SYNTHESIS OF THERMOCHROMIC FORMAZANS OF A NUMBER OF BENZAZOLES

Yu. A. Rybakova and N. P. Bednyagina

UDC 547.785.5'789.6'556.9.07

In a search for compounds that have thermochromic properties, a group of formazans that contain benzimidazolyl (benzothiazolyl), methyl (phenyl), and hydroxydinitrophenyl (anthraquinoyl) groups in the 1-, 3-, and 5-positions, respectively, were synthesized. Benzimidazolylformazans with a picramic acid residue in the 5-position have thermochromic properties.

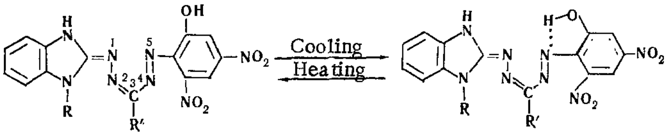
In [1] it was noted that 1-(1-benzyl-2-benzimidazolyl)-5-(2-hydroxy-4,6-dinitrophenyl)-3-methylformazan in chloroform solution changes from violet at the boiling point of the solution to blue on cooling. In a search for new compounds that have thermochromic properties we synthesized a series of 1-benzazolylformazans (Tables 1 and 2).

The formazans were synthesized by azo coupling in neutral or alkaline media of benzenediazonium salts with the corresponding benzazolylhydrazones. The formazans were deeply colored, crystalline products.

Benzimidazolylformazans with a picramic acid residue in the 5-position have thermochromic properties. These formazans have negative thermochromism in solutions of nonpolar or slightly polar solvents (chloroform and benzene). Thus chloroform solutions of formazans with a methyl group in the 3-position have a violet color on heating, while formazans with a phenyl group in the 3-position are blue-violet. When the solutions are cooled from 0 to −10°, the color changes to bright-blue and blue-black, respectively (Table 3).

The cycle of the thermochromic transformations is repeated many times without any changes.

The absorption spectra in the visible region, recorded in chloroform solutions, each contain two maxima: at 540-545 nm and at 640-645 nm. The intensity of these bands changes on heating or cooling, and an isopiestic point is observed, which indicates the presence of two forms. The proposed structures of these forms are as follows:

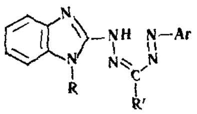


The forms differ with respect to the presence or absence of hydrogen bonding between the nitrogen atom in the 5-position and the hydrogen of the hydroxyl group. The deepening in color on cooling can be explained by the formation of a hydrogen bond [2] and by the coplanar structure of the entire molecule [3]. The following facts are evidence in favor of the proposed explanation of the thermochromic phenomena. Formazans in solutions of oxygen-containing solvents (acetone and dioxane) do not display an appreciable change in color, since the hydrogen of the hydroxyl group of the formazan is apparently linked by a hydrogen bond to the oxygen atom of the solvent, and the formation of two forms does not occur in heating and cooling. The spectra of formazans in oxygen-containing solvents contain one maximum at 540 nm, and a

---

S. M. Kirov Ural Polytechnical Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 970-973, July, 1971. Original article submitted October 14, 1970.

TABLE 1.



Comp.	R	R′	Ar	mp	Crystallization solvent	Empirical formula	Found %			Calculated %			Yield, %
							C	H	N	C	H	N	
I	$CH_2C_6H_5$	H	PA*	241—242	Acetone	$C_{21}H_{16}N_8O_5 \cdot 3H_2O$	48,94	3,71	21,92	49,02	4,31	21,78	70
II	$CH_2C_6H_5$	CH_3	"	201—202	Chloroform + ethanol	$C_{22}H_{18}N_8O_5$	55,28	3,88	—	55,69	3,82	—	87
III	$CH_2C_6H_5$	C_6H_5	"	197—198	Pyridine	$C_{27}H_{20}N_8O_5 \cdot 1/2C_5H_5N$	61,45	4,04	—	61,50	3,93	—	40
IV	C_2H_5	CH_3	"	193—194	Acetone	$C_{17}H_{16}N_8O_5 \cdot H_2O \cdot \cdot 1/2CH_3COCH_3$	48,35	4,76	24,41	48,36	4,60	24,39	80
V	C_2H_5	C_6H_5	"	187—188	Aqueous acetone	$C_{22}H_{18}N_8O_5 \cdot 2H_2O$	51,49	4,42	—	51,76	4,34	—	60
VI	CH_3	CH_3	"	193	Chloroform	$C_{16}H_{14}N_8O_5$	48,04	3,68	—	48,24	3,54	—	70
VII	CH_3	C_6H_5	"	243	Ethanol	$C_{21}H_{16}N_8O_5 \cdot 4H_2O$***	47,11	4,31	—	47,36	4,54	—	90
VIII	$CH_2C_6H_5$	CH_3	A†	261—262	Chloroform + ethanol	$C_{30}H_{22}N_6O_2 \cdot 1/2\ C_2H_5OH$	71,23	4,76	—	71,38	4,83	—	80
IX	$CH_2C_6H_5$	C_6H_5	"	230	The same	$C_{35}H_{24}N_6O_2 \cdot 1/2\ H_2O$	73,31	4,34	14,63	73,73	4,42	14,75	70

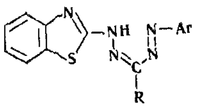
---

*Picramic acid residue (2-hydroxy-4,6-dinitrophenyl).

† 1-Anthraquinoyl.

‡ Found %: H_2O 13.3. Calculated %: H_2O 13.5.

TABLE 2.



Comp.	R	Ar	mp	Crystalliza. solvent	Empirical formula	Found %			Calc. %			Yield, %
						C	H	S	C	H	S	
X	CH_3	ПАК	198—200	Acetone	$C_{15}H_{11}N_7O_5S \cdot \cdot (CH_3)_2CO$	47,12	3,88	6,84	47,05	3,72	6,96	70
XI	C_6H_5	ПАК	>350	Acetone	$C_{20}H_{13}N_7O_5S$	—	—	—	—	—	—	70
XII	C_6H_5	A	272	Dimethylformamide	$C_{28}H_{17}N_5O_2S$	68,85	3,71	6,67	68,97	3,51	6,57	75

TABLE 3. Thermochromic Transformations of 1-Benzimidazolyl-3-methyl (phenyl)-5-(2-hydroxy-4,6-dinitrophenyl)formazans

Compound	Color in $CHCl_3$ solution		λ_{max} ($CHCl_3$) at 20° C, nm
	on boiling	at -10°	
II	Violet	Blue	538, 642
III	Blue-violet	Blue	*
VI	Violet	Blue	546, 640
VII	Blue-violet	Blue-black	*
IV	Violet	Blue	545, 640
V	Blue-violet	Blue-black	550, 600

---

*The compounds are only slightly soluble.

barely noticeable inflection of weak intensity is present at 650 nm. The 1,3-diphenyl-5-(2-hydroxy-4,6-dinitrophenyl)formazan (XIII) synthesized as a model is not thermochromic, since, like triphenylformazan [4,5], it has a chelate ring that is not disrupted during temperature changes.

EXPERIMENTAL

1-(1-Ethyl-2-benzimidazolyl)-3-methyl-5-(2-hydroxy-4,6-dinitrophenyl)formazan (IV). A diazonium solution obtained from 2 g of picramic acid, 16 ml of water, 0.4 g of NaOH, 3 ml of concentrated hydrochloric acid, and 0.8 g of sodium nitrite was added to a cooled solution of 1.9 g of the 1-ethylbenzimidazolylhydrazone of acetaldehyde in 100 ml of alcohol containing 3.2 g of sodium acetate. After 2 h, the precipitate was filtered and washed with water and alcohol to give 3 g (80%) of fine, fibrous, needles with a dark-green luster (from acetone). Compounds I, II, and VI were similarly obtained.

1-(1-Methyl-2-benzimidazolyl)-3-phenyl-5-(2-hydroxy-4,6-dinitrophenyl)formazan (VII). A suspension of a diazonium salt (from 2 g of picric acid) was added to a cooled solution of 2.5 g of the 1-methylbenzimidazolylhydrazone of benzaldehyde in 100 ml of ethanol containing 3.2 g of sodium acetate. After all of the diazonium salt had been added, the solution was made alkaline to pH 8-9 with 2 N NaOH. After several hours, the mass was diluted with water, and the black precipitate was filtered to give 4 g (90%) of fine, black needles with a red-brown luster (from ethanol).

Products V and X were similarly obtained.

1-Benzothiazolyl-3-phenyl-5-(2-hydroxy-4,6-dinitrophenyl)formazan (XI). A diazonium salt prepared from 1 g of picramic acid was added to a solution of 1.25 g of benzaldehyde benzothiazolylhydrazone in a mixture of ethanol and 2 N hydrochloric acid (added until the mixture gave a slightly acid reaction). The mass was carefully made alkaline with 2 N NaOH until it gave an alkaline reaction. The green solution was diluted with water and neutralized with 2 N HCl. The precipitate was filtered and washed with water to give 1.9 g of fine, black needles with a violet luster (from acetone).

1,3-Diphenyl-5-(2-hydroxy-4,6-dinitrophenyl)formazan (XIII). A suspension of a diazonium salt (from 2 g of picramic acid) was added to a cooled solution of 1.96 g of benzaldehyde phenylhydrazone in 50 ml of pyridine. The red precipitate was filtered and washed with water to give 3 g (70%) of dark-red needles with a green luster (from benzene) and mp 176.5-177°. Found %: C 53.76; H 3.83; N 20.14. $C_{19}H_{14}N_6O_5 \cdot 2H_2O$. Calculated %: C 53.77; H 3.80; N 19.80.

Products III, IX, and XII were similarly obtained, while VIII was obtained in alcohol solution.

LITERATURE CITED

1. Yu. A. Rybakova and N. P. Bednyagina, Khim. Geterotsikl. Soedin., 421 (1965).
2. N. P. Bednyagina and G. N. Lipunova, Khim. Geterotsikl. Soedin., 877 (1969).
3. Yu. Sh. Moshkovskii, T. N. Ignatovich, N. S. Spasokutskii, and M. V. Deichmeister, Khim. Geterotsikl. Soedin., 246 (1965).
4. R. Kuhn and J. Hausser, Ber., 82, 815 (1949).
5. M. I. Ermakova, E. I. Krylov, and I. Ya. Postovskii, Zh. Obshch. Khim., 30, 849 (1960).