Chemistry of Heterocyclic Compounds, Vol. 32, No. 5, 1996

POLYCYCLIC ROD-SHAPED AZO DYES BASED ON AMINOPHENYLPYRIMIDINES

V. F. Sedova, V. P. Borovik, M. A. Mikhaleva, and O. P. Shkurko

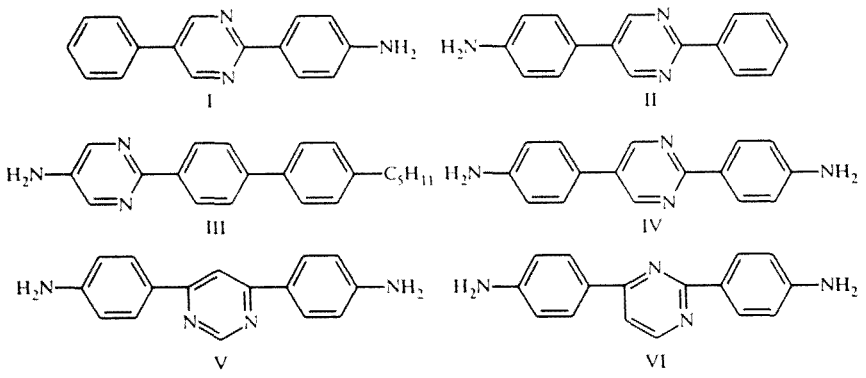
We have synthesized rod-shaped tricyclic monoazo and bisazo dyes based on amino derivatives of arylpyrimidines and N,N-dialkylanilines or p-*nitroso-N,N-dialkylanilines. We have shown that the process of azo coupling of the diazonium salt obtained from 2,5-bis(*p*-aminophenyl)pyrimidine is accompanied by dediazoniation, with substitution of the diazonium group by hydrogen or an aryl group. The monoazo dyes obtained display mesomorphic properties which are absent in the bisazo dyes.*

Among polycyclic compounds constructed from successively coupled aromatic and heterocyclic rings and including chromogenic spacer groups, a prominent position is occupied by azo compounds. As dichroic dyes, they are included within the composition of liquid crystalline materials used in display devices for color display of information [1-3]. Data on application of azo derivatives of the azine series are limited to individual examples [1,4-6]. Azoaryl- and arylazopyrimidines with a rod-shaped structure and not containing donor groups in the pyrimidine ring are a not very well studied class of compounds. Previously investigated derivatives of the pyrimidine series as dichroic dyes in a liquid-crystalline matrix (2-aryl-5-arylazopyrimidines [1] and 5-aryl-2-(arylazoaryl)pyrimidines [4,5]) have high order parameters, while the 5-aryl-2-arylazopyrimidines which are isomeric to the latter compounds are characterized by lower order parameters and substantial hypsochromic shifts of the long-wavelength absorption maximum in the UV spectra [6].

Bisazo dyes, compared with mono derivatives, have lower stability with respect to UV light and poorer solubility in a liquid-crystalline matrix, but due to higher geometric anisotropy have good order parameters and longer-wavelength absorption in the UV region [1,3]. In the series of bisazo dyes from pyrimidine derivatives, only the bisazo derivative of naphthalene is known, containing a pyrimidinylphenyl moiety bonded to one of the azo groups [4]. No bisazo derivatives of the pyrimidine series are known with symmetric location of the azo group relative to the pyrimidine ring.

Continuing the work on synthesis and study of the properties of azo derivatives of arylpyrimidines [6], we have synthesized tricyclic monoazo- and bisazoarylpyrimidines based on amino derivatives of arylpyrimidines I-VI, and we have compared their optical and mesomorphic properties with the properties of known bicyclic azo derivatives of pyrimidine.

By coupling of the diazonium salts Ia and IIa obtained from 2(*p*-aminophenyl)-5-phenyl- (I) and 5-(*p*-aminophenyl)-2-phenylpyrimidines (II) with dimethylaniline or N-pentyl-N′-phenylpiperazine, we synthesized the aminoazo dyes VII, VIII, and IX. Compound IX was also obtained by reaction of aminophenylpyrimidine I with N-pentyl-N′-(*p*-nitrosophenyl)piperazine.



Novosibirsk Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences, Novosibirsk 630090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 693-702, May, 1996. Original article submitted January 25, 1996.

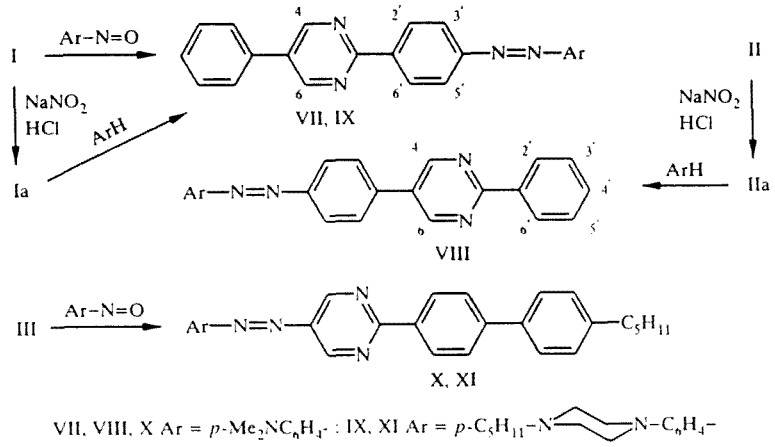
 0009-3122/96/3205-0596$15.00

TABLE 1. UV Absorption Spectra of Azo Derivatives of Pyrimidine

Соединение	Solvent	λ_{max}, nm	lg ε
	Bicyclic monoazo derivatives		
XII	$CHCl_3$	370	4.44
XIII	$CHCl_3$	454	4.53
XIV	$CHCl_3$	444	4.66
	Tricyclic monoazo derivatives		
VII	$CHCl_3$	440,	4.59,
	DMF	455	4.52
VIII	$CHCl_3$	438	4.50
IX	$CHCl_3$	423	4.57
X	$CHCl_3$	460	4.58
XI	$CHCl_3$	430	4.48
	Tricyclic bisazo derivatives		
XVI	$CHCl_3$	460*,	—
	DMF	480	4.81
XVII	DMF	470	4.80
XVIII	DMF	470	4.83

*For saturated solution.

By condensation of 5-amino-2-(4-pentylbiphenyl-4′-yl)pyrimidine (III) with *p*-nitroso-N,N-dimethylaniline or N-pentyl-N′-(*p*-nitrosophenyl)piperazine in superbasic medium, we synthesized the azo dyes X and XI respectively.



VII, VIII, X Ar = *p*-$Me_2NC_6H_4$- ; IX, XI Ar = *p*-C_5H_{11}-N⟨⟩N-C_6H_4-

Comparison of the UV absorption spectra of the monoazo derivatives of pyrimidine (Table 1) shows that in a bicyclic system, the location of the azo group affects the position of the absorption maximum: compared with the 2-azo derivative (XII) for 5-azo derivatives of pyrimidine (XIII and XIV), we observe a strong bathochromic shift. In a tricyclic system (compound X) when retaining the azo group in the 5 position of the pyrimidine ring, a small bathochromic shift occurs (compare with compounds XIII and XIV).

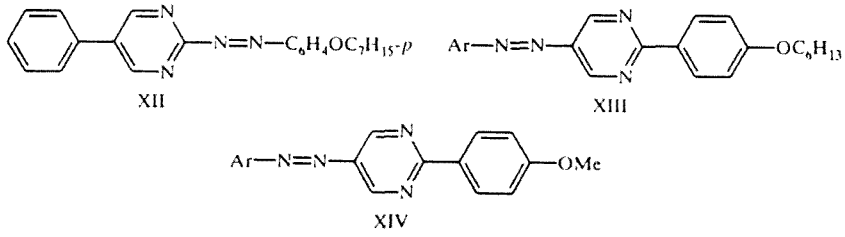


TABLE 2. Characteristics of Synthesized Compounds

Compound	T_{mp}, °C*	Empirical formula	Found / Calculated, %			Yield, %
			C	H	N	
I	199-201	$C_{16}H_{13}N_3$	77.9 77,7	5.18 5,30	17.1 17,0	94
II	162-168	$C_{16}H_{13}N_3$	78.1 77,7	5.19 5,30	17.2 17,0	93
III	200-202	$C_{21}H_{23}N_3$	79.2 79,5	7.35 7,30	13.2 13,2	85
VII	308-310 N-320 *I* decomp.	$C_{24}H_{21}N_5$	76.0 76,0	5.54 5,58	18.5 18,5	60
VIII	280 *N*...300 *I*	$C_{24}H_{21}N_5$	75.2 76,0	5.76 5,58	18.3 18,5	41
IX	222 S-235 *N* > 280 decomp.	$C_{31}H_{34}N_6$	75.9 75,9	7.05 6,98	16.8 17,1	33
X	225-350 *N*	$C_{29}H_{31}N_5$	77.4 77,5	7.02 6,95	14.7 15,6	76
XI	302-306	$C_{36}H_{44}N_6$	77.1 77,1	7.96 7,91	15.0 15,0	77
XIV	198-200	$C_{19}H_{19}N_5O$	68.6 68,7	5.75 6,07	21.0 21,3	30
XV	> 100 decomp.	$C_{16}H_{10}N_8$	61.4 61,1	3.07 3,21	35.6 35,6	94
XVI	310-315 decomp.	$C_{32}H_{30}N_8$	72.9 73,0	5.76 5,74	20.9 21,3	80
XVII	280-283	$C_{32}H_{30}N_8$	72.9 73,0	5.93 5,74	20.8 21,3	80
XVIII	314-318	$C_{32}H_{30}N_8$	72.8 73,0	5,84 5,74	20,9 21,3	93

*Compounds I, II were recrystallized from ethanol; compounds VII, VIII were recrystallized from DMSO; compounds IX, X, XI, XIV were recrystallized from benzene; compounds XV, XVI, XVII, XVIII were recrystallized from DMF. Compound III was purified by filtration of a solution in benzene through a bed of Al_2O_3. Symbols: *N*) nematic mesophase; *S*) smectic mesophase; *I*) isotropic liquid.

The presence of a phenylene bridge between the azo group and the 5 position of the pyrimidine ring (the tricyclic system of compound VIII) leads to a hypsochromic shift of the absorption band compared not only with the tricyclic isomeric skeleton of compound X, but also with the bicyclic system of 5-azopyrimidine (compounds XIII and XIV). Earlier, an anomalously low position of the absorption band was noted in the UV spectrum of bicyclic compounds with a 2-azopyrimidinyl moiety (compound XII) [6]. Introduction of a phenylene bridge between the azo group and the 2 position of the pyrimidine ring leads to a bathochromic shift of the long-wavelength absorption band (compare compounds VII and XII). We should note that in the tricyclic 2,5-diphenylpyrimidine system, the location of the azo groups in isomeric dyes VII and VIII has practically no effect on the position of the absorption maximum in the UV spectrum.

From comparison of the UV absorption spectra of the azo dyes VII and IX, X, and XI we see that substitution of the dimethylamino group by a piperazine ring leads to a hypsochromic shift of the absorption maximum (up to ~30 nm), which is consistent with observations made for other classes of compounds [7]. The hypsochromic shift is explained by weakening of the conjugation in the aniline part of the molecule between the phenyl group and the *p* orbital of the nitrogen atom, due to the presence of the more rigid conformational requirements of the piperazine ring.

Diazotization of 2,5-bis(*p*-aminophenyl)pyrimidine (IV) in an acetic acid—HCl mixture leads to the bisdiazonium salt IVa, which was confirmed by reaction of the latter with sodium azide and formation of 2,5-bis(*p*-azidophenyl)pyrimidine (XV) in high yield. The behavior of the diazonium salt IVa upon coupling with aniline derivatives to a significant degree depends on the reaction conditions and the chemical nature of the azo components.

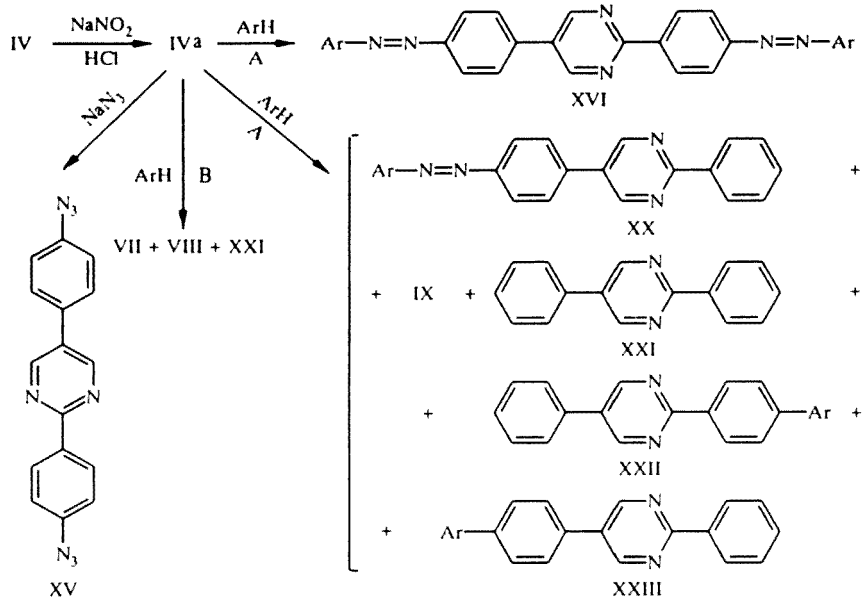
TABLE 3. PMR Spectra of Synthesized Compounds, Chemical Shifts, d, ppm (spin—spin coupling constants, J, Hz)

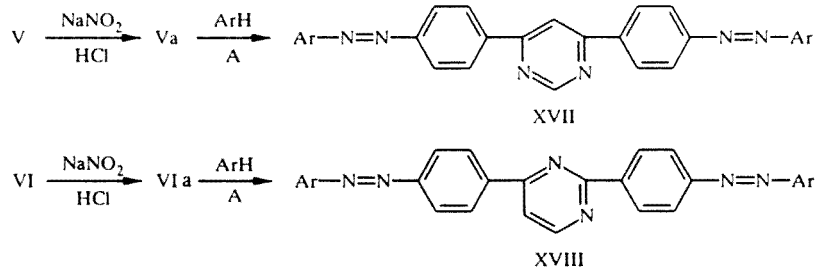
Compound	Solvent	H_{pyrim}		H_{arom}			H_{aliph}*	
		H-2 and H-5	H-4, H-6	Het-C_6H_4— H-2', H-6', d	—C_6H_4—$NAlk_2$-p H-m, d (J = 9.0 Hz)	other H	—$NAlk_2$	—C_5H_{11}
VII	CF_3COOH	–	9,57 (2H, s)	8,62 (2H, 9,0 Hz)	7,36 (2H)	7,67 - 8,23 (9H,m)	3,71 (6H, s, CH_3)	–
VIII	CF_3COOH	–	9,65 (2H, s)	8,45 (2H, d. d), 7,5 and 1,5 Hz)	7,30 (2H)	7,74 - 8,22 (9H,m)	3,67 (6H, s, CH_3)	–
IX	$CDCl_3$	–	9,02 (2H, s)	8,60 (2H, 8,5 Hz)	6,96 (2H)	7,97 (2H,d, 8,5Hz), 7,91 (2H, d, 9,0 Hz), 7,40 - 7,68 (5H,m)	3,39 (4H, t, CH_2), 2,61 (4H, t, CH_2)	2,39 (2H, t), 1,75 - 1,14 (6H, m), 0,88 (3H, t)
XVI	CF_3COOH	–	9,63 (2H, s)	8,65 (2H, 9,0 Hz)	7,31 (2H), 7,35 (2H)	7,99 - 8,29 (10H,m)	3,73 (6H, s, CH_3), 3,69 (6H, s, CH_3)	–
XVII	CF_3COOH	9,50 (1H,s), 8,77 (1H,s)	–	8,50 (4H, 9,0 Hz)	7,37 (4H)	7,93 - 8,29 (8H,m)	3,73 (12H, s, CH_3)	–
XVIII	CF_3COOH	8,39 (1H, d) (3,5 Hz)	8,94 (1H, d) (3,5 Hz)	8,71 (4H, 9 Hz)	7,32 (4H)	7,95 - 8,27 (8H,m)	3,72 (12H, s, CH_3)	–
XX†	$CDCl_3$	–	9,07, s	8,48, m	6,96	7,74 (1H, d. 8,5 Hz), 7,97 (1H,d, 8,5Hz), 7,89 (1H, d, 9,0Hz), 7,65 - 7,48 m	3,42 (4H, t), 2,65 (4H, t)	2,43 (2H, t), 1,60 - 1,31 (6H, m), 0,90 (3H, t)
XXII‡	$CDCl_3$	–	9,00 s	8,49 (8,5 Hz)	7,00	7,75 - 7,39 m	3,27 (4H, t), 2,60 (4H, t)	2,38 (2H, t), 1,67 - 1,16 (6H, m), 0,90 (3H, t)
XXIII†	$CDCl_3$	–	9,04 s	8,48 m	6,99	7,65 - 7,48 m		2,43 (2H, t), 1,60 - 1,31 (6H, m), 0,90 (3H, t)

*For signals from the piperazine ring, J = 5 Hz; for the N—CH_2—Alk signal, J = 7.7 Hz; for the signal from the CH_3 group in the alkyl substituent, J = 6.7 Hz.

†Assignments of signals were made from the spectrum of a mixture of compounds IX, XX, XXII, and XXIII, 9:9:1:1 ratio.

‡Assignments of signals were made from the spectrum of a mixture of compounds IX and XXII, 9:1 ratio.





XVI–XVIII Ar = p-$Me_2NC_6H_4$; XX, XXII, XXIII Ar = p-C_5H_{11}-N⟨⟩N-C_6H_4

Upon addition of the bisdiazonium salt IVa to dimethylaniline ("reverse order" of mixing of the reagents, conditions A), we obtained the bisazo dye XVI in high yield.

Similarly, upon diazotization of compounds V and VI followed by coupling with dimethylaniline, we obtained the bisazo dyes XVII and XVIII. Under the same conditions, the reaction of the bisdiazonium salt IVa with N-pentyl-N′-phenylpiperazine, occurring very slowly, did not lead to formation of 2,5-bis{4-[4-(4-*n*-amyl-1-piperazinyl)phenyl]-azophenyl}pyrimidine (XIX). From the complex mixture of products, we isolated a mixture of two monoazo derivatives in ~1:1 ratio (according to the PMR spectra): one was identified as compound IX, and the other was identified as the isomeric compound XX. Furthermore, we obtained 2,5-diphenylpyrimidine (XXI) as the product of deamination of compound IV. In purification of the mixture of compounds (IX + XX), we also observed the presence of difficultly soluble products for which, based on the mass spectrum and PMR spectrum, we may propose the following structures for the isomeric compounds: 2-[4-(4-pentyl-1-piperazinyl)biphenyl-4′-yl]-5-phenylpyrimidine (XXII) and 5-[4-(4-pentyl-1-piperazinyl)biphenyl-4′-yl]-2-phenylpyrimidine (XXIII).

Formation of compounds XXI and XXII was also observed upon coupling of the monodiazonium salt Ia with N-pentyl-N′-phenylpiperazine.

As we should also expect, we obtained complex reaction mixtures for the normal order of mixing of the reagents. Thus, from the bisdiazonium salt IVa and dimethylaniline (conditions B), the bisazo dye XVI was not observed in the reaction mixture. By chromatographic separation, from the reaction mixture we isolated in significant amounts a mixture of the corresponding isomeric monoazo dyes VII and VIII in 1:1 ratio, and also 2,5-diphenylpyrimidine (XXI).

Synthesis of the salt IVa by diazotization of the amine IV in nitrosylsulfuric acid (conditions C) followed by coupling leads to formation of up to 40% of a mixture of the monoazo derivatives VII and VIII, and also a significant amount of the bisazo product XVI. In all cases, unidentified products were present.

Formation of the monoazo dyes VII, VIII, IX, and XX, the diphenylpyrimidine XXI, and the compounds XXII and XXIII during diazotization of the diamino derivative IV followed by coupling of the salt IVa indicates decomposition of the latter under the reaction conditions, with exchange of the diazonium group by hydrogen and occurrence of the arylation reaction.

Along with reductive deamination of diazonium salts [8], exchange of a diazonium group by hydrogen often occurs under different conditions even without addition of a reducing agent [8-10]. Examples have been described for dediazoniation of diazonium salts in the presence of acids [9,11,12]. The dediazoniation reaction is considered as a radical chain process [10], and alkyl groups may act as the source of hydrogen (for example, of acetic acid [12], alkylanilines [13], or alkylbenzenes [14]).

The literature data presented may explain the formation in the studied reaction of a large amount of the monoazo derivatives VII and VIII in acid media; and the appearance of products of the accompanying process of radical arylation in the reaction mixture of compounds XXII and XXIII indicates a radical mechanism for decomposition of the salt IVa. The lowered reactivity of the diazonium salt IVa, and also the low reactivity of alkyl-substitute phenylpiperazine probably favor the occurrence of side reactions of decomposition during azo coupling.

In the UV absorption spectra of the bisazo dyes XVI-XVIII, we observe a bathochromic shift of the absorption maximum compared with monoazo dyes (compounds VII, VIII, and XVI) (Table 1).

The monoazo dyes obtained display mesomorphic properties. The isomeric compounds VII and VIII form a nematic mesophase; in this case, the presence of a bridging *trans* azo group in the planar 2-phenylpyrimidinyl moiety gives an unstable compound, decomposing upon transition to the isotropic liquid, with a narrow temperature range for the mesophase. The opposite situation, i.e., addition of a *trans* azo group to the nonplanar 5-arylpyrimidinyl moiety [15], gives a more stable liquid crystal with a lower temperature for transition to the mesophase and a range for the existence of the mesophase which is twice as wide.

The azo dye IX, having high geometric anisotropy and including a *trans* piperazine moiety promoting the formation of a layer with closer packing [16], already displays smectic properties. Transition to the nematic mesophase in this compound occurs at a lower temperature than for the liquid crystals VII and VIII, and the thermodynamic stability of the nematic phase is high, since compound IX decomposes upon heating (as does 2-arylazopyrimidine VII), never reaching the nematic to isotropic liquid transition.

The monoazo compound X has a nematic mesophase over a wide temperature range, while its piperazine analog XI does not display mesomorphism.

EXPERIMENTAL

The PMR spectra of compounds VII, VIII, and the mixtures of compounds (VII + VIII) and (IX + XX + XXII + XXIII) were recorded on a Bruker AC-200 instrument. The PMR spectra of compounds (IX + XII) were recorded on a Bruker WP-200SY using $CHCl_3$ (7.24 ppm) or CH_2Cl_2 (5.32 ppm) as an internal standard. The IR spectra were taken on a Specord M-80 in KBr pellets. The UV spectra were taken on a Specord UV-vis spectrophotometer. The mass spectra were recorded on a Finnigan MAT-8200 spectrometer. The physicochemical and spectral characteristics of the compounds are presented in Tables 1-3. The compounds obtained in different experiments were identified by TLC on Silufol UV-254 plates and from the IR spectra. Mixtures of samples obtained by different methods did not show any depression of the melting point.

The starting compounds were obtained as follows: IV according to the technique in [17], V according to [18], VI according to [19]. The synthesis of compounds XII and XIII is described in [6].

2-(*p*-Aminophenyl)-5-phenylpyrimidine (I) and 5-(*p*-Aminophenyl)-2-phenylpyrimidine (II) were obtained by amination of the corresponding bromophenyl derivatives of pyrimidine with aqueous ammonia in an autoclave in the presence of CuBr at 160°C, as in [18,19].

5-Amino-2-(4-*n*-pentylbiphenyl-4′-yl)pyrimidine (III). 2 ml piperidine were added to a mixture of 1.0 g (3.3 mmoles) of 4′-n-pentylbiphenylamidine hydrochloride and 0.57 g (4.1 mmoles) of the sodium salt of nitromalonaldehyde in 24 ml 50% aqueous dioxane. This was stirred at room temperature for 3 h. The precipitate was filtered, washed with water, and dried. Obtained: 0.90 g (80%) 5-nitro-2-(4-*n*-pentylbiphenyl-4′-yl)pyrimidine, T_{mp} 248-251°C (from benzene). Found, %: N 12.3. $C_{21}H_{21}N_3O_2$. Calculated, %: N 12.1.

A mixture of 1.0 g (3 mmoles) of the nitro derivative of pyrimidine obtained, 0.6 g iron powder, 7.5 ml ethanol, and 1.4 ml glacial acetic acid were heated at 100°C with rapid stirring for 7 h. This was poured into 300 ml water; the precipitate was filtered off, washed with water, and dried. Obtained: 0.8 g amino derivative of pyrimidine III.

N-Pentyl-N′-(*p*-nitrosophenyl)piperazine. A solution of 3.3 g (48 mmoles) $NaNO_2$ in 34 ml water was added dropwise at 5°C to a mixture of 9.9 g (43 mmoles) N-pentyl-N′-phenylpiperazine, 34 ml conc. HCl, and 41 g ice. This was stirred at 5°C for 0.5 h, then a saturated solution of $NaHCO_3$ was added until a green precipitate (the hydrochloride of the nitroso derivative) fell out of solution. Then 60 ml ether was added and the result was neutralized with an $NaHCO_3$ solution at 10°C. The ether layer was removed and it was again extracted several times with ether (3 × 75 ml). The extract was dried and evaporated. Obtained: 9.4 g (84%) of a dark green viscous oil, which was used without purification to obtain the azo dyes IX and XI.

Synthesis of the Diazonium Salts Ia, IIa, IVa, Va, and VIa. The corresponding aminophenylpyrimidine (3.8 mmoles) was dissolved in acetic acid with heating up to 70°C, then 15 ml of 6N HCl was added. To the suspension formed at 0-5°C was added dropwise a saturated aqueous solution of $NaNO_2$ (4.2 mmoles for compounds I and II, 8.4 mmoles for compounds IV, V, VI). The reaction mixture was stirred at this temperature for 1 h, the excess $NaNO_2$ was removed by addition of urea. The solutions obtained were used for coupling with aromatic amines using methods A and B.

Synthesis of the Diazonium Salt IVa in H_2SO_4. 1.4 g (20 mmoles) $NaNO_2$ was dissolved in 20 ml H_2SO_4. Then 2.6 g (10 mmoles) of diamine IV was added to the solution in a single portion. The reaction mixture was stirred at room temperature until the diamine dissolved, then 80 g ice was added and it was allowed to stand for 1.5 h. The solution of the diazonium salt IVa was used in coupling with amines according to method C.

2-[4-(*p*-Dimethylaminophenyl)azophenyl]-5-phenylpyrimidine (VII) and 5-[4-(*p*-dimethylaminophenyl)azophenyl]-2-phenylpyrimidine (VIII). A solution of the diazonium salt Ia or IIa was added dropwise to a solution of 0.54 g (4.5 mmoles) dimethylaniline in 8 ml of 1N HCl at 0-5°C. This was stirred at that temperature for 1 h, then the reaction mixture was neutralized to pH 5 by addition of a saturated soda solution and stirred for 2 h at 0-5°C and then for 3 h at 20°C. Then it was neutralized to pH 8 by a saturated soda solution, extracted with chloroform (4 × 100 ml). The extract was washed with water, dried, evaporated down to 50 ml, and eluted on a column with SiO_2 with chloroform. Obtained: the azo dyes VII or VIII.

2-[4-(4-[4-*n*-Pentyl-1-piperazinyl]phenyl)azophenyl]-5-phenylpyrimidine (IX). Conditions A. A 5% NaOH solution was added to a solution of 1.0 g (4.4 mmoles) N-amyl-N′-phenylpiperazine in 10 ml of a 10% HCl solution until reaching pH 5. This was cooled down to 2°C and then a solution of the diazonium salt Ia was added dropwise over the course of 1 h, maintaining pH 5 in the solution by steady addition of a 5% NaOH solution. This was stirred for 3 h at a temperature of 2°C, then it was stirred for 24 h at room temperature. The reaction mixture was neutralized with a saturated $NaHCO_3$ solution. The precipitate was filtered off, washed with water, dried, and chromatographed on a column with SiO_2, sequentially separating the fractions: 1) (eluents pentane, pentane—chloroform, 5:2) 0.12 g (13%) diphenylpyrimidine XXI, T_{mp} 179-181°C (according to the data in [20], T_{mp} 180-181°C); 2) (eluents pentane—chloroform, 3:5, then 1:5) unidentified impurities; 3) (eluents chloroform, then chloroform—methanol, 9:1) 0.70 g of a mixture of compounds IX (high-resolution mass spectrum M^+ 490.2882, calculated for $C_{31}H_{34}N_6$ M 490.2844) and XXII (M^+ 462.2773, calculated for $C_{31}H_{34}N_4$ M 462.2783). The ratio of compounds IX and XXII in the mixture was 9:1, T_{mp} 202-220°C (from benzene). The pure compound IX was obtained by additional purification using HPLC (Silasorb 600, Bruker chromatograph, UV detector at 320 nm) in the gradient elution regime, from chloroform to a 1:1 chloroform—methanol mixture.

Azo Dye IX. A mixture of 0.35 g (1.4 mmoles) compound I and 0.36 g (1.4 mmoles) N-pentyl-N′-(*p*-nitrosophenyl)piperazine in 2 ml acetic acid and 2 ml ethanol was heated for 2.5 h at 80°C. The reaction mixture was decanted into 30 ml water, extracted with chloroform (3 × 30 ml), washed with an $NaHCO_3$ solution and then with water, then dried and evaporated. The residue was chromatographed on a column with SiO_2 (eluents chloroform, then chloroform—ethanol, 10:1). Obtained: 0.15 g (22%) azo dye IX, T_{mp} 222-230°C (from benzene).

2-(4-*n*-Pentylbiphenyl-4′-yl)-5-(4-dimethylaminophenylazo)pyrimidine (X). A mixture of 0.4 g (1.26 mmoles) pyrimidine III and 0.2 g (1.3 mmoles) *p*-nitrosodimethylaniline in 2.5 ml 40% NaOH solution was heated to boiling, and then 0.3 ml DMSO was added. This was boiled for 10 min and then cooled. The precipitate was filtered off, washed with water and then with alcohol, dissolved in chloroform, passed through a bed of Al_2O_3, and evaporated. Obtained: 0.4 g of product X.

2-(4-*n*-Pentylbiphenyl-4′-yl)-5-[4-(4-*n*-pentyl-1-piperazinyl)phenylazo]pyrimidine (XI) was obtained similarly to compound X from pyrimidine III and N-pentyl-N′-(*p*-nitrosophenyl)piperazine.

5-(*p*-Dimethylaminophenylazo)-2-(*p*-methoxyphenyl)pyrimidine (XIV) was obtained similarly to compound X from 5-amino-2-(*p*-methoxyphenyl)pyrimidine and *p*-nitrosodimethylaniline.

2,5-Bis(*p*-azidophenyl)pyrimidine (XV). A solution of 0.56 g (8.6 mmoles) NaN_3 in 3 ml water was added with stirring to a solution of the diazonium salt IVa at a temperature of −3°C in a single portion. The suspension obtained was stirred for 0.5 h at 0-5°C, then for 1 h at room temperature. This was decanted into 150 ml water and then neutralized with conc. NH_4OH to pH 7. The precipitate was filtered off and washed with water, then ethanol, and then ether. Obtained: 1.12 g. IR spectrum (KBr): 2105, 2145 cm^{-1} (N_3).

2,5-Bis[4-(*p*-dimethylaminophenyl)azophenyl]pyrimidine (XVI), 4,6-bis[4-(*p*-Dimethylaminophenyl)azophenyl]-pyrimidine (XVII), 2,4-bis[4-(*p*-Dimethylaminophenyl)azophenyl]pyrimidine (XVIII). Conditions A. A solution of the bisdiazonium salt IVa, Va or VIa was added dropwise at a temperature of 0-5°C to a suspension of 1.1 g (9.0 mmoles) dimethylaniline in a mixture of 5 ml acetic acid, 10 ml [sic] and 4.5 g sodium acetate. The reaction mixture was stirred at this temperature for 2 h and then allowed to stand overnight. On cooling with ice, it was neutralized with 150 ml of a 10% NaOH solution, then with a saturated soda solution. The precipitate was filtered, washed with water and then ethanol, crystallized from DMF or reprecipitated by pouring the hot solution of the material in DMF into ethanol.

Azo Coupling of the Diazonium Salt IVa under Conditions B. A solution of 1.1 g (9.0 mmoles) dimethylaniline in 3.0 ml acetic acid was added dropwise at a temperature of 0-5°C to a solution of the diazonium salt IVa. This was stirred at that temperature for 0.5 h, then 17 g sodium acetate in 50 ml water was added dropwise. This was stirred with cooling for 2 h and then held for 2 days at room temperature. The reaction mixture was neutralized with 100 ml of a 10% NaOH solution and then with a saturated Na_2CO_3 solution, and then extracted with chloroform (100 ml × 4). The extract was washed with water, dried, and evaporated. The residue was chromatographed on an SiO_2 column, obtaining two fractions: 1) (eluent pentane—chloroform, 1:2), compound XXI, 0.1 g (10%); 2) (eluents chloroform, chloroform—ethylacetate, 1:1) a mixture of monoazo dyes VII+VIII 0.7 g (47%), T_{mp} 240-278°C (from DMSO), M^+ 379. According to the PMR and IR spectra, this completely corresponds to the mixture of compounds VII and VIII (1:1) obtained from compounds I and II. UV spectrum, λ_{max} (log e): ($CHCl_3$) 438 nm (4.16).

Azo Coupling of the Diazonium Salt IVa under Conditions C. 2.4 g (20 mmoles) dimethylaniline was dissolved in 5 ml of a 3N HCl solution, and a solution of the diazonium salt IVa in H_2SO_4 was filtered into it. The dark red solution obtained was allowed to stand for 24 h, then was filtered and neutralized with a soda solution to pH 6. The precipitate was filtered off and washed with water, then ether, and then ethanol. Obtained: 3.5 g product (a mixture of dyes).

The product obtained (1.0 g) was boiled with a benzene—chloroform—ethanol mixture, 5:3:3, in order to remove residues of diphenylpyrimidine XXI and unidentified dyes. The residue was boiled in 150 ml DMF. The hot solution was filtered and cooled. The precipitate was removed and 0.45 g (30%) bisazo derivative XVI was obtained. The mother liquor was concentrated under vacuum down to 1/3 volume and then cooled. The precipitate was filtered off: a mixture of monoazo derivatives VII and VIII, 0.43 g (39%) (mass spectrum, *m/z* 379).

Azo Dye IX and 5-[4-(4-[4-*n*-Pentyl-1-piperazinyl]phenyl)azophenyl]-2-phenylpyrimidine (XX). A solution of the diazonium salt IVa (obtained from 0.5 g (2.0 mmoles) compound IV) was added dropwise over the course of 5 h at a temperature of 0-5°C with stirring to a mixture of 1.0 g (4.3 mmoles) N-amyl-N′-phenylpiperazine, 2.5 ml acetic acid, 2.1 g sodium acetate, and 5 ml water. This was stirred for 10 h at that temperature and then for 24 h at room temperature. The reaction mixture was neutralized with a 10% NaOH solution and a saturated $NaHCO_3$ solution, then filtered and washed with water. Obtained: 0.5 g of a mixture of products. The mixture was chromatographed on a column with SiO_2 (eluents were sequentially: pentane—chloroform, 1:1, 1:3, chloroform), obtaining 50 mg of the compound and 80 mg (8.5%) of a mixture of the monoazo dyes IX, XX, and biphenyl derivatives XXII and XXIII in the ratio (9:9:1:1). High resolution mass spectra M^+ 490.2780, calculated for compounds IX and XX, $C_{31}H_{34}N_6$, M 490.2844 and M^+ 462.2761, calculated for compounds XXII and XXIII, $C_{31}H_{34}N_4$, M 462.2783. UV spectrum ($CHCl_3$), λ_{max} (log e): 318 (4.37), 420 nm (4.49).

This work was done with the financial support of the International Science Foundation and the Russian government, grant NQN300.

REFERENCES

1. A. V. Ivashchenko, Dichroic Dyes for Liquid Crystal Displays, CRC Press, Boca Raton (1994).
2. S. Wu, J. D. Margerum, M. Ho, and B. M. Fung, Appl. Phys. Lett., **64**, 2191 (1994).

3. Dichroic Dyes for Liquid-Crystal Displays. Aniline Dye Industry Series [in Russian], Rev. Inf. MNPO NIOPiK; NIITÉKhIM, Moscow (1987).
4. M. Kaneko, T. Ozawa, T. Yoneyama, S. Imazeki, A. Mucoh, and M. Sato, Eur. Pat. Appl. 76,633; Chem. Abstr., **99**, 46062 (1983).
5. M. Kaneko, T. Yoneyama, J. Iwanami, S. Imazeki, A. Mukoo, and M. Sato, Eur. Pat. Appl. 98,522; Chem. Abstr., **100**, 148633 (1984).
6. M. A. Mikhaleva, G. A. Igonina, V. T. Lazareva, V. G. Rumyantsev, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 2, 209 (1993).
7. L. Z. Gandel'sman, S. V. Shelyazhenko, L. A. Nechitailo, Yu. A. Fialkov, and T. S. Plyusnina, Ukr. Khim. Zh., **54**, 608 (1988).
8. Houben-Weyl, Methods of Organic Chemistry [in German], Georg Thieme Verlag, Stuttgart/New York (1990); Vol. E 161/2, p. 1052.
9. D. F. De Tar and M. N. Turetzky, J. Am. Chem. Soc., **77**, 1745 (1955).
10. C. Galli, Chem. Rev., **88**, 765 (1988).
11. H. Gies and E. Pfeil, Lieb. Ann., **578**, 11 (1952).
12. R. Nishiyama, Tetrahedron Lett., No. 15, 1403 (1967).
13. J. H. Gorvin, J. Chem. Soc., No. 7, 1693 (1951).
14. I. Takagishi, Y. Hashida, and K. Matsui, Bull. Chem. Soc. Jpn., **52**, 2635 (1979).
15. G. Winter, H. Hartung, W. Brandt, and M. Jaskolski, Mol. Cryst. Liq. Cryst., **150b**, 289 (1987).
16. S. Takenaka, T. Hirobata, and S. Kusabayashi, Bull. Chem. Soc. Jpn., **58**, 1079 (1985).
17. V. P. Borovik, V. A. Semikolenov, and V. P. Mamaev, Izv. Sibirsk. Otdel. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 4, 94 (1988).
18. V. P. Borovik, A. I. Shadrina, and V. P. Mamaev, Sibirsk. Khim. Zh., No. 6, 77 (1991).
19. V. P. Borovik, S. G. Baram, E. Yu. Kozlova, and V. P. Mamaev, Izv. Sibirsk. Otdel. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 5, 97 (1985).
20. R. M. Wagner and C. Jutz, Chem. Ber., **104**, 2975 (1971).