REACTION OF 1,2-DIAMINOIMIDAZOLES WITH ISATINS. DEGREE OF ORDERLINESS OF COMPOUNDS IN A LIQUID-CRYSTAL MATRIX AS A CRITERION OF THEIR STRUCTURE

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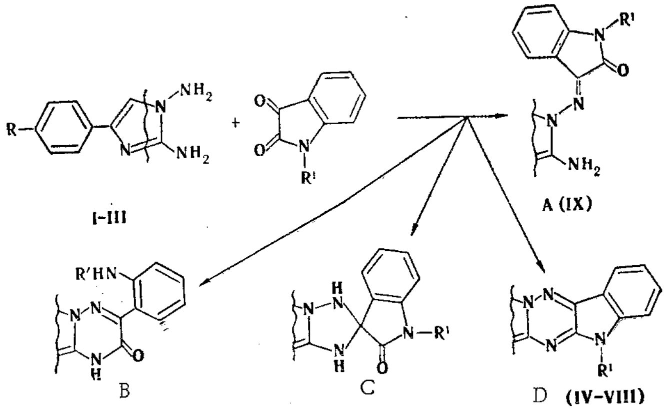
The reaction of 1,2-diamino-4-arylimidazoles with isatin and N-methylisatin, as a result of which the corresponding imidazo[1',2':2,3]-1,2,4-triazino[6,5-b]indoles were obtained, was studied. The corresponding Schiff base was also isolated in the case of the reaction of 1,2-diamino-4-(p-tert-butylphenylene)imidazole with N-methylisatin. The electronic and IR spectra of the synthesized compounds were studied. The possibility of the use of the degree of orderliness of the synthesized compounds in a liquid-crystal matrix as an additional spectral method in proving the structures of the compounds is demonstrated.

It has been reported that, in addition to indolo[2,3-b]quinoxalines and their analogs, Schiff bases, 2(1H)-quinoxalinone derivatives [1-4], or spiro compounds [5-9] are formed as a result of the reaction of aromatic or heterocyclic o-diamines with isatins. Continuing our investigation of this reaction we studied the reaction of 1,2-diaminoimidazoles (I-III) with isatin and N-methylisatin. Taking into account the data in [1-9], as well as the increased activity of the 1-NH_2 group of 1,2-diaminoimidazoles [10, 11] and the 3-CO group of isatins [12, 13], we assumed that the products of the indicated reaction may be the corresponding Schiff base (A), 2(1H)-imidazo[1,2-b]-1,2,4-triazinones (B), spiro-(imidazo[1,2-b]triazoline-2,3'-indoline)-2'-ones (C), or imidazo[1',2':2,3]-1,2,4-triazino[6,5-b]indoles (D).



I, IV, IX R=tert-C_4H_9; II, V, VII R=C_7H_{15}; III, VI, VIII R=4-$C_8H_{17}C_6H_4$; IV—VI, IX R'=CH_3; VII, VIII R'=H

Two products are formed when 1,2-diaminoimidazole I is heated with N-methylisatin in ethanol or benzene in the presence of acetic acid, whereas primarily one product is formed in the reaction of diamines II and III with isatin and N-methylisatin under the indicated conditions, as well as in acetic acid.

To ascertain the compositions and structures of the synthesized compounds we used the results of elementary analysis (Table 1) and data from the IR and electronic spectra.

The IR spectrum of a dilute solution in $CHCl_3$ is one of the compounds obtained as a result of the reaction of 1,2-diaminoimidazole I with N-methylisatin and the IR spectra of dilute solutions in $CHCl_3$ of the compounds obtained as a result of the reaction of 1,2-di-

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TAБLE 1. Characteristics of IV-IX

Compound	mp,* °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
IV†	249,0—250,0	74,1	6,0	19,9	$C_{22}H_{21}N_5$	74,3	5,9	19,7	25
V	216,0—217,0	75,5	6,8	17,7	$C_{25}H_{27}N_5$	75,5	6,9	17,6	38
VI	225,0—226,0	78,9	6,9	14,4	$C_{32}H_{33}N_5$	78,8	6,8	14,4	41
VII	358,0—360,0	75,3	6,5	18,8	$C_{24}H_{25}N_5$	75,2	6,6	18,2	52
VIII	333,5—335,0	78,4	6,8	14,5	$C_{31}H_{31}N_5$	78,6	6,6	14,8	55
IX	215,5—250,0	71,0	6,0	19,1	$C_{22}H_{23}N_5O$	70,8	6,2	18,8	17

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*The compounds were recrystallized: IV, V, and VI from ethanol, VII and VIII from ethanol—chlorofrom, and IX from benzene.

†Compound IV had R_f 0.54, and IX had R_f 0.31 [benzene—acetone (4:1)].

amines II and III with isatin and N-methylisatin do not contain absorption bands of a carbonyl group. These compounds are consequently imidazotriazinoindoles (IV-VIII).

The IR spectrum of a dilute solution in $CHCl_3$ of another compound obtained as a result of the reaction of 1,2-diamine I with N-methylisatin contains a $\nu_{C=O}$ band at 1704 cm^{-1} and two ν_{NH} bands at 3540 and 3435 cm^{-1}. These data do not make it possible to choose unambiguously between structures A-C (R = tert-C_4H_9, R^1 = CH_3).

In addition to absorption bands in the UV region, the electronic spectrum of this compound (Table 2) contains intense bands in the visible region (470-500 nm) of the spectrum. This constitutes evidence that it is not a 2(1H)-imidazo[1,2-b]-1,2,4-triazinone derivative (B), since the known representatives of this series [14] have a long-wave absorption band in their electronic spectra at 395 nm. The compound obtained consequently can have only structures A and C, which differ markedly from one another with respect to their "linearity." This structural difference in the indicated compounds makes it possible to use the "guest—host" effect in liquid crystals for definitive proof of its structure. In conformity with the existing concepts regarding this effect [15], the degree of orderliness of an investigated substance (the "guest") in a liquid crystal (the "host") increases as the linearity of the "guest" increases, i.e., as the structure of the latter approaches the structure of the "host." The dichroism [$S(\lambda)$] of the absorption band (λ), which shows up spectrally in different optical densities of this band in the electronic spectrum of the "guest" when the measurement is made parallel ($D_\parallel$) and perpendicular ($D_\perp$) to the director of the "host" and is determined from Eq. (1) [16]

$$S(\lambda)=\frac{D_\parallel-D_\perp}{D_\parallel+2D_\perp}. \qquad (1)$$

may serve as a criterion of the degree of orderliness of the "guest."

In conformity with the "linearity" of A, C, and D one should have expected that $S_A \ll S_C \leq S_D$. In fact, depending on the aryl substituent, the dichroism of the long-wave absorption bands of IV-VIII ranges from 0.5 to 0.68, whereas S = 0.17 for the investigated compound (Table 2). This constitutes evidence that the second product obtained as a result of the reaction of 1,2-diamine I with N-methylisatin is Schiff base IX, and the ν_{NH} bands in its IR spectra are due to the symmetrical and asymmetrical stretching vibrations of the amino group. The structure of the latter is also confirmed by its conversion to imidazotriazinoindole VD when it is melted, since spiro compounds of the C type do not undergo any changes when they are melted [8, 9].

EXPERIMENTAL

The individuality of the synthesized compounds was monitored by thin layer chromatography (TLC) on Silufol UV-254 plates. The electronic absorption spectra of $1\cdot10^{-4}$ M solutions of the compounds in chloroform were recorded with a Specord UV-vis spectrophotometer. The IR spectra of $5\cdot10^{-3}$ M solutions of the compounds in chloroform were recorded with a UR-20 spectrometer. The electronic spectra of 3% solutions of the compounds in an oriented liquid-crystal matrix were measured with a Hitachi spectrophotometer by the method in [16]. A mixture of 4-alkyl- and 4-alkoxy-4'-cyanodiphenyls with a nematic meso phase interval of 0-60°C

TABLE 2. Electronic Spectra of IV-IX

Compound	λ_{max}, nm (log ε) in chloroform	Degree of orderliness, S(λ), in a liquid-crystal matrix
IV	278 (4,43), 369 (4,27), 469 (4,04), 500* (3,97)	0,53 (386), 0,53 (480)
V	278 (4,19), 357 (3,99), 440 (3,71), 500* (3,62)	0,66 (400), 0,57 (480)
VI	286 (4,67), 385 (4,74), 472 (4,58), 500* (4,52)	0,68 (395), 0,68 (485)
VII	271 (4,71), 372 (4,67), 465 (4,51), 488* (4,39)	0,57 (384), 0,50 (474)
VIII	278 (4,51), 380 (4,19), 465 (4,06), 492* (4,00)	0,63 (395), 0,56 (476)
IX	282 (4,25), 328 (3,92), 348* (4,16), 478 (4,04)	0,17 (490)

*Shoulder.

was used as the liquid-crystal matrix. 1,2-Diaminoimidazoles I-III were obtained by the method in [14].

Reaction of 1,2-Diaminoimidazoles with Isatins. A 5-mmole sample of I-III and 5 mmole of isatin or N-methylisatin were refluxed in 100 ml of ethanol or in 100 ml of an aromatic hydrocarbon (benzene, toluene, or xylene) in the presence of 1 ml of acetic acid or in 50 ml of acetic acid for 2 h, after which the mixture was cooled, and the precipitate was removed by filtration and recrystallized from the minimum amount of solvent to give, respectively, V-IX. The mother liquor was evaporated to dryness *in vacuo*, and the residue was dissolved in the minimum amount of acetone—chloroform (2:1) and chromatographed on Chemapol L 40/100 silica gel with acetone—chloroform (1:10). The unchanged isatin or N-methylisatin (up to 1 mmole) and an additional amount of V-IX, as well as IV, were isolated. The characteristics of IV-IX are presented in Table 1. The maximum yields of IV-IX were obtained when the reaction was carried out in an aromatic hydrocarbon in the presence of acetic acid.

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