SYNTHESIS AND INVESTIGATION OF THIOCARBOHYDRAZIDE DERIVATIVES

V. SYNTHESIS AND INVESTIGATION OF 3-MERCAPTOFORMAZANS FROM 1,5-DI(ARYLAMIDOTHIOCARBO)THIOCARBOHYDRAZIDES*

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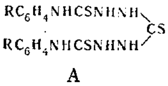
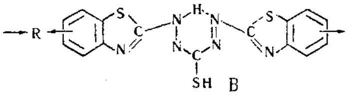
Reaction of thiocarbohydrazide with aryl isothiocyanates gives 1,5-di(arylamidothiocarbo) thiocarbohydrazides. Oxidation of the latter with potassium ferricyanide gives symmetrical norcyanines, which exhibit positive solvatochromism. They give a bathochromic shift of the absorption maximum both on protonation and on removal of a proton. S-Methyl derivatives of norcyanines have been obtained, and their structures proved.

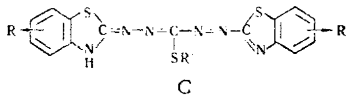
Substituted 1,5-diphenylformazans are widely used as dyes and indicators [1]. It is of particular interest to synthesize unknown heterocyclic derivatives of formazans containing a mercapto group in the 3-position by starting from symmetrically substituted 1,5-di(phenylamidothiocarbo)thiocarbohydrazides. The latter (A) were prepared by a modification of the method of Guha [2,11] from thiocarbohydrazide and aryl isothiocyanates.



A



B



C

The compounds A (I-VII, Table 1) were colorless, crystalline solids which were readily soluble in alkalis (being reprecipitated from their solutions by acids), and sparingly soluble in organic solvents. Reaction of A with potassium ferricyanide in aqueous alcoholic alkali gave violet-colored crystalline compounds with a metallic luster, readily soluble in most organic solvents. The color of the solution deepens

TABLE 1. 1,5-Di(arylamidothiocarbo)thiocarbohydrazides (A)

Compound	R	mp, °C	Molecular formula	N, %		Yield, %
				Found	Calculated	
I	o-CH_3	158	$C_{17}H_{20}N_6S_3$	20,4	20,8	73
II	p-C_2H_5	185	$C_{19}H_{24}N_6S_3$	19,8	19,4	84
III	p-$C(CH_3)_3$	184	$C_{23}H_{32}N_6S_3$	17,6	17,2	70
IV	p-C_4H_9O	185	$C_{23}H_{32}O_2N_6S_3$	16,6	16,2	95
V	m-Cl	181	$C_{15}H_{14}Cl_2N_6S_3$	18,5	18,9	82
VI	p-I	164	$C_{15}H_{14}O_2N_6S_3$	13,6	13,4	83
VII	p-C_2H_5OOC	181	$C_{21}H_{24}O_4N_6S_2$	16,4	16,2	96

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* For part IV, see [12].

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TABLE 2. 1,5-Di(6-R-2'-benzothiazolidene)-1,2,4,5-tetraaza-3-R'-mercaptopentamethionenorcyanines (C)

Compound	R	R'	mp, °C	Molecular formula	Elements	Found, %	Calculated %	Yield, %
VIII	H	H	149—50	$C_{15}H_{10}N_6S_3$	C	48,8	48,6	85
					H	3,1	2,7	
IX	6-CH_3	H	168—69	$C_{17}H_{14}N_6S_3$	N	20,4	21,1	80
X	6-C_2H_5O	H	133—34	$C_{19}H_{18}N_6O_2S_3 \cdot 2H_2O$	N	17,0	16,9	88
XI	6-Cl	H	165—66	$C_{15}H_{18}Cl_2N_6S_3$	Cl	15,9	16,1	80
XII	6-NO_2	H	169—70	$C_{15}H_{18}N_4O_2S_3$	N	24,1	24,3	79
XIII	6-CH_3	CH_3	75—76	$C_{18}H_{16}N_6S_3$	S	22,8	23,3	97
XIV	6-C_2H_5O	CH_3	95—96	$C_{20}H_{20}N_6O_2S_3 \cdot 2H_2O$	S	19,0	18,9	78
XV	6-Cl	CH_3	135—36	$C_{16}H_{10}N_6S_3Cl_2$	Cl	14,9	15,6	98

TABLE 3. Absorption Maxima of Alcoholic Solutions of 3-Mercaptopentamethinenorcyanines (C)

Compound	λ_{max} (log ε) in alcohol*	$\lambda_1$max(log ε_2) in 10^{-4} N alcohol·HCl	$\lambda_2$max (log ε_2) in 10^{-5} N alcohol·HCl
IX	506 (3,81)	540 (3,90)	545 (3.82)
X	548 (3.81)	580 (4,00)	580 (3,57)
XI	536 (3.30)	566 (3,37)	560 (3.49)

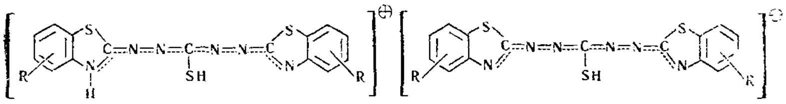
*Concentration of dyestuff $5 \cdot 10^{-5}$M.

on passing from less polar to more polar solvents (positive solvatochromism). Bearing in mind that thioamides on treament with potassium ferricyanide undergo oxidative cyclization to give benzothiazoles [3], we assigned to compounds VIII-XII (Table 2) the structure 1,5-di-(2'-benzothiazolyl)-3-mercaptoformazan (B), or 1,5-di-(2'-benzothiazolidene)-1,2,4,5-tetraaza-3-mercaptopentamethinenorcyanine (C) [4]. Similar tetraazapentamethine benzothiazole dyestuffs bearing a hydrogen atom in the meso position have been described [4, 5].

The IR spectra of B do not show the characteristic NH frequency (3500-3400 cm^{-1}), either in chloroform solution or in the solid state. This appears to be due to hydrogen bonding, which is characteristic of formazans with a chelate structure [8-10].

We expected methylation of these norcyanines to give two products, the N- and S-methyl derivatives. We obtained violet-colored crystalline compounds which were readily soluble in organic solvents. Like the starting norcyanines, they showed positive solvatochromism and indicator properties (XIII-XV, Table 2). In order to establish the structures of the methylation products, their IR spectra were taken, and reactions at the mercapto group were carried out [6]. The IR spectra showed strong bands at 695 cm^{-1}, characteristic of the $>C{-}S{-}C<$ group [7]. Positive reactions for the presence of the methylmercapto group indicated S-methylation.

Both attachment and removal of a proton led to equalization of the electron density over the whole of the conjugated ring, resulting in a bathochromic shift of the absorption maxima similar to that observed in 1,5-dibenzimidazolylformazans [10]. These compounds, therefore, possess characteristics similar to the onium and acylhalochromic cyanine dyes. We see from Table 3 that, irrespective of the sign of the charge, they possess almost identical absorption spectra.



EXPERIMENTAL

1,5-Di(o-tolylamidothiocarbo)thiocarbohydrazide (I). To a solution of 1.06 g (0.01 mole) of thiocarbohydrazide in 4 ml of water was added a solution of 2.98 g (0.02 mole) of o-tolyl isothiocyanate in alcohol. The mixture was heated on a water bath for 30 min, cooled, and the precipitate which separated was filtered off, washed with dil HCl followed by water until neutral, and then with alcohol and ether. Yield 2.94 g (73%).

Compounds II-VII (Table 1) were obtained in a similar manner.

1,5-Di(6'-ethoxy-2'-benzothiazolidene)-1,2,4,5-tetraaza-3-mercaptopentamethinenorcyanine (X). To a suspension of 1.4 g (3 mmole) of 1,5-di(p-phenethylamidothiocarbo)thiocarbohydrazide in a 1:1 mixture of alcohol and water (20 ml) was added 0.6 g (7.5 mmole) of NaOH. The resulting cherry-red solution was added with stirring to a solution of 4.9 g (7.5 mmole) of potassium ferricyanide in 30 ml of water. The mixture was stirred for 1 hr at room temperature, and the precipitate filtered off and washed with water followed by small quantities of alcohol and ether. After drying in vacuo, the yield was 1.2 g (88%).

Compounds VIII-XII (Table 2) were obtained in similar manner.

1,5-Di-(6'-ethoxy-2'-benzothiazolidene)-1,2,4,5-tetraaza-3-methylmercaptopentamethinenorcyanine (XIV). To 0.26 g (0.5 mmole) of X was added 0.3 ml of 10% alcoholic KOH and 0.2 ml (3 mmole) of methyl iodide. The dark-blue precipitate was filtered off and washed with the minimum amount of alcohol and ether. The yield after drying in vacuo was 0.18 g (78%).

Compounds XIII and XV were obtained in a similar manner (Table 2).

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