SYNTHESIS OF 1,2-DIAMINOIMIDAZOLE DERIVATIVES BY THE REACTION OF BENZALDEHYDE GUANYLHYDRAZONE WITH α-HALOALKYL ARYL KETONES

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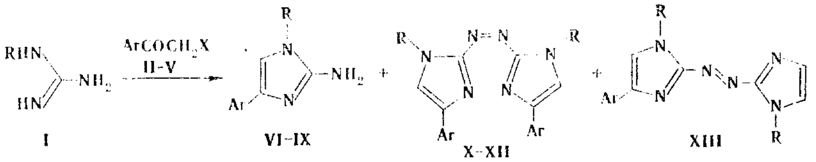
2-Amino-1-benzylideneamino-4-arylimidazoles were obtained by the reaction of benzaldehyde guanylhydrazone with 4-alkyl- and 4-aryl-ω-haloacetophenones. Side products of this reaction were cis- and trans-1,1'-bis(benzylideneamino)-4,4'-diaryl-2,2'-azoimidazoles. The corresponding 2-amino-1-benzylideneaminoimidazole and 1-benzylideneaminoimidazo[1,2-a]imidazole were obtained in the reaction of α-bromopropiophenone with benzaldehyde guanylhydrazone. The 2-amino-1-benzylideneamino-4-arylimidazoles were converted by successive reactions to 1,2-diamino-4-arylimidazoles and then to imidazo[1,2-b]-1,2,4-triazine derivatives — dyes for liquid crystals with positive dichroism.

The first information regarding the reaction of benzaldehyde guanylhydrazone with ω-bromo- and 4,ω-dibromoacetophenone, as a result of which it was reported [1] that benzaldehyde [4(5)-aryl-2-imidazolyl]hydrazones were obtained, proved to be erroneous. It was later shown that the products of the reaction of benzaldehyde and acetophenone guanylhydrazone with ω-chloro-, ω-chloro-4-bromo, 4,ω-dibromo-, 4,ω-dichloro-, and ω-chloro-4-methylacetophenone are 2-amino-1-arylideneaminoimidazole derivatives [2]. The structures of these compounds were confirmed by alternative synthesis by condensation of benzaldehyde with 1,2-diamino-4-arylimidazoles; the latter were obtained by hydrolysis of 2-amino-1-acylamino-4-arylimidazoles formed by the action of ammonia on 2-amino-3-aracyl-1,3,4-oxadiazole halides [2, 3]. The reaction of α-bromovalerophenone with benzaldehyde guanylhydrazone gives 1-benzylideneamino-3,6-diphenyl-2,5-dipropylimidazo[1,2-a]imidazole, the structure of which was confirmed by spectral methods and several transformations [4, 5].

In the present research we studied the reaction of benzaldehyde guanylhydrazone with ω-chloro- (II-V, X = Cl) and ω-bromoacetophenones (II-V, X = Br) in hot alcohol. In the first case we obtained 2-amino-1-benzylideneaminoimidazoles (VI-IX) in 47-65% yields. Compounds VI-IX are also formed in the case of bromo ketones (II-V, X = Br) but in lower yields (17-21%); as in [2], 2,2'-azoimidazole derivatives (X-XIII) were isolated as side products of this reaction in 1-2% yields.



R=C_6H_5CHN—, II, VI Ar=4-tert-$C_4H_9C_6H_4$; III, VII, X Ar=4-C_6H_{13}—C_6H_4; IV, VIII, XI Ar=4-C_7H_{15}—C_6H_4; V, IX, XII, XIII Ar=4-(4-C_8H_{17}—C_6H_4)C_6H_4

Let us note that in the reaction of hydrazone I with bromo ketone V we were able to isolate two dyes (XII, XIII). The same dyes are also formed in the oxidation of 2-aminoimidazole IX with manganese oxide in an aromatic hydrocarbon with removal of the water by azeotropic distillation. Whereas primarily 2,2'-azoimidazole XII is formed as a result of the reaction of hydrazone I with bromo ketone V, primarily 2,2'-azoimidazole XIII is obtained as a result of the oxidation of 2-aminoimidazole IX.

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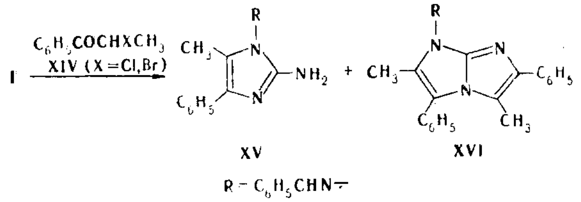
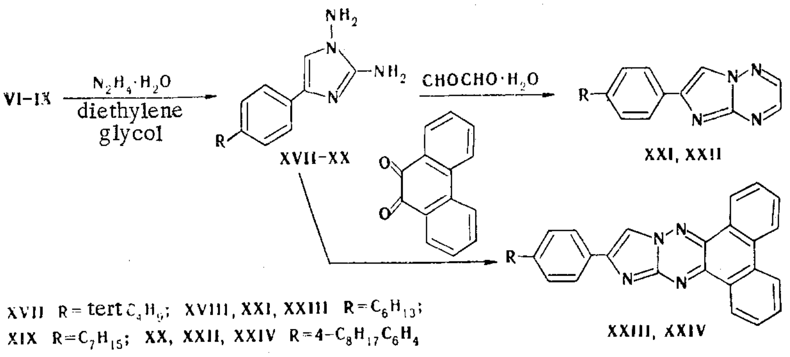
The compositions and structures of VI-XIII are confirmed by the results of elementary analysis and the similarity in their electronic spectra and the spectra of known analogs [2, 4, 5] (Table 1), as well as by their subsequent transformations.

The conclusion regarding the cis (XII) and trans (XIII) forms of 2,2'-azoimidazoles was drawn on the basis of a comparison of their electronic spectra, since the long-wave bands in the spectrum of the trans form (XIII) are shifted bathochromically as compared with the corresponding absorption bands in the spectrum of the cis form (XII). A comparison of the electronic spectra of 2,2'-azoimidazoles XII and XIII with the spectra of 2,2'-azoimidazoles formed as a result of the reactions of hydrazone I with bromo ketones III and IV makes it possible to assume that the latter have the cis form (X, XI). Judging from the electronic spectra, the 2,2'-azoimidazole derivatives obtained in [2] evidently also have the cis form.

Under the conditions indicated above α-chloropropiophenone (XIV, X = Cl), does not react with hydrazone I. However, the products of the reaction of the latter with α-bromopropiophenone (XIV, X = Br) are 2-amino-1-benzylideneamino-5-methyl-4-phenylimidazole (XV) and 1-benzylideneamino-2,5-dimethyl-3,6-diphenylimidazo[1,2-a]imidazole (XVI), which are formed in a ratio of 1:1.4.



The results of the latter reaction confirm the previously expressed assumption that 1-benzylideneamino-3,6-diphenyl-2,5-dipropylimidazo[1,2-a]imidazole, which was obtained in [4, 5], is the product of the reaction of α-bromovalerophenone with 2-amino-1-benzylideneamino-4-phenyl-5-propylimidazole, which was not isolated [4, 5]. The formation as a result of the reaction of hydrazone I with α-bromoalkyl aryl ketones of primarily 1-benzylideneaminoimidazo[1,2-a]imidazoles can be explained by the higher rate of reaction of 2-amino-1-benzylideneaminoimidazoles with α-bromoalkyl aryl ketones as compared with the rate of the reaction of the latter with benzaldehyde guanylhydrazone.



We converted 2-amino-1-benzylideneaminoimidazoles VI-IX to 1,2-diaminoimidazoles XVII-XX by the method described in [2], from which we obtained imidazo[1,2-b]-1,2,4-triazines XXI and XXII and imidazo[1,2-b]phenanthreno[9,10-e]-1,2,4-triazines XXIII and XXIV.

The results of elementary analysis and data from the electronic and IR spectra confirm the structure of XVII-XXIV (Table 1). Thus the electronic spectra of 1,2-diaminoimidazoles XVII-XX are similar to the electronic spectra of their known analogs [4, 5], and the IR spectra of XXI-XXIV do not contain CO and NH absorption bands.

The structure of XXI-XXIV is similar to the structure of liquid-crystal molecules [6]. However, they do not form a liquid-crystal meso phase but, like normal compounds, are converted immediately to an isotropic liquid when they are melted. Considering the fact that they absorb in the visible region, we studied the possibility of their use as dichromic dyes for liquid-crystal materials. The latter are becoming increasingly attractive to researchers attempting to create polychromic electrooptical devices based on liquid crystals [7].

TABLE 1. Results of Analysis and Electronic Spectra of the Synthesized Compounds

Compound	mp,[a] °C	Electronic spectra of ethanol solutions, λ_{max}, nm (log ε)	Found, %			Empirical formula	Calc., %			Yield, %, by method	
			C	H	N		C	H	N	A	B
VI	206[c]	204 (4,39), 215[d] (4,28), 238 (4,07), 283 (4,40), 362 (4,05)	75,6	7,1	17,6	$C_{20}H_{22}N_4$	75,4	7,0	17,6	51	25
VII	189[c]	204 (4,38), 215 (4,27), 238 (4,06), 283 (4,44), 362 (4,05)	76,4	7,5	16,4	$C_{22}H_{26}N_4$	76,3	7,5	16,2	47	28
VIII	204[c]	204 (4,38), 215 (4,25), 238 (4,04), 283 (4,38), 362 (4,04)	76,6	7,5	15,8	$C_{23}H_{28}N_4$	76,6	7,8	15,5	54	17
IX	202[c]	207 (4,68), 293 (4,57), 365 (4,30)	80,3	7,7	15,4	$C_{30}H_{34}N_4$	80,0	7,6	12,4	66	21
X	184—185	278 (4,55), 389 (4,43), 523 (4,18)	76,5	7,1	16,4	$C_{44}H_{48}N_8$	76,7	7,0	16,3	2	
XI	184—186	281 (4,57), 385 (4,42), 526 (4,13)	76,8	7,1	15,7	$C_{46}H_{52}N_8$	77,1	7,3	15,6	2	
XII	213—215	263 (4,37), 289 (4,37), 395 (4,18), 512 (3,82), 526[d] (3,80)	80,0	7,1	12,7	$C_{60}H_{64}N_8$	80,3	7,2	12,5	2	
XIII	232—233	237[d] (4,59), 303 (4,66), 416 (4,57), 531 (4,14)	79,8	7,0	12,3	$C_{60}H_{64}N_8$	80,3	7,2	12,5	—	
XV	186[c]	207 (4,44), 215[d] (4,33), 282 (4,39), 357 (3,74)	74,0	5,9	20,5	$C_{17}H_{16}N_4$	73,9	5,8	20,3	10	
XVI	192—193	208 (4,74), 248[d] (4,47), 254 (4,48), 276 (4,35), 349 (4,50)	80,1	5,6	14,4	$C_{26}H_{22}N_4$	80,0	5,7	14,3	14	
XVII	234[c]	201 (4,33), 220 (4,06), 282 (4,01)	67,7	8,0	24,6	$C_{13}H_{18}N_4$	67,8	7,9	24,3	88	
XVIII	234[c]	201 (4,34), 220 (4,04), 282 (4,00)	69,5	8,8	21,4	$C_{15}H_{22}N_4$	69,7	8,6	21,7	97	
XIX	220[c]	201 (4,35), 220 (4,06), 282 (4,02)	70,6	8,6	20,8	$C_{16}H_{24}N_4$	70,5	8,9	20,6	68	
XX	250[c]	255 (4,18), 310 (4,40)	76,5	8,2	15,7	$C_{23}H_{30}N_4$	76,2	8,3	15,4	72	
XXI	118—120	210 (4,51), 218 (4,39), 249 (4,26), 395 (4,15)	72,9	7,5	20,2	$C_{17}H_{20}N_4$	72,8	7,2	20,0	15	
XXII	190—192	209 (4,59), 227[d] (4,35), 278 (4,43), 397 (4,33)	78,4	7,5	14,3	$C_{25}H_{28}N_4$	78,1	7,3	14,6	35	
XXIII	198—199	238[d] (4,43), 256 (4,50), 276 (4,63), 465 (4,41), 493 (3,37)	81,1	6,0	13,2	$C_{29}H_{26}N_4$	80,9	6,1	13,0	16	
XXIV	199—201	212 (4,77), 258 (4,78), 265 (4,81), 315 (4,07), 463 (3,68), 478[d] (3,61)	83,4	6,6	10,5	$C_{36}H_{34}N_4$	83,1	6,4	10,5	40	

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[a] The compounds were recrystallized: VI from toluene, VII-IX from chloroform, X-XVI from benzene, XVII-XIX and XXII-XXIV from ethanol, and XXI from heptane. [b] The spectra of XX and XXIII were obtained from solutions in $CHCl_3$. [c] With decomposition. [d] Shoulder.

It is apparent from Fig. 1 that the intensities of the absorption bands in the electronic spectra of liquid crystal solutions of XXII and XXIV in the case of measurements parallel (D) and perpendicular ($D_{\perp}$) to the axis of nematic order of the liquid crystal differ. Calculations of the dichroism (the S parameter, which characterizes the effectiveness of the dichroic dye) of the long-wave absorption bands of these compounds (Table 2), made from Eq. (1) [8] constitute evidence that an increase in the length of the dye molecules leads to an increase in S, whereas broadening of the molecules leads to a decrease in S.

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

where S(λ) is the dichroism of the absorption band with a maximum at λ in nanometers, and $D_{\parallel}$ and $D_{\perp}$ are the optical densities at wavelength λ in the case of measurement parallel and perpendicular to the axis of nematic order.

As expected, dye XXII has the greatest dichroism, while dye XXIII has the minimum dichroism. Let us note that the practical application of the dichroic dyes obtained, particularly XXII, which has very high dichroism, is limited by their low photostability in the liquid crystal. However, the data obtained constitute evidence that the search for dyes with positive dichroism (S > 0) in series of polycondensed azaheterocyclic systems is a promising pursuit.

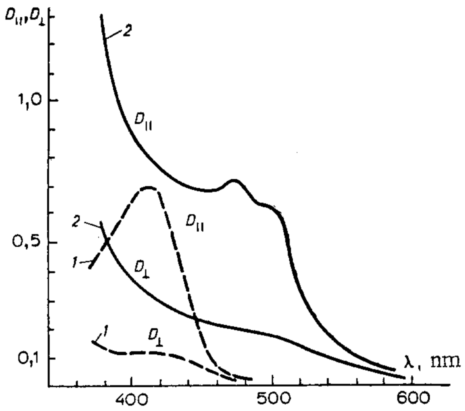

Fig. 1. Electronic spectra of 0.5% solutions of XXII (1) and XXIV (2) in an oriented liquid-crystal matrix in the case of measurements parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) to the axis of nematic order.

EXPERIMENTAL

The individuality of the synthesized compounds was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates. The electronic absorption spectra of 10^{-4} M solutions of the compounds in ethanol and chloroform were recorded with a Specord UV-vis spectrophotometer. The IR spectra were recorded with a UR-20 spectrometer. The electronic spectra of solutions of XXI-XXIV in an oriented liquid-crystal matrix were recorded with a Hitachi spectrophotometer by the method in [8]. A mixture of 4-alkyl- and 4-alkoxy-4'-cyanodiphenyls was used as the liquid-crystal matrix.

2-Amino-1-benzylideneaminoimidazoles (VI-IX). A) Chlorine, which was obtained from 104 g of $KMnO_4$ and 680 ml of HCl, was passed into a solution of 0.96 mole of the corresponding acetophenone in 220 ml of acetic acid, after which the reaction mixture was poured into water, and the organic layer was extracted with benzene. The extract was washed with water and dried with anhydrous Na_2SO_4. The benzene was removed by distillation, and the residue was distilled *in vacuo*. This method gave II-IV in 70-75% yields. Compound II had bp 142-146°C (1 mm) and n_D^{20} 1.534, III had bp 156-158°C (1 mm) and n_D^{20} 1.540, and IV had bp 166-168°C (2 mm) and n_D^{20} 1.530. After chlorination of 4-acetyl-4'-octyldiphenyl, the reaction mixture was diluted with water, and the precipitate was removed by filtration, washed on the filter with water, dried, and recrystallized from heptane to give V in 72% yields. A mixture of 0.08 mole of benzaldehyde guanylhydrazone, 0.04 mole of chloro ketone II-V, and 60 ml of ethanol was refluxed for 3 h, after which it was cooled, and the precipitate was removed by filtration, washed on the filter with 10 ml of ethanol, and recrystallized from the appropriate solvent. Compounds VI-IX were obtained in this way (Table 1).

B) A 9.6-g sample of bromine was added with stirring at 40°C to a solution of 0.06 mole of the corresponding acetophenone in 20 ml of acetic acid, and the mixture was stirred until the color due to the bromine disappeared. It was then poured into water, and the organic layer was extracted with chloroform. The extract was washed successively with water, a 5% aqueous solution of sodium carbonate, and water and dried with anhydrous Na_2SO_4. The chloroform was removed by vacuum distillation to give crude bromo ketones II-IV, which were used immediately in the next step. Bromo ketone V was isolated by dilution of the reaction mixture with water, removal of the precipitate by filtration, and recrystallization from heptane. Ethanol (100 ml) and 0.12 mole of benzaldehyde guanylhydrazone were added to the bromo ketone (II-V), and the reaction mixture was refluxed for 2 h. It was then cooled, and the precipitate was removed by filtration and recrystallized two to three times from chloroform to give VI-IX. The mother liquors obtained after recrystallization of VII-IX were evaporated *in vacuo*, and the residue was dissolved in the minimum amount of chloroform and chromatographed on Chemapol L 40/100 silica gel with benzene—acetone (10:1). The crimson-colored fraction was collected and evaporated, and the residue was recrystallized from acetic anhydride to give X and XI and a mixture of XII and XIII, respectively. The mixture of XII and XIII was dissolved in the minimum amount of chloroform and chromatographed again as indicated above. Two fractions were collected and evaporated to give XII (R_f 0.13) and XIII (R_f 0.48) [R_f on Silufol, benzene—acetone (10:1)].

TABLE 2. Dichroism of the Long-Wave Absorption Bands in the Electronic Spectra of XXI-XXIV

Compound	XXI	XXII	XXIII	XXIV
S (λ, nm)	0,46 (410)	0,78 (410)	0,26 (466), 0,25 (498)	0,49 (475), 0,50 (500)

1,1'-Bis(benzylideneamino)-4,4'-bis(4-octyl-4'-diphenylene)-cis- (XII) and 1,1'-Bis-(benzylideneamino)-4,4'-bis(4-octyl-4'-diphenylene)-trans-2,2'-azoimidazole (XIII). A 31.9-g (0.071 mole) sample of IX was oxidized with 50 g of manganese oxide [9] in 2 liters of benzene by heating with removal of the water by azeotropic distillation in the course of 3.5 h. The mixture was then filtered, and the precipitate was washed on the filter with 200 ml of hot benzene. The filtrates were combined and evaporated *in vacuo* to a volume of 700 ml, and the concentrate was cooled. The precipitate was removed by filtration and dissolved in the minimum amount of chloroform. The chloroform solution was chromatographed on activity II aluminum oxide by elution with benzene—acetone (10:1). The second and third fractions were collected and evaporated, and the residues were recrystallized from the minimum amount of benzene to give 1.920 g (6%) of XIII (from the second fraction, R_f on Silufol 0.48 [benzene—acetone (10:1)]) and 0.032 g (0.01%) of XII (from the third fraction, R_f on Silufol 0.13 [benzene—acetone (10:1)]).

1,2-Diaminoimidazoles (VII-XX). A mixture of 0.02 mole of I-IV and 20 ml of hydrazine hydrate in 50 ml of diethylene glycol was heated to the boiling point with stirring, and the mixture was refluxed until a homogeneous solution formed (~3 h). The mixture was cooled, and the precipitate was removed by filtration, washed on the filter with water, and recrystallized from ethanol. This method was used to prepare XVII-XX.

Imidazo[1,2-b]-1,2,4-triazines (XXI, XXII) and Imidazo[1,2-b]phenanthreno[9,10-e]-1,2,4-triazines (XXIII, XXIV). A mixture of 0.01 mole of XVII or XX and 0.01 mole of glyoxal monohydrate or phenanthrenequinone in 100 ml of ethanol was refluxed for 3 h, after which the hot mixture was filtered, and the solvent was removed by distillation *in vacuo*. The residue was recrystallized twice from the minimum amount of ethanol. This method was used to obtain XXI-XXIV.

2-Amino-1-benzylideneamino-5-methyl-4-phenylimidazole (XIV) and 1-Benzylideneamino-2,5-dimethyl-3,6-diphenylimidazo[1,2-a]imidazole (XV). A 2.2-ml (0.042 mole) sample of bromine was added with stirring to a solution of 5.68 g (0.042 mole) of propiophenone in 10 ml of acetic acid, and the mixture was maintained at 20°C for 1 h. Water (50 ml) was added, and the organic layer was extracted with chloroform. The extract was washed successively with water, a 5% aqueous solution of sodium carbonate, and water and dried with anhydrous sodium sulfate. The chloroform was removed by vacuum distillation, and 50 ml of ethanol and 13.5 g (0.084 mole) of I were added to the resulting α-bromopropiophenone (XIV). The resulting solution was refluxed for 3 h, after which it was cooled, and the precipitate was removed by filtration, washed on the filter with 10 ml of ethanol, and recrystallized from the minimum amount of benzene—ethanol (4:1), twice from the minimum amount of benzene, and, finally, from the minimum amount of ethanol to give 0.51 g of XV. The mother liquors from the crystallizations were combined and evaporated *in vacuo*, and the residue was dissolved in the minimum amount of benzene. The solution was separated chromatographically on Chemapol L 40/100 silica gel by elution with benzene to give an additional 0.7 g of XV and 1.13 g of XVI with R_f 0.09 and 0.66, respectively ($CHCl_3$).

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