmetric formazans in some respects resemble onium and acihalochromic cyanine dyes. It is characteristic that the onium and acihalochromic carbocyanines also have almost identical spectra, independent of the sign of the charge distributed along the chain [8, 9].

Experimental

Hydrochlorides of formazans III, IV, VI, VII. 1 ml conc. HCl was added to a solution of 0.0005 mole formazan in 30 ml Me_2CO. A precipitate of hydrochloride immediately formed, was filtered off, and washed with ether. Yield almost quantitative. The formazans III, VI, VII are obtained as dark violet needles with a green glance, while formazan IV formed long fibrous needles, green with a red reflex. The hydrobromides of formazans II, IV were prepared similarly.

Sodium salt of formazan III. A few drops of a 30% NaOH solution were added to a solution of 0.0005 mole formazan in 30 ml EtOH, when blackish-blue glistening plates separated, which were filtered off and washed with a small amount of EtOH, yield 80%, mp 175–178° C (decomp). Found: C 63.12; H 5.61; N 19.28%. Calculated for $C_{30}H_{25}N_8Na \cdot 3H_2O$: C 62.64; H 5.43; N 19.48%.

Sodium salt of formazan VI. A solution of 0.001 mole formazan VIII (prepared by autoxidation of 2-hydrazinobenzimidazole in EtOH [10]) in 10 ml EtOH and 1 ml 30% NaOH was mixed with 0.001 mole MeI, and left to stand for a day. Dark blue shining needles of formazan VI Na salt separated, yield 80–90%, mp 251–253°C. The salt was stable, and could be recrystallized from EtOH. Found: C 53.42; H 5.41; N 28.18; H_2O 8.88% (from loss in weight on drying at 200°). Calculated for $C_{18}H_{17}N_8Na \cdot 2H_2O$: C 53.46; H 5.23; N 27.71; H_2O 8.91%. The same Na salt was formed by adding 30% NaOH to an EtOH solution of formazan VI.

Sodium salt of formazan VII. Prepared similarly to the above, by ethylating formazan VIII with EtI in ethanolic alkali. Dark violet rhombs, with a golden reflex, mp 251–252° C, unstable, and on dilution with aqueous EtOH, it readily hydrolyzed to formazan VII. Found: C 60.11; H 5.96; N 28.22%. Calculated for $C_{20}H_{21}N_8Na$: C 60.59; H 5.33; N 28.26%.

The visible spectra of the compounds were measured with a SF-10 spectrophotometer, formazan concentration 10^{-4} M, layer thickness 3.05 mm. When measuring the spectra in acid or alkaline solution, 50 ml formazan solution was made acid or alkaline to the required pH, by adding a few drops (which caused only an insignificant change in volume, which was neglected) of conc. HCl or 30% NaOH.

REFERENCES

1. N. P. Bednyagina, G. N. Tyurenkova, and Yu. A. Rybakova, ZhOKh, 34, 1288, 1964.
2. Yu. A. Rybakova and N. P. Bednyagina, KhGS [Chemistry of Heterocyclic Compounds], 421, 1965.
3. N. P. Bednyagina and Yu. A. Rybakova, KhGS [Chemistry of Heterocyclic Compounds], 425, 1965.
4. E. N. Yurchenko, K. V. Aglitskaya, N. P. Bednyagina, E. P. Darienko, and I. I. Kalinichenko, ZhFKh (in press).
5. M. I. Ermakova, E. I. Krylov, and I. Ya. Postovskii, ZhOKh, 30, 849, 1960.
6. I. W. Le Fevre, I. B. Sousa, and R. L. Werner, Austral. J. Chem., 9151, 1956.
7. S. Hünig, F. Brühne, and E. Breither, Ann., 667, 72, 1963.
8. W. König, Z. Angew, Chem., 38, 1, 1925.

9. V. A. Izmail'skii, Khim. nauka i prom., 3, 232, 1958.
10. Yu. A. Rybakova and N. P. Bednyagina, in: Problems of Organic Synthesis [in Russian], 210, 1965.

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