RESEARCHES ON BENZ- AND NAPHTHAZOLES

XVII. Unsymmetrical Formazans of the Benzothiazole and Benzoxazole Series*

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1-Benzothiazolyl- and 1-benzoxazolyl-3-methyl(or phenyl)-5-arylformazans are synthesized. The depth of the color of the similarly structured 1-benzazolyl-5-arylformazans depends on the nature of the benzazole group. The power of the chromophores decreases in the following order: 1-alkyl-benzimidazole > benzothiazole > benzoxazole. Unsymmetrical 1-benzazolyl-5-arylformazans exhibit positive solvatochromism.

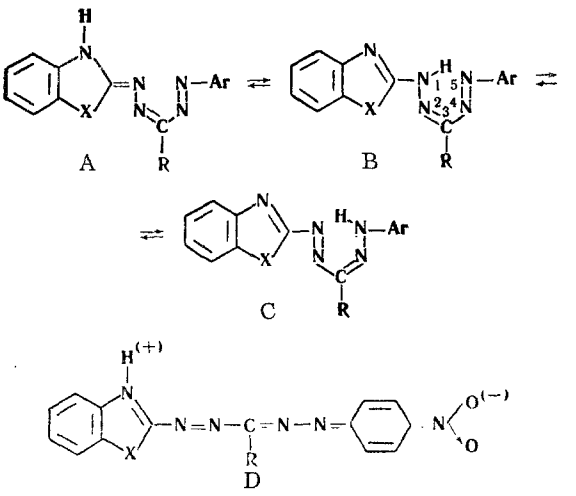
It is only quite recently that a start has been made with the study of unsymmetrical formazans of the azole and benzazole series with heterocyclic groups at position 1(5), thiazole, selenazole, and oxazole formazans [1, 2]. The formazans of the benzazole series which have been prepared are 1-benzimidazolyl-3-methyl-5-arylformazans [3].

Continuing previous work [3], we have prepared unsymmetrical formazans of the benzothiazole and benzoxazole series by coupling aryl diazonium salts with benzothiazolyl(3)- and benzoxazolyl(2)-hydrazones of acetaldehyde and benzaldehyde (Table 1).

Like 1-benzimidazolyl-5-arylformazans [3], formazans of the benzothiazole and benzoxazole series are decomposed and decolorized in acid solution, while in ethanolic sodium hydroxide they are converted into deeply colored sodium salts. These formazans also exhibit a capacity to retain in the composition of the molecule a component of crystallization, most frequently water. The substituent at position 3 in the formazan ring powerfully affects the color of the compound: 3-phenyl derivatives are more deeply colored (by 50–70 mμ) than the corresponding 3-methyl derivatives. The nature of the substituent in the aryl group (position 5) is also of great significance: the nitro group evokes considerable deepening of the color as compared with the methyl group.

For unsymmetrical formazans, where positions 1 and 5 are occupied by substituents of different accepting capacity, it is hardly possible to speak of a strong equality of bonds in the chelate formazan ring. On the other hand, if one substituent is much more electronegative, than the other, polarization of the molecule and breaking of the chelate ring must occur. Then mutual interconversions of spatial isomers can also occur in solution.

Unlike 1, 5-diarylformazans, heterocyclic formazans can also exhibit tautomerism, and obviously depending on the natures of the heterocyclic ring and of the substituents in the aryl group, equilibrium can be displaced towards one side or the other.



The given formazans can be regarded as internally ionized dyes, where limiting structures with unseparated charges (A, B, or C) predominate over bipolar ion structures (e.g., D). Such dyes should exhibit positive solvatochromism, according to the data of [4]. Actually, when determining the absorption spectra in the visible region of 1-benzazolyl-3-methyl-5-p-nitrophenylformazans, a bathochromic shift of the absorption maximum with increasing solvent polarity can be observed (Table 2).

When comparing the colors of dyes of one type of structure, where is a striking regularity: formazans of the benzothiazole series are more deeply colored than formazans of benzoxazole, but with respect to depth and intensity of color, they are both exceeded by benzimidazole formazans. Probably the depth of color is directly connected with the basicity of the heterocyclic ring. The new formazans prepared are being studied as ligands for chelate complexing.

EXPERIMENTAL

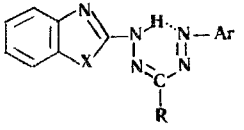
2-Hydrazinobenzothiazole was prepared from 2-chlorobenzothiazole (by boiling with hydrazine hydrate as described in [5]). Mp 195–196° (the literature gives 205° [6]).

Acetaldehyde benzothiazolylhydrazone was obtained by adding 0.02 mole acetaldehyde to an EtOH solution of 0.01 mole 2-hydrazinobenzothiazole and keeping the mixture at 30° for 1/2 hr. Yield 90%, mp 194–195° (ex n-heptane). Found: N 21.39%. Calculated for $C_9H_9N_3S$: N 21.98%.

*For Part XVI see [3].

Table 1

1-Benzothiazolyl- and 1-Benzoxazolyl-5-arylformazans



Compound no.	X	R	Ar	mp. °C	λ_{max}, mμ (ε · 10⁻⁴)		Formula	Found, %			Calculated, %			Yield, %
					Neutral solvent $CHCl_3$	Alkaline ethanol solvent		C	H	N	C	H	N	
I	S	CH_3	p-$C_6H_4CH_3$	136—137	422 (1.61)	514 (5.045)	$C_{16}H_{15}N_5S$*	62.38	4.93	22.60	62.13	4.85	22.65	75
II		CH_3	p-$C_6H_4NO_2$	229—230	478 (3.43)	510 (4.57)	$C_{15}H_{12}N_6O_2S \cdot CO(CH_3)_2$	54.34	4.26	20.86	54.26	4.55	21.10	53
III		CH_3	o-C_6H_4COOH	228—229	476 (3.86)	512 (5.105)	$C_{16}H_{13}N_5O_2S \cdot H_2O$**	53.60	4.26	20.17	53.63	4.19	19.55	41
IV		C_6H_5	p-$C_6H_4CH_3$	161—162	476 (1.44)	520 (4.28)	$C_{21}H_{17}N_5S \cdot 1^1/_2H_2O$	63.00	5.02	17.89	63.31	5.02	17.59	81
V		C_6H_5	p-$C_6H_4NO_2$	213—214	562 (3.07)	608 (5.50)	$C_{20}H_{14}N_6O_2S$	60.47	3.58	21.29	59.70	3.48	20.89	84
VI	O	CH_3	p-$C_6H_4CH_3$	115—116	410 (1.51)	488 (4.03)	$C_{16}H_{15}N_5O \cdot H_2O$	62.55	5.64	22.54	61.72	5.46	22.50	51
VII		CH_3	p-$C_6H_4NO_2$	193—195	448 (1.49)	566 (3.32)	$C_{15}H_{12}N_6O_3 \cdot H_2O$	52.09	4.08	24.60	52.63	4.09	24.54	55
VIII		CH_3	o-C_6H_4COOH	157—158	476 (3.35)	484 (3.38)	$C_{16}H_{13}N_5O_3 \cdot H_2O$	56.67	4.69	20.43	56.30	4.39	20.52	30
IX		C_6H_5	p-$C_6H_4CH_3$	158—159	456 (2.26)	498 (3.74)	$C_{21}H_{17}N_5O$	70.48	4.97	20.16	70.98	4.79	19.71	50
X		C_6H_5	p-$C_6H_4NO_2$	174—175	512 (1.38)	547 (4.57)	$C_{20}H_{14}N_6O_3$	61.42	4.09	21.75	61.91	3.63	21.76	57

*Found: 10.57%; Calculated S 10.35%.

**Found: S 8.96%. Calculated S 8.94%.

Table 2

Absorption Spectra of 1-Benzazolyl-3-methyl-5-p-nitrophenyl-formazans in Various Solvents

Compound	λ_{max}, mμ (ε · 10⁻⁴)		
	Benzene	Acetone	Nitrobenzene
1-Benzylbenzimidazolyl [3]	510 (4.19)	522 (4.53)	530 (3.77)
Benzothiazolyl (II)	466 (2.00)	468 (3.96)	480 (3.79)
Benzoxazolyl (VII)	440 (1.84)	444 (2.61)	456 (2.08)

Benzaldehyde benzothiazolylhydrazone was prepared by heating a solution of 0.05 mole 2-hydrazinobenzthiazole in 30 ml EtOH with 0.05 mole benzaldehyde. Yield quantitative, mp 221°–222° (ex EtOH). Found: N 16.99%. Calculated for $C_{14}H_{11}N_3S$: N 16.60%.

1-Benzothiazolyl-3-methyl-5-p-tolylformazan (II). A diazo solution, from 0.005 mole p-toluidine, was added to a cooled solution of 0.005 mole acetaldehyde benzothiazolylhydrazone in 50 ml EtOH. The mixture was brought to pH 5–6 with 2 N NaOH, and left for the formazan to separate out. It formed a fine crystalline reddish-brown powder (ex petrol ether).

Formazans (II–IV). These were prepared similarly to above. The coupling with the nitrobenzenediazonium salt proceeded in more acid solution. Compound II—brown needles (ex acetone), III—red needles (ex EtOH), IV and V—brown and dark brown minute needles (ex EtOH).

2-Hydrazinobenzoxazole was prepared from benzoxazolylsulfonic acid, by boiling with hydrazine hydrate*, mp 153°–154° (the literature [6] gives mp 154°–155°).

Acetaldehyde benzoxazolylhydrazone was prepared by mixing 2-hydrazinobenzoxazole and acetaldehyde in ether. Yield quantitative, mp 159°–164° (ex dilute EtOH). Found: N 23.56%. Calculated for $C_9H_9N_3O$: N 24.00%.

Benzaldehyde benzoxazolylhydrazone was prepared by heating together in ethanol equimolecular amounts of 2-hydrazinobenzoxazole and benzaldehyde. Yield quantitative. Mp 208°–209° (ex MeOH). Found: N 17.76%. Calculated for $C_{14}H_{11}N_3O$: N 17.72%.

1-Benzoxazolyl-3-methyl-5-p-tolylformazan (VI). A diazo solution made from 0.5 g p-toluidine, 7 ml 2 N HCl, and 0.35 g $NaNO_2$ was added to a cooled solution of acetaldehyde benzoxazolylhydrazone in 40 ml EtOH. After 20 min stirring the reaction products had turned dark red. 2 N NaOH was added dropwise, to bring the solution to pH 5–6, then about 30 ml water added, and the whole left overnight. The formazan which separated as a reddish-brown powder was recrystallized from dilute EtOH.

The other benzoxazole formazans were prepared similarly. Compound VII—minute brown crystals (ex dilute acetone), VIII—violet-brown powder (ex dilute EtOH), IX—dark brown, and X—brownish-violet fine crystalline powder (ex MeOH).

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