TAUTOMERISM OF 1,5-DIBENZAZOLYLFORMAZANS

N. P. Bednyagina, G. N. Lipunova,
and G. M. Petrova

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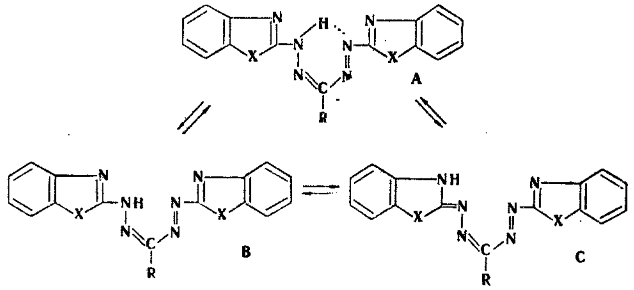
The structures of new symmetrical and asymmetrical 1,5-dibenzazolylformazans were investigated by IR and electronic spectroscopy. It is shown that 1,5-dibenzimidazolylformazans, regardless of the substituent in the 3 position (methyl, phenyl), display the presence of the tautomeric imino form in solutions. 1,5-Dibenzothiazolylformazans display a high tendency to form chelate forms. The stability of the chelate increases on passing from the 3-methyl to the 3-phenyl derivative.

In [1, 2] it was established that the substituent attached to the meso carbon atom in unsymmetrical 1-benzothiazolyl (or oxazolyl)-5-phenylformazans has a decisive effect on the structure of the formazan group. Formazans that contain a phenyl group in the 3 position are chelated, while 3-methylformazans have an open structure. In contrast to this, 1-benzimidazolylformazans, regardless of the substituent in the 3 position, are open and exist in the imino form. It has been shown [2] that the ν_{NH} frequencies in the IR spectrum (in $CHCl_3$ or CCl_4) at 3440-3450 cm^{-1} pertain to the imino form, while those in the 3350-3360-cm^{-1} region pertain to the tautomeric amino form. The chelate form does not display ν_{NH} frequencies at 3100-3500 cm^{-1}.

Formazans I-VI were synthesized in order to ascertain the effect of a substituent in the 3 position (methyl, phenyl) and the character of the heteroring in the 1,5 positions (benzimidazole, benzothiazole, and benzoxazole) on the structure of the formazan chain in a number of 1,5-dibenzazolylformazans.

The first four compounds may exist in the following three tautomeric forms: chelate (A), the amino form (B), and the imino form (C):



A ν_{NH} frequency corresponding to the imino form (C) is detected in the IR spectra of symmetrical formazans of benzimidazole (Table 1). As in the unsymmetrical benzimidazolylformazans [1], the color of the symmetrical formazans of benzimidazole (I, II) is practically independent of the substituent attached to C_3.

The formazans of benzothiazole do not have ν_{NH} bands at 3100-3500 cm^{-1}; this is associated with the presence of a chelate form (A). The chelate ring in 1,5-dibenzothiazolyl-3-methylformazan (III) is unstable and is converted by the action of alkali or acid, respectively, to the anion or cation, which, as shown for 1,5-dibenzimidazolylformazans [3], have a cyanine structure. The chelate ring in 1,5-dibenzothiazolyl-

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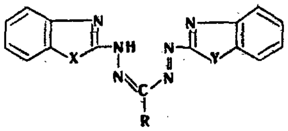
S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 699-701, May, 1973. Original article submitted May 4, 1972.

TABLE 1. Spectral Characteristics of 1,5-Dibenzazolylformazans



Compound	X	Y	R	ν_{NH}, cm^{-1} CHCl$_3$	λ_{max}, nm (acetone)		
					neutral medium	NaOH, pH 12–13	HCl, pH 1–2
I	$NCH_2C_6H_5$	$NCH_2C_6H_5$	CH_3	3420	530	570, 605	580, 610
II	$NCH_2C_6H_5$	$NCH_2C_6H_5$	C_6H_5	3468	540—550	570, 600	590, 620
III	S	S	CH_3	None	526	570, 600	580, 610
IV	S	S	C_6H_5	None	580—600	580—600	—*
V	$NCH_2C_6H_5$	S	CH_3	3442	552	572, 598	584, 606
VI	$NCH_2C_6H_5$	O	CH_3	3401	542	574, 608	580, 614

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*There is no clearly expressed maximum in the spectrum.

3-phenylformazan (IV) is so stable that, like the triphenylformazan ring, it is not susceptible to the action of alkali. The deeper color of III in acetone as compared with IV is also explained by opening of the chelate under the influence of the solvent (Table 1).

For asymmetrical formazans V and VI, the factor that determines the structure is the basicity of the benzimidazole heteroring. Despite the increase in the number of possible tautomeric forms (six forms), form C with a hydrogen atom attached to the nitrogen atom of the benzimidazole ring is the most probable form for these compounds. The presence in the IR spectra of a ν_{NH} absorption band at 3442 and 3401 cm^{-1} for formazans V and VI, respectively, speaks in favor of this sort of structure.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer, while the electronic spectra in the visible region were recorded with an SF-10 spectrophotometer. 1,5-Di(1-benzylbenzimidazolyl)-3-methylformazan (I) was obtained by the method in [4].

1,5-Dibenzothiazolyl-3-methylformazan (III). This compound was obtained by the method in [5]. A solution of 0.02 mole of acetaldehyde 2-benzothiazolylhydrazone and 0.02 mole of 2-hydrazinobenzothiazole in 250 ml of ethanol, prepared at 50-60°, was filtered, and a solution of 2 g of sodium acetate in 5 ml of ethanol was added to it. The solution gradually became colored on standing in air, and a dark-brown crystalline precipitate formed. After 6-7 days, the mixture was filtered to give formazan III, with mp 213-215° (from ethanol), in 70% yield. Found: C 54.6; H 3.7; N 23.3; S 17.6%. $C_{16}H_{12}N_6S_2$. Calculated: C 54.5; H 3.4; N 23.8; S 18.2%.

1,5-Di(1-benzylbenzimidazolyl)-3-phenylformazan (II). This compound was obtained by the method in [5] from 0.001 mole of benzaldehyde 1-benzyl-2-benzimidazolylhydrazone and 0.001 mole of 1-benzyl-2-hydrazinobenzimidazole by autooxidation in 100 ml of pyridine. The reaction mixture was diluted after a month with alcohol and water to give formazan II with mp 168-170° (from aqueous ethanol). Found: C 75.4; H 5.5%. $C_{35}H_{28}N_8$. Calculated: C 76.0; H 5.0%.

1,5-Dibenzothiazolyl-3-phenylformazan (IV). A diazonium salt solution obtained from 0.001 mole of 2-aminobenzothiazole was added to a solution of 0.001 mole of benzaldehyde 2-benzothiazolylhydrazone in a mixture of 100 ml of pyridine and 100 ml of methanol. Water (200 ml) was then added to the mixture at 5-10° after 12 h to give a product with mp 151-153° (from aqueous ethanol). Found: C 60.7; H 3.6; S 14.9%. $C_{21}H_{14}N_6S_2$. Calculated: C 60.8; H 3.4; S 15.5%.

1-Benzylbenzimidazolyl-3-methyl-5-benzothiazolylformazan (V). A 0.01-mole sample of 1-benzyl-2-benzimidazolylhydrazine and 0.01 mole of acetaldehyde benzothiazolylhydrazone were dissolved in 50 ml of slightly heated distilled pyridine. The violet solution was filtered and allowed to stand in the air for 5-6 days. The precipitate was removed by filtration. Removal of about half the solvent from the mother liquor by distillation gave another small amount of product. The formazan was crystallized from ethanol to give beautiful large shiny green crystals with mp 207-208° in 71% yield. Found: C 64.4; H 5.2; N 21.8; S 7.1%. $C_{23}H_{19}N_7S$. Calculated: C 64.9; H 4.5; N 23.0; S 7.5%.

1-Benzylbenzimidazolyl-3-methyl-5-benzoxazolylformazan (VI). This compound was obtained by the method used to prepare V. The solution was allowed to stand for a week. The precipitate was removed by filtration and crystallized from ethanol to give a finely crystalline lilac-colored product with mp 264-265° in 12% yield (based on the hydrazine). Found: C 67.5; H 5.1; N 23.0%; $C_{23}H_{19}N_7O$. Calculated: C 67.5; H 4.7; N 23.9%. Removal of part of the solvent from the mother liquor by distillation gave another 45% of product as a crystalline powder with mp 140° (from alcohol). The formazan contained two molecules of pyridine as a crystallization component. Found: C 69.8; H 5.2; N 22.2%. $C_{23}H_{19}N_7O \cdot C_5H_5N$. Calculated: C 70.0; H 5.2; N 21.8%.

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