

INVESTIGATIONS IN THE BENZAZOLE AND  
NAPHTHAZOLE SERIES

XXX.\* STRUCTURE AND COLOR OF 1-BENZAZOLYL-3-  
PHENYL(METHYL)-5-(p-NITRO)[DIMETHYLAMINO]-  
PHENYLFORMAZANS

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The introduction of electron-accepting or electron-donating groups in the phenyl ring of unsymmetrical benzazolyformazans causes deepening of the color of the formazans and their complexes with metals. Nitro- and dimethylamino-substituted formazans have a nonchelate structure with predominance of imino tautomeric forms for the benzimidazolyl and amino forms for the benzothiazolyl or benzoxazolylformazans.

The effect of electron-accepting (nitro) or electron-donating (dimethylamino) groups on the structure and color of benzazolyformazans and their salts and metal complexes was investigated by us for formazans I-XII (Table 1).

It has been previously established [2-4] that, depending on the nature of the heterocycle and the substituent in the 3 position (methyl, phenyl), unsymmetrical benzazolyformazans have an open or chelate structure. It was established that  $\nu_{\text{NH}}$  in the  $3450\text{ cm}^{-1}$  region for open formazans is due to the imino tautomeric form with the hydrogen on the nitrogen of the benzazole ring, while  $\nu_{\text{NH}}$  in the  $3350\text{ cm}^{-1}$  region is due to the amino tautomeric form with the hydrogen on  $N_1$  of the formazan group.

As seen from the IR spectral data (Table 1), the introduction of both nitro and dimethylamino groups, regardless of the nature of the heterocycle and the substituent in the 3 position, leads to opening of the chelate ring. Moreover, judging from the position of the  $\nu_{\text{NH}}$  frequencies for I-IV, the imino form prevails, while the amino tautomeric form dominates for V-VIII and IX-XII.

Both the nitro and dimethylamino groups introduce considerable perturbations in the  $\pi$ -electron system of formazans. Compounds I-XII are much more deeply colored in solution than the corresponding unsubstituted formazans. The greatest deepening of color is observed for benzothiazolyl- and benzoxazolylformazans with a nitro group (V, VII, IX, and XI,  $\Delta\lambda_{\text{max}} = 100\text{--}160\text{ nm}$ ). For XI there are two absorption maxima (456, 566) in the visible region of the spectrum, while the IR spectrum has two  $\nu_{\text{NH}}$  frequencies; this is evidence for the presence of a mixture of amino and imino forms in  $\text{CHCl}_3$  solutions.

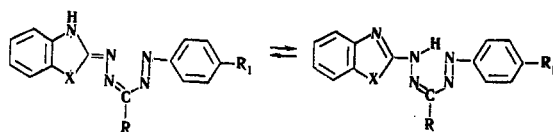
In contrast to unsubstituted formazans, formazans with a nitro group have different bathochromic effects during the formation of sodium salts, depending on the heterocycle. The effect is rather large for benzimidazolylformazans (75-105 nm), while for benzothiazolyl- and benzoxazolylformazans it is very small or completely absent.

It may be assumed that the structure of the dipolar ion (A) makes an appreciable contribution to the imino tautomeric form for benzimidazolylformazans, as evidenced by the large dipole moment of these

\*For Communication XXIX, see [1].

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TABLE 1.



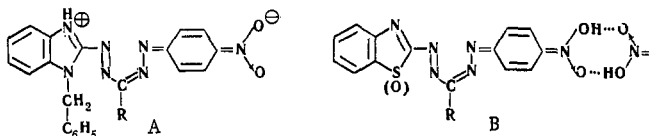
Comp.	X	R	R <sub>1</sub>	ν <sub>NH</sub> , cm <sup>-1</sup> (CHCl <sub>3</sub> )	λ <sub>max</sub> , nm			λ <sub>max</sub> (nm) of metal complexes		
					Alcohol	Δλ <sub>max</sub> Alcoholic NaOH	Alcoholic NaOH	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Co <sup>2+</sup>
I	NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	NO <sub>2</sub>	3464	554	80	628	678	666	680—710
II	NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	3450	508	34	556	660	466; 586; 750	—800
III	NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	NO <sub>2</sub>	3440; 3340	522	58	628	674	568	422; 700
IV	NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	3450	510	46	548	652	520	584; 750
V	S	C <sub>6</sub> H <sub>5</sub>	NO <sub>2</sub>	3308	586	116	608	676	668	670—690
VI	S	C <sub>6</sub> H <sub>5</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	3328	532	62	542	482; 672	482; 662	464; 750
VII	S	CH <sub>3</sub>	NO <sub>2</sub>	3230; 3185	510	100	510	546	486	550; 670
VIII	S	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	3340	500	90	554	670	528	610; 750
IX	O	C <sub>6</sub> H <sub>5</sub>	NO <sub>2</sub>	3315	572	142	574	660	640	560; 670
X	O	C <sub>6</sub> H <sub>5</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	3340	500	70	522	480; 648	480; 630	610; 750
XI	O	CH <sub>3</sub>	NO <sub>2</sub>	3440; 3360	456; 566	46	566	640	516	540; 656
XII	O	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	3350	476	160	526	640	514	596; 750

\*Bathochromic shift in λ<sub>max</sub> as compared with unsubstituted formazans (R<sub>1</sub> = H).

TABLE 2. Characteristics of the Formazans Obtained

Comp.	mp (crystallization solvent)	Empirical formula	Found, %			Calc., %		
			C	H	N	C	H	N
I	112—14 (alcohol)	C <sub>27</sub> H <sub>21</sub> N <sub>7</sub> O <sub>2</sub> · C <sub>2</sub> H <sub>5</sub> OH	66,74	5,33	19,22	66,76	4,99	18,80
II	188—90 (alcohol)	C <sub>29</sub> H <sub>27</sub> N <sub>7</sub>	73,22	5,65	20,77	73,57	5,70	20,71
IV	114—115 (isoamyl alcohol)	C <sub>24</sub> H <sub>25</sub> N <sub>7</sub> · C <sub>8</sub> H <sub>11</sub> OH	69,71	7,57	19,59	69,73	7,41	19,63
VI	114—16 (alcohol)	C <sub>22</sub> H <sub>20</sub> N <sub>6</sub> S · C <sub>2</sub> H <sub>5</sub> OH	64,75	5,20	18,91	64,57	5,52	18,83
VIII	212—13 (alcohol)	C <sub>17</sub> H <sub>18</sub> N <sub>6</sub> S · H <sub>2</sub> O	60,33	5,62	25,22	60,35	5,32	24,85
X	188—90 (alcohol)	C <sub>22</sub> H <sub>20</sub> N <sub>6</sub> O · 0,5H <sub>2</sub> O	67,27	5,43	20,79	67,17	5,34	21,37
XII	178—80 (aqueous acetone)	C <sub>17</sub> H <sub>18</sub> N <sub>6</sub> O	63,33	5,62	26,14	63,35	5,59	26,08

formazans [5]. A structure with the nitro group in the aci form with intermolecular hydrogen bonds (B) is most likely for benzothiazolyl- and benzoxazolylformazans V, VII, IX, and XI:



The formation of a sodium salt in this case does not introduce changes in the electronic state of the molecule and therefore does not cause a bathochromic effect. Also confirming this is the weak resolution of the IR spectra (LiF prism) and the high lability of the proton which is bonded here with oxygen rather than nitrogen (the pK<sub>a</sub> for VII is 8.1, that for XI is 7.7, while for the remaining formazans with a methyl group in the 3 position it is 12–13).

The introduction of a nitro or dimethylamino group induces a deepening in the color not only of formazans themselves but also of their metal complexes. The nickel complexes are more deeply colored by 30-40 nm, but the bathochromic effect is particularly large for cobalt complexes of formazans containing a dimethylamino group since  $\lambda_{\max}$  for them lies in the 750-800 nm region.

The formazans were obtained by coupling of benzazolyhydrazones with diazonium salts (Table 2). The synthesis of V, VII, IX, III, and XI was previously described in [6, 7].

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