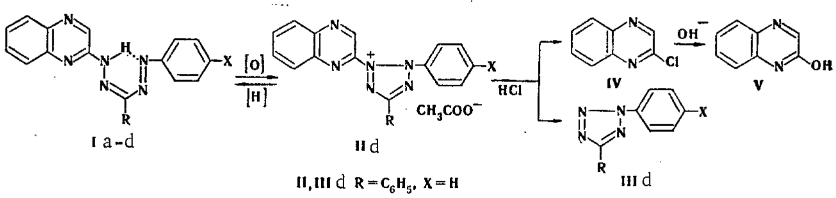
SYNTHESIS, STRUCTURE, AND PROPERTIES OF N-QUINOXALYLFORMAZANS

Yu. A. Sedov, A. I. Zabolot-skaya, and N. V. Koba

UDC 547.863.1'796.1.07:543.422.6

The first representatives of the previously unknown N-quinoxalylformazans were synthesized. Their chemical properties were investigated, and their structure and chromaticity are discussed.

The aim of the present research was an investigation of the properties of the previously unknown N-quinoxalylformazans (I), which we obtained by azo coupling of the corresponding 2-quinoxalylhydrazones with arenediazonium chlorides. The structure of Ia-d was confirmed by oxidation of formazan Id to tetrazolium salt IId with lead tetraacetate and subsequent reduction of tetrazolium acetate IId to the starting formazan with ascorbic acid [1]. The identical character of the product of reduction of tetrazolium salt IId and the starting formazan (Id) was proved by spectroscopy. The structure of formazans Ia-c is confirmed by the similarity between their UV spectra and the spectrum of formazan Id. Like benzimidazolyltetrazolium salts [2], quinoxalyltetrazolium salt IId is readily decomposed with dilute hydrochloric acid at 30°C to give 2-quinoxalone V and 2,5-diphenyltetrazole IIId via the following scheme:



The structure of the latter was confirmed by comparison of them with genuine samples [3, 4].

The maxima of the $\pi \rightarrow \pi^*$ transitions in the absorption spectra of alcohol solutions of formazans I in the visible region (Table 1) are shifted to the short-wave region as compared with the spectra of benzene solutions; this is due to the decrease in the dipole moments of I during the electron transitions. A hypsochromic shift is also observed for formazans Ia, b, d in dioxane with respect to the spectra of benzene solutions; this can be explained by a decrease in the energy of the intramolecular hydrogen bond (IHB) of formazans due to the proton-acceptor action of dioxane and, because of this, destruction of the quasi-aromatic character of the formazyl grouping. Formazan Ic, with a strong IHB, the decrease in which is not reflected in the quasi-aromatic character of the formazyl grouping, is an exception to this. The strong IHB is explained by the increased electron density on the N_5 atom of the formazyl grouping due to the donor dimethylamino group.

TABLE 1. Spectra of Ia-d in the Visible Region

Compound	R	X	λ_{max}, nm ($\varepsilon \cdot 10^4$)				
			benzene	dioxane	alcohol	KOH + alcohol, pH > 14	concn. H_2SO_4
a	CH_3	H	435 (2,5)*	425 (2,6)	410 (4,3)	535 (6,10)	491 (1,60)
b	CH_3	CH_3	435 (2,0)*	408 (2,6)	398 (4,0)	538 (5,85)	530 (0,32)
c	CH_3	$N(CH_3)_2$	492 (4,46)	490 (4,92)	488 (4,8)	558 (6,05)	404 (2,25)
d	C_6H_5	H	476 (1,54)	460 (0,74)	452 (1,37)	538 (5,75)	643 (1,85)

Tyumen' Industrial Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1705-1707, December, 1973. Original article submitted January 31, 1973.

TABLE 2. Compounds Ia-d

Compound	mp, °C	Empirical formula	Found, %		Calc., %		Yield, %
			C	H	C	H	
Ia	185—187[a]	$C_{16}H_{14}N_6$	66,2	5,1	66,2	4,9	35
Ib	193—195[b]	$C_{17}H_{16}N_6$	67,0	5,2	67,1	5,3	31
Ic	185—187[c] (dec.)	$C_{18}H_{19}N_7$	65,2	6,6	64,9	5,7	41
Id	191—193[d]	$C_{21}H_{16}N_6$[e]	—	—	—	—	78

[a] From dioxane–ethanol (3 : 2). [b] From propyl alcohol. [c] From ethanol. [d] From ethanol–butyl alcohol (1 : 2). [e] Found: N 24.2%. Calculated: N 23.9%.

The expected – in accordance with chromaticity theory [5] – sequence of deepening of the color of formazans I with increasing donor character of the substituents in the p position of the phenyl group attached to N_5 is not noted in even one of the solvents presented above. However, the expected sequence is observed in the spectra of the anions of Ia-c (Table 1); this also indicates the presence of an IHB in formazans I. From the data from the absorption spectra of anions of formazans of the quinoxaline series (I), it can be supposed that they have a structure similar to that of the anions of formazans of the aryl and benzazole series [6]. The slight difference (Δ 3 nm) in the positions of the absorption maxima of the anions of formazans Ia and Id with methyl and phenyl groups attached to the C_3 atom of the formazyl grouping should be ascribed to the noncoplanarity of the benzene ring in the anion of formazan Id; this is confirmed by the decrease in the absorption intensity.

From a comparison of the absorption spectra of formazans I and formazans of the aryl and benzazole series in concentrated sulfuric acid, a structure similar to that of the cations of benzazolyl formazans [6] was assigned to the cations of formazans I. At room temperature, the cations of formazans I gradually decompose in concentrated sulfuric acid. In 1 h, 0.2-2% of the cations undergo decomposition, compared with 4-10% and 10-71% after 2 h and 24 h, respectively. The most stable cation is that of formazan Ic, while the cation of formazan Ia is less stable.

Formazans I form complexes with a number of metal cations (Cu, Ni, Co, etc.). A complex (VI) of formazan Id with nickel, which probably has a chelate structure similar to that of complexes of benzimidazolylformazans [7], was isolated.

EXPERIMENTAL

Formazans Ia-d. Sodium hydroxide solution (2 N) was added by drops to a cooled mixture of solutions of 0.02 mole of benzaldehyde or acetaldehyde 2-quinoxalylhydrazone in 150 ml of dimethylformamide and 0.02 mole of benzenediazonium salt in 20 ml of 18% HCl in such a way that the temperature of the solution did not exceed 0°. The acidity of the medium was brought up to pH 9-10, after which the mixture was held at 0° for 2-3 h and allowed to stand overnight. It was then diluted with a threefold amount of water and neutralized to pH 7-7.5. The precipitate was removed by filtration, washed with water, and recrystallized. Data on Ia-d are presented in Table 2.

Oxidative Cleavage of Formazan Id. A 0.45-g (1 mmole) sample of lead tetraacetate was added with stirring to a solution of 0.47 g (1.3 mmole) of formazan Id in 10 ml of glacial acetic acid, during which the solution changed from red to pale yellow. The acetic acid was vacuum-evaporated at 50°, and the residue, which contained tetrazolium acetate IId, was treated with 30 ml of 18% HCl and allowed to stand at 30° for 30 min. The precipitate was extracted with 30 ml of hot alcohol, and the extract was filtered. The alcohol was removed by distillation, and the residue was dissolved in 20 ml of 2 N NaOH. The undissolved 2,5-diphenyltetrazole (IIId) was removed by filtration, washed with water, and crystallized from alcohol. The yield of tetrazole IIId, with mp 101-102° (mp 101.5-102° [4]), was 0.26 g (88%). The alkaline solution was neutralized with acetic acid to precipitate 0.17 g (88%) of colorless needles of 2-quinoxalone V with mp 264-265° (mp 265° [3]).

Complex of 1-(2-Quinoxalyl)-3,5-diphenylformazan with Nickel (VI). A hot solution of 0.05 g (0.14 mmole) of formazan Id in 50 ml of acetone was mixed with 0.1 g (0.34 mmole) of $Ni(NO_3)_2 \cdot 6H_2O$ in 5 ml of water, and the mixture was heated to the boiling point and cooled. The crystalline precipitate was removed by filtration and washed with warm alcohol and distilled water to give green prisms. Spectrum in the visible region (in benzene): λ_{max} 664 nm, ε $4.05 \cdot 10^4$. The yield of product with mp 248-250° was 0.07 g (64%). Found: C 66.3; H 3.9; Ni 7.9%. $(C_{21}H_{15}N_6)_2Ni$. Calculated: C 66.6; H 4.0; Ni 7.7%.

LITERATURE CITED

1. R. Kuhn and H. M. Weitz, Chem. Ber., 86, 1199 (1953).
2. Yu. A. Sedov and I. Ya. Postovskii, Zh. Organ. Khim., 5, 781 (1969).
3. D. J. Shiho and S. Tagami, J. Am. Chem. Soc., 82, 4044 (1960).
4. O. Dimroth and S. Mazzbacher, Chem. Ber., 40, 2402 (1907).
5. A. I. Kiprianov, Introduction to the Electronic Theory of Organic Compounds [in Russian], Naukova Dumka, Kiev (1965), p. 158.
6. N. P. Bednyagina and Yu. A. Rybakova, Khim. Geterotsikl. Soedin., 283 (1966).
7. V. T. Panyushkin, A. D. Garnovskii, O. A. Osipov, N. P. Bednyagina, and R. I. Nikitina, Zh. Obshch. Khim., 38, 1161 (1968).