RESEARCH IN THE BENZAZOLE AND NAPHTHAZOLE SERIES

XXXVIII.* EFFECT OF AN o-NITRO GROUP ON THE STRUCTURE AND PROPERTIES OF BENZOTHIAZOLYLFORMAZANS

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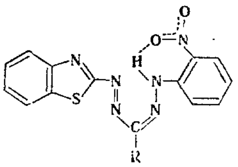
The ortho effect of a nitro group in newly synthesized 1-benzothiazolyl-5-(o-nitrophenyl) formazans was investigated. It is shown that these compounds exist in solution as chelates with the participation of the nitro group. The acid–base and thermochromic properties of the formazans were studied.

The effect of ortho substituents (CH_3, OH, COOH) in the 5 position of the phenyl ring on the structure and properties of benzothiazolylformazans was examined in [2, 3]. It was noted that in all cases one observes a steric effect of the substituent that also affects the structure of the formazans and their complexing properties. Our investigations have shown that the introduction of a nitro group into the ortho position has a substantial effect on the state of the tautomeric equilibria of the formazans.

The ortho effect of the nitro group was studied for a series of benzothiazolyl formazans (Table 1) as compared with the analogous previously described [1] compounds containing a nitro group in the para position relative to $N_{(5)}$. A distinct band of ν_{NH} vibrations is observed in the IR spectra of I-V in CCl_4 at 3200-3500 cm^{-1} (Table 1). The decrease in the frequency of the stretching vibrations by 40-60 cm^{-1} as compared with the ν_{NH} bands of formazans containing a p-nitro group [1] makes it possible to assume the presence of an intramolecular hydrogen bond of the type:



A

i.e., the o-nitro group is included in the formation of a chelate ring (structure A). This sort of intramolecular hydrogen bond in molecules with π conjugation should cause a bathochromic shift of the absorption band in the electronic spectra similar to that which was established in [4, 5] in a study of the structure and electronic spectra of o-nitroaniline. In fact, the long-wave absorption band for I-V in neutral solvents (CCl_4 and benzene) is shifted bathochromically by 20-30 nm as compared with the para analogs.

The ionization constants of I-VI were measured (see Table 1 for the pK_a values). The acid properties of formazans containing an o-nitro group are reduced as compared with p-nitrophenylformazans. The linear relationship between $\Delta\nu_{NH}$ and ΔpK_a of the formazans (Fig. 1) is a confirmation that the differences between the compounds are due to intramolecular hydrogen bonding. The deviation of point 4 from this line is associated with the fact that it is difficult to evaluate the $\Delta\nu_{NH}$ and ΔpK_a values for IV, inasmuch as the presence of intermolecular hydrogen bonds [1] that affect the magnitude of the pK_a value of the formazan and the position of the ν_{NH} frequency is characteristic for 1-benzothiazolyl-3-H-5-(p-nitrophenyl)formazan.

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*See [1] for communication XXXVII.

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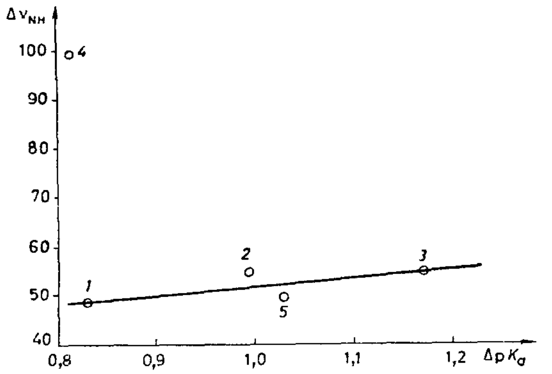


Fig. 1

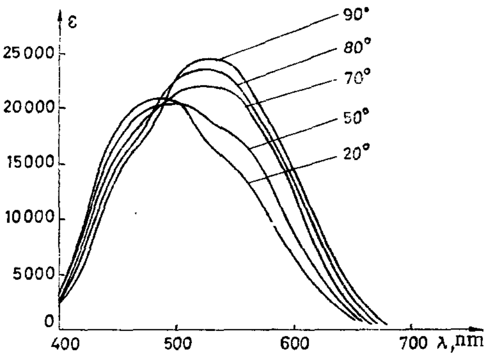


Fig. 2

Fig. 1. Dependence of ΔpK_a on $\Delta\nu_{NH}$ [$\Delta pK_a = pK_a$ of 1-benzothiazolyl-5-(o-nitrophenyl) formazan (o)$-pK_a$ of 1-benzothiazolyl-5-(p-nitrophenyl)formazan (p), $\Delta\nu_{NH} = \nu_{NH(p)} - \nu_{NH(o)}$]: 1) I; 2) II; 3) III; 4) IV; 5) V.

Fig. 2. Light-absorption curves of formazan I in a propanol-buffer solution (pH 8.6) at various temperatures.

The presence of a phenyl group attached to the meso carbon atom in II and of an electron-acceptor nitro group in benzothiazole V promotes partial opening of the chelate ring of structure A and the appearance of a tautomeric form with a free amino group [the IR spectra contain a second ν_{NH} band at 3340 (V) and 3335 (II) cm^{-1}, Table 1].

The behavior of 1-benzothiazolyl-3-methyl-5-(2,4-dinitrophenyl)formazan (VI), for which the o- or p-nitro group has the dominant effect on the structure and properties, depending on the character of the solvent, is peculiar. Only the ν_{NH} absorption band at 3290 cm^{-1} characteristic for o-nitrophenylformazans I-V is observed in the IR spectrum of formazan VI. The electronic spectra of VI in nonpolar solvents are also similar to the spectra of formazan I, while the nitro group in the para position has the maximum effect on the acid properties and the color of the compounds in polar solvents. The pK_a values of VI and 1-benzothiazolyl-3-methyl-5-(p-nitrophenyl)formazan (VII) are close (Table 1), and the electronic spectra of formazan VI in alcohol and acetone contain the absorption band of the anionic form (λ_{max} 644 nm).

All of the information stated above provides a basis for assuming that the presence of an intramolecular hydrogen bond, the possibility of the formation of which was previously assumed [6] for arylformazans with an o-nitro group, is characteristic for formazans containing an o-nitro group.

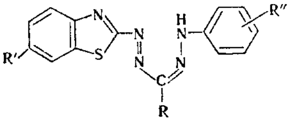
It was of interest to investigate the thermochromic properties of I-VI in order to compare them with the previously studied thermochromism of 1-benzothiazolyl-5-(p-nitrophenyl)formazans [1] in aqueous alcohol solution. It was found that formazans I-VI do not undergo a change in color on heating in aqueous alcohol solutions. Thermochromic transitions (red-violet) were observed when alcohol buffer solutions with pH values close to the pK_a values of the compounds were used, but the transitions were less distinct than in the case of p-nitrophenylformazans. Thus an isopiestic point is absent in the spectrum of I, and the bathochromic shift between the thermally induced and starting forms is 60 nm (Fig. 2), while it reaches 120 nm for 1-benzothiazolyl-3-methyl-5-(p-nitrophenyl)formazan. The reason for the smaller thermal induction effect of I-V is, on the one hand, the bluer color of the starting form, which has a chelate structure (λ_{maxVII} 475, λ_{maxI} 510 nm), and, on the other hand, the deeper color of the thermally induced form, which is an anion (λ_{maxVII} 606 nm, λ_{maxI} 568 nm). In contrast to I-V, an isopiestic point is observed in the spectrum when an alcohol buffer solution of formazan VI (pH = 8.2) is heated, and the bathochromic shift is 180 nm, i.e., it is close to VII with respect to its thermochromic properties.

Thus the unique character of the o-nitro group is manifested both in the structure of the formazans and in their properties.

EXPERIMENTAL

The IR spectra of saturated CCl_4 solutions were recorded with a UR-20 spectrometer at 3200-3500 cm^{-1} (LiF prism). The electronic spectra were recorded with an SF-4 spectrophotometer. The pK_a values of the compounds were determined as in [1].

TABLE 1



Compound	R	R′	R″	ν_{NH}, CCl_4, cm^{-1}	λ_{max}, nm					pK_a
					CCl_4	benzene	acetone	alcohol	alcohol, NaOH	
I	CH_3	H	o-NO_2	3305	470 530*	480 560*	470 560*	510	568	9,03±0,05
II	C_6H_5	H	o-NO_2	3335 3280	550	520—580	508 570*	508 580*	580	9,93±0,04
III	$CH(CH_3)_2$	H	o-NO_2	3295	546	548	540	560	558	10,69±0,07
IV	H	H	o-NO_2	3285	504	488 550*	476	506	560	8,19±0,03
V	CH_3	NO_2	o-NO_2	3340 3290	510 564	486—510	482 606	564	564	7,76±0,05
VI	CH_3	H	o,p-Di-NO_2	3290	480 562*	480 540*	464 640	466 644	644	8,35±0,02
VII[1]	CH_3	H	p-NO_2	3435 3354	458	480	468	475	606	8,20±0,02

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* Shoulder

TABLE 2. Characteristics of the Compounds Obtained

Compound	mp, °C	Empirical formula	Found, %			Calc., %		
			C	H	N	C	H	N
I	220[a]	$C_{15}H_{12}N_6O_2S$	53,5	3,6	—	52,9	3,5	—
II	205[a]	$C_{20}H_{14}N_6O_2S$[d]	59,9	3.7	—	59,7	3,5	—
III	198[a]	$C_{17}H_{17}N_6O_2S$	55,7	4,4	22,9	55,6	4,6	22,7
IV	235[b]	$C_{14}H_{10}N_6O_2S$	51,1	3,1	25,8	51,5	3,1	25,8
V	250[c]	$C_{16}H_{12}N_7O_4S$	46,3	3,0	24,8	46,7	2,9	25,4
VI	255[c]	$C_{16}H_{12}N_7O_4S$	46,9	3,0	25,1	46,7	2,9	25,4

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[a] From alcohol. [b] From nitromethane–alcohol (1 : 1). [c] From nitromethane. [d] Found: S 7.7%. Calculated: S 7.9%.

1-Benzothiazolyl-3-H-5-(o-nitrophenyl)formazan (IV). This compound was obtained by the method used to prepare 1-benzothiazolyl-3-H-5-(p-nitrophenyl)formazan [1]. Formazans I-III, V, and VI were obtained by coupling of the appropriate hydrazones with a solution of the o-nitrobenzenediazonium salt. The results of elementary analysis and the melting points of the compounds are presented in Table 2.

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