BENZAZOLES AND NAPHTHAZOLES

XXXVII.* STRUCTURE AND THERMOCHROMIC PROPERTIES OF 1-BENZOTHIAZOLYL-5-(p-NITROPHENYL)FORMAZANS

G. N. Lipunova, N. N. Gulemina,
A. P. Zeif, and N. P. Bednyagina

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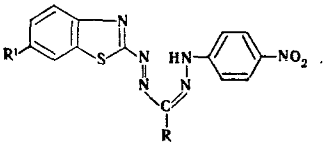
1-Benzothiazolyl-5-(p-nitrophenyl)formazans, which have thermochromic properties, were synthesized. The structure of the compounds was studied by means of IR and UV spectroscopy and quantum-mechanical calculations, the state of the tautomeric equilibrium was established, and the most probable planar conformations of the formazans as a function of the character of the substituent in the 3-position of the formazan chain were found. It is shown that the thermochromism of these compounds in solution is related to dissociation of the hydrogen of the NH bond of the formazan grouping and that the deeply-colored thermally induced form is the anionic aci form.

More and more attention has been directed to the problem of the photochromism and thermochromism of compounds in recent years [2]. The photochromism of formazans was first studied in the triarylformazan series [3]. Both photochromic [4] and thermochromic [5] compounds were found among the formazans of the benzazole series. 1-Benzothiazolyl-3-methyl(phenyl)-5-(p-nitrophenyl)formazans had positive thermochromism, but the nature of the phenomenon and the effect of the substituent in the 3-position remained unstudied.

This communication is devoted to a study of the interrelationship between the structure and thermochromic properties in formazans of the general formula



I–V

I R = CH_3; II R = C_6H_5; III R = $CH(CH_3)_2$; IV R = H; V R = CH_3;
I–IV R′ = H; V R′ = NO_2

Two ν_{NH} bands, which can be assigned to the absorption of the amine (ν_{NH} 3350-3360 cm^{-1}) and imine (ν_{NH} 3450-3460 cm^{-1}) tautomeric forms on the basis of previous investigations [6-8], are observed in the IR spectrum of formazan I in CCl_4 at 3100-3500 cm^{-1} (Table 1). One should note the low intensity of the bands as compared with the spectrum of 1-benzothiazolyl-3-methyl-5-phenylformazan. The decrease in intensity is not associated with the formation of an intramolecular hydrogen bond, inasmuch as the electronic spectrum in the visible region of formazan I in CCl_4 (Table 1) is identical to the spectrum of its methylation product (λ_{max} 456 nm).

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*See [1] for communication XXXVI.

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 492-499, April, 1974. Original article submitted December 26, 1972.

TABLE 1. Physicochemical Characteristics of 1-Benzothiazolyl-5-(p-nitrophenyl)formazans

Compound	IR spectrum, ν_{NH}, cm^{-1}*	Electronic spectrum, λ_{max}, nm					
		CCl_4	benzene	alcohol	alcoholic NaOH	absolute acetone	60% acetone
I	3435, 3354	458	480	475‡	600	468	600
II	None	540—600	540—600	510—590	610	486, 580†	500, 598†
III	3350	522, 570†	520, 570†	504, 570†	616	504, 570†	510, 600†
IV	3485	484 in $CHCl_3$	468	484, 600	608	488	600
V	3343	474 in $CHCl_3$	425	600	590	630	—

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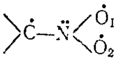
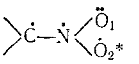
*Compounds I-III in CCl_4; IV and V in $CHCl_3$.

†The long-wave band is an inflection.

‡A different value was erroneously presented in [8].

TABLE 2

Group	Element	$\nu_{\mu\mu}$, eV	$-\beta_{\mu\nu}$, eV	$-W_{\mu}$, eV
	N	15,43	$\ddot{N}—\dot{O}$ 2,37	8,21
	O_1, O_2	18,89		19,8
	C	11,13	$\ddot{N}—\dot{C}$ 2,02	9,94
	N	15,43		14,56
	O_1	18,89	$\dot{N}—\dot{O}$ 2,37	20,9
	O_2	18,89	$\dot{N}—\ddot{O}$ 2,37	19,8
	C	11,13	N—C 2,816	9,94

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*One π electron was assumed to be delocalized over the entire π system.

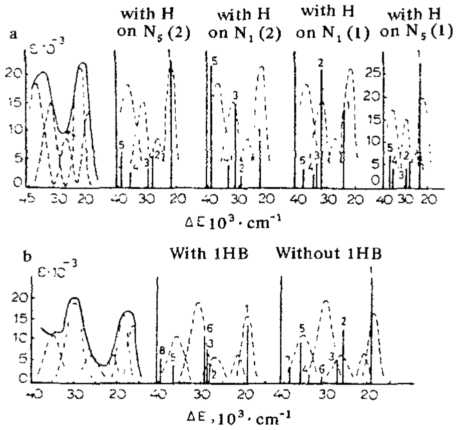

Fig. 1. Electronic absorption spectra of I (a) and II (b) in CCl_4 and their calculated spectra in the anti,trans (1) and syn,trans (2) configurations (H attached to N_1 and H attached to N_5 indicate the amino form with the hydrogen atom attached to N_1 or to N_5; "with IHB" indicates with allowance for the intramolecular hydrogen bond, while "without IHB" indicates disregarding the IHB. The x_{th} value for (2) with H attached to N_1 is 0.964).

The absence of a ν_{NH} band for II in CCl_4 and the appearance of a low-intensity ν_{NH} band at 3308 cm^{-1} in $CHCl_3$ [8] makes it possible to assume a chelate structure with a weak intramolecular hydrogen bond for this compound. When the electronic spectrum of II in CCl_4 was broken down into Gaussian components by the method in [9], we were able to isolate two absorption bands in the visible region at 18,750 cm^{-1} (533 nm) and 21,250 cm^{-1} (470 nm) (Fig. 1). The most intense long-wave band at 18,750 cm^{-1} can be linked to the absorption of the deeply-colored chelate form, while the low-intensity band at 21,250 cm^{-1} characterizes the amino form. The intensity of the absorption at 21,250 cm^{-1} increases in the electronic spectra of formazan II in polar solvents (alcohol and acetone); this can be explained by opening of the chelate ring.

An isopropyl group attached to the meso carbon, like a phenyl group, promotes chelation of the formazan chain; this was previously noted in the arylformazan series [10]. The electronic spectra of formazan III in various solvents have the same character as those of formazan II (Table 1). However, in contrast to II, a low-intensity ν_{NH} band, which attests to the presence in solution of an open amino form in addition to a chelate form, appears in the IR spectrum of formazan III in CCl_4.

Formazan IV behaves unusually. There is only the ν_{NH} band of the imino form at 3485 cm^{-1} in the IR spectrum, and this band is diffuse in character; this may be as-

TABLE 3

Transition	f_{exp}/f_{th} raio for the calculated configurations			
	syn-trans		anti-trans	
	H to N_1	H to N_5	H to N_1	H to N_5
(1) π_1—π_1*	1,48	0,446	0,784	0,312
(2) π_2—π_1*	1,18	0,424	0,14	0,628
(3) Φ_2—π_1*	0,51	3,13	2,23	3,2
(5) π_1—NO_2*	0,558	1,86	11,1	1,72

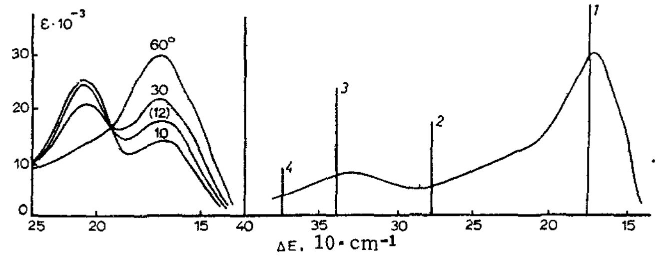

Fig. 2. Temperature variations of the electronic spectra of I in aqueous alcohol solution (the temperature of the reverse transition is indicated in parentheses); experimental spectrum for aqueous alcohol solution at 60° and calculated spetrum for aci form I.

sociated with the presence of intermolecular hydrogen bonds between the nitro and NH groups. Two absorption maxima (Table 1), of which the long-wave band that coincides in position with the absorption maximum of the Na salt of IV is probably affiliated with the aci form that arises due to intermolecular proton transfer, are observed in the electronic spectra of an alcohol solution of formazan IV.

The introduction of an NO_2 group into the 6-position of the benzothiazole ring causes a shift in the amine-imine equilibrium to favor the amine form. The position of the long-wave absorption band in the electronic spectra of V depends markedly on the nature of the solvent. In nonpolar solvents, V absorbs at 435 or 475 nm as compared with 600 nm in polar solvents.

To precisely determine the structure of the formazans we performed quantum-mechanical calculations of their π-electron systems by the Pariser—Parr—Pople method with the use of parameters previously employed for compounds of this class [11]. The parameters of the nitro and aci-nitro groups, which were found by the method in [12, 13], are presented in Table 2. The angles and interatomic distances were assumed to be the same as those in nitrobenzene [14]. Because of the absence of x-ray diffraction data for the aci-nitro group, we used the bond lengths and valence angles of similar compounds [14]. All of the compounds were assumed to be coplanar.

The site of localization of the acid hydrogen of the formazan grouping had to be precisely determined. In [15] it was shown that the hydrogen in 1-phenyl-5-(p-nitrophenyl)formazan is attached to the nitrogen atom linked to the p-nitrophenyl grouping. The amino forms of formazans I and II were therefore calculated for a model with a hydrogen atom attached to the N_1 and N_5 atoms.

Proceeding from the IR and electronic spectral data, we calculated I for the amine tautomeric form of the anti-trans and syn-trans configurations relative to the C = N bond of the formazan ring, which differ most from one another with respect to calculations of the electronic spectra [11]. Inasmuch as the anti-trans form excludes the chelate structure, the calculation of II was made for the syn-trans configuration of the amino form with intramolecular hydrogen bonding and without it.

The experimental spectrum of formazan I in CCl_4 was broken down into its Gaussian components, as in the case of II (Fig. 1).†

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† Long-wave absorption bands at 16,800 and 16,750 cm^{-1}, respectively, the assignment of which is not discussed in this paper, were isolated during the analysis of the spectra of I and II in CCl_4.

TABLE 4

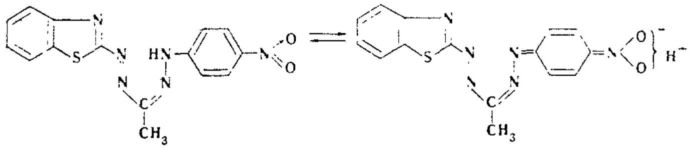
Compound	I	II	III	IV	V
pK_a	8,20 ±0,02	8,94 ±0,04	9,53 ±0,02	7,38 ±0,04	6,73 ±0,04

A comparison of the experimental and calculated spectra of I and II, which are presented in Fig. 1, shows that I exists in CCl_4 as an equilibrium mixture of tautomeric forms of syn-trans configurations with the hydrogen atom attached to N_1 or N_5, while predominance of the chelate form is characteristic for II. Moreover, as in [11], the long-wave band is affiliated with the (1) $\pi_1-\pi_1^*$ transition from the upper filled π_1 level, localized on Φ_1, to the lower vacant π_1^* level, localized on the formazan grouping. The following bands are affiliated with the transitions: (2) $\pi_2-\pi_1^*$; (3) $\Phi_2-\pi_1^*$; (4) $\Phi_1-\pi_1^*$; (5) $\pi_1-NO_2^*$; (6) $(\Phi_1+\Phi_3)-\pi_1^*$; (7) $P-\pi_1^*$; (8) $NO_2-\pi_1^*$. Here, Φ_1 and Φ_2 are the states localized in the p-nitrophenyl and benzothiazole residues, respectively. The symbols and localization of the remaining states are the same as in [11]. The correctness of the selection of the configurations for formazan I (syn-trans rather than anti-trans) is confirmed by the f_{theor} ratio (Table 3).

Formazans I-IV display positive thermochromism, and the ease of the thermochromic transitions depends on the structure. The most distinct thermochromic transitions in the change in color from red ($\lambda_{\max}$ 475 nm) to blue ($\lambda_{\max}$ 600 nm) were obtained for I in 75% alcohol for formazan I concentrations of $5 \cdot 10^{-5}$ to $5 \cdot 10^{-4}$ mole/liter (Fig. 2). In contrast to I, the thermochromic transitions of formazans II and III under the same conditions are not so distinct. There is no isopiestic point in the electronic spectra, and the thermochromic transition is characterized only by an increase in the absorption intensity at 600 nm. Heating of an alcohol solution of IV is accompanied by an increase in the absorption intensity at 480 nm and a decrease in the absorption at 600 nm (Fig. 3), i.e., in this case there is an irreversible transition of the blue form to the red form. However, after water is added, subsequent heating of the dilute solution leads to thermochromic transitions that are similar to the transitions for formazan I. Formazan V does not have thermochromic properties, inasmuch as it has an absorption maximum at 600 nm (blue form) in aqueous alcohol solution.

The nature of the thermochromic transitions was investigated in greater detail in the case of formazan I. Its light-absorption curves have a distinct isopiestic point at 524 nm, which is evidence for equilibrium of two forms in solution (Fig. 2). As established above, I exists in the amino form ($\lambda_{\max}$ 475 nm) in alcohol solution, and the color is shifted bathochromically in alcoholic alkali; the electronic spectrum of the anion coincides with the spectrum of the thermally induced form with respect to the position of the maximum and the intensity. The introduction of a nitro group into the phenyl ring in the para-position relative to the N_5 atom increases the acidity of the N–H bond (pK_a 8.2) as compared with unsubsitituted 1-benzothiazolyl-3-methyl-5-phenylformazan (pK_a 9.1). Thermochromic transitions appear for I only in aqueous alcohol solutions, the pH of which is 8.3, i.e., a value close to the pK_a of I, and are absent in alcohol solution (pH 7.1).

All of this provides a basis for assuming that both the Na salt and the blue tautomeric form have close electronic structures and that the thermochromism is related to dissociation of the formazan at the NH bond and transition of the starting amino form (I) to the aci form (2) [sic]. A similar sort of mechanism was presented in [16] for the explanation of the photochromism of dinitrobenzylpyridine.



To precisely determine the structure of the blue tautomeric form we made quantum-mechanical calculations of the π-electron system of I in the aci form (the parameters are presented in Table 2).

A comparison of the experimental and calculated spectra of I (Fig. 2) confirms that the long-wave absorption band at 600 nm (the blue form) is affiliated with the $\pi_1-\pi_1^*$ transition of the aci form.

Proceeding from the above assumption regarding the mechanism of the thermochromic transitions, it was of interest to examine the thermochromic properties of the remaining formazans at pH values of aqueous alcohol solutions that are close to the pK_a values. For this, we measured the apparent ionization constants of I-V, the pK_a values of which are presented in Table 4.

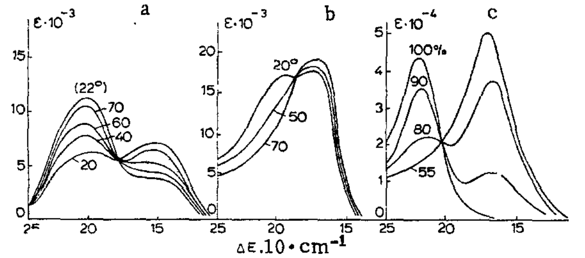


Fig. 3. Temperature variations of the electronic spectra of formazans IV (a) and II (b); electronic spectrum of I in acetone as a function of the percentage of water (c).

The ionization constants obtained are in good agreement with the data on the structure of I-V. The acid properties of II and III are weakened, while there is a general tendency for an increase in the acid properties in the 5-(p-nitrophenyl)-substituted formazans.

The temperature dependence of the electronic spectrum of II in an alcohol buffer solution with pH 8.8, which is close to the pK_a value, is presented in Fig. 3 and shows that the pattern of the thermochromic transitions is more distinct than in an aqueous alcohol solution with pH 8.15. A similar dependence is also characteristic for III.

A comparison of the long-wave absorption band in the experimental spectrum of the thermally induced II and III forms with the λ_{max} values of the Na salts of the formazans shows that the thermochromism is due to dissociation and a shift of the tautomeric equilibrium of the amino and aci forms in these cases also. The appearance of the aci form when aqueous alcohol solutions of II and III with pH values far from the pK_a values are heated is hampered because of the presence in the solutions of the tautomeric chelate form, and this also explains the indistinct spectral characteristics of the thermochromic transitions.

The pK_a values of formazans IV and V are lower than the pH values of their alcohol solutions, and the aci form is observed (IV) or predominates (V) for them even in cold solutions.

An investigation of the effect of the solvent on the thermochromic behavior of I-V showed that the shift in the equilibrium to favor the aci form in aqueous acetone solutions depends to a marked degree on the acetone–water ratio, even without heating (Fig. 3 and Table 1). In this case, first of all, the increase in the pH of the aqueous acetone solution as a function of the percentage of water and, secondly, the increase in the lability of the proton of the NH bond due to the acceptor character of acetone probably affect the shift of the equilibrium. Heating of 70-80% acetone solutions is characterized by distinct thermochromic transitions for formazans I, II, and IV.

EXPERIMENTAL

The electronic spectra of solutions of I-V ($5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ M) were recorded with VSU-2P*, SF-4, and SF-2M spectrophotometers. The IR spectra of saturated solutions of the formazans in CCl_4 in the LiF region were obtained with a UR-20 spectrometer. The π-electron systems were calculated with a Minsk-2 computer. The apparent ionization constants of the formazans were measured spectrophotometrically [17] in 50% alcohol buffer solutions (ammonia–acetate buffer); the working concentration of the formazans was $5 \cdot 10^{-5}$ M, the temperature was 22°, and the analytical wavelength was 600 nm.

The synthesis of I and II is described in [8].

Isobutyraldehyde 2-Benzothiazolylhydrazone. A 0.025-mole sample of isobutyraldehyde was added to a suspension of 0.02 mole of 2-hydrazinobenzothiazole VII in 40 ml of alcohol, after which the reaction mixture was heated for 10 min, during which all of the solids dissolved. The mixture was cooled to precipitate the hydrazone. Workup gave 65% of VI with mp 165° (alcohol). Found: C 60.5; H 6.0; N 18.8%. $C_{11}H_{13}N_3S$. Calculated: C 60.3; H 5.9; N 19.2%.

1-Benzothiazolyl-3-isopropyl-5-(p-nitrophenyl)formazan (III). A diazonium salt solution, prepared from 0.05 mole of p-nitroanaline, was added gradually with cooling to a solution of 0.05 mole of IV in alcohol–pyridine (2 : 1) containing 0.01 mole of CH_3COONa. Compound III was precipitated by bringing the pH of the solution up to 7 by treatment with 2 N NaOH. Workup gave 45% of III with mp 172° (nitromethane). Found: C 55.8; H 4.5; N 22.8%. $C_{17}H_{16}N_6O_2S$. Calculated: C 55.6; H 4.6; N 22.7%.

Acetaldehyde 6-Nitro-2-benzothiazolylhydrazone. This compound was obtained by the method used to prepare VI. The yield of product with mp 288-290° (alcohol) was 60%. Found: C 45.9; H 3.6; N 23.8%. $C_9H_8N_4O_2S$. Calculated: C 45.8; H 3.4; N 23.7%.

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*The authors thank V. I. Minkin for allowing us to use this spectrophotometer.

1-(6-Nitrobenzothiazolyl)-3-methyl-5-(p-nitrophenyl)formazan (V). This compound was obtained by the method used to prepare III, but the isolation was carried out at pH 5-6. Workup gave 56% of V with mp 237° (nitromethane). Found: C 45.7; H 3.3%. $C_{15}H_{11}N_7O_4S \cdot H_2O$. Calculated: C 46.0; H 3.3%.

Nitroformaldehyde p-Nitrophenylhydrazone (VIII). This compound was obtained by the method in [18].

1-Benzothiazolyl-5-(p-nitrophenyl)formazan (IV). Saturated solutions, each containing 0.05 mole of VII and VIII in pyridine, were mixed, and the mixture was heated for 15 min and allowed to stand for 15 days. The resulting precipitate was removed by filtration and washed with a small amount of alcohol. Workup gave 75% of V with mp 250° (dimethylformamide). Found: C 51.4; H 3.3; N 26.0%. $C_{14}H_{10}N_6O_2S$. Calculated: C 51.5; H 3.0; N 25.8%.

LITERATURE CITED

1. L. P. Sidorova and N. P. Bednyagina, Khim. Geterotsikl. Soedin., 1138 (1972).
2. G. Hayasi and K. Maeda, Kagaku-no Reiki, 22, No. 1, 1 (1968).
3. I. Hausser, D. Jerhel, and K. Kuhn, Ber., 84, 651 (1951).
4. N. P. Bednyagina, G. N. Lipunova, and G.A. Mokrushina, USSR Author's Certificate No. 241,442 (1969); Byul. Izobr., No. 14, 23 (1969).
5. Yu. A. Rybakova, G.N. Lipunova, and N. P. Bednyagina, USSR Author's Certificate No. 296,791 (1971); Byul. Izobr., No. 9, 86 (1971).
6. N. P. Bednyagina and G. N. Lipunova, Khim. Geterotsikl. Soedin., 877 (1969).
7. A. P. Zeif, L. N. Shchegoleva, G.N. Lipunova, A.P. Novikova, and N. P. Bednyagina, Zh. Organ. Khim., 6, 1332 (1970).
8. N. P. Bednyagina, N. V. Serebryakova, and G.N. Lipunova, Khim. Geterotsikl. Soedin., 342 (1967).
9. V. D. Vdovenko (editor), Spectroscopic Methods in the Chemistry of Complexes [in Russian], Khimiya, Moscow–Leningrad (1964), p. 102.
10. F. Neugebauer and H. Frischmann, Ann., 706, 107 (1967).
11. A. P. Zeif, G. N. Lipunova, N. P. Bednyagina, L. N. Shchegoleva, and L. I. Chernyavskii, Zh. Organ. Khim., 6, 2590 (1970).
12. J. Fischer, H. Olmers, and M. Sundbom, Acta, Chem. Scand., 22, 607 (1968).
13. O. Gropek and P. N. Scancke, Acta Chem. Scand., 23, 2695 (1969).
14. Tables of Interatomic Distances, Spec. Pull., London, No. 11 (1958).
15. F. A. Neugebauer and M. Jenne, Tetrahedron Lett., 10, 771 (1969).
16. J. D. Magarum, L. J. Miller, E. Saito, M. Brown, and R. Hardwick, J. Phys. Chem., 66, 2434 (1962).
17. A. Albert and E. Serjeant, Ionization Constants of Acids and Bases, Barnes and Noble, Inc. (1962).
18. R. I. Ogloblina, N. P. Bednyagina, and N. N. Gulemina, Khim. Geterotsikl. Soedin., 393 (1972).