ARYLAZOPYRIMIDINES AS DICHROIC DYES FOR LIQUID CRYSTALS

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Substituted 5-arylazopyrimidines and 2-arylazopyrimidines have been synthesized and investigated as dichroic dyes with positive dichroism, for liquid crystals. A promising series of 2-aryl-5-arylazopyrimidine dyes has been found, and a method is proposed for their synthesis by condensation of 2-aryl-5-aminopyrimidines with nitrosobenzenes in a superbasic medium.

The use of dichroic dyes in liquid-crystal displays in order to obtain color images may simplify their manufacture and improve their operating reliability by eliminating the use of polaroids. The dichroic dyes function primarily through realization of a "guest–host" electrooptical effect [1]. The efficiency of a dye is most often rated by the order parameter S of the guest (the dye), which is uniaxially oriented in the liquid-crystal matrix. This parameter is a quantitative measure of the degree of parallelism of the long-wave transition oscillator of the dye molecule to the direction of orientation of the host [2], and it is determined from the polarization absorption spectrum of the solution of the dye in the matrix.

One of the most important and commercially significant classes of such dyes is a class of dichroic azo dyes having a structure very similar to that of rodlike nematic liquid crystals.

In the work reported here, we synthesized a number of substituted 5-arylazopyrimidines I and 2-arylazopyrimidines II for testing as dichroic dyes with positive dichroism (L type [3]) for liquid crystals. In these dyes, the presence of the pyrimidine ring, the dipole moment of which is directed along the long axis of the molecule, may result in obtaining dyes with a good value of the order parameter S.

There are not many L-type dichroic azo dyes based on heterocyclic systems, and only individual derivatives in certain series fit this classification (for example, in the pyridine and thiazole series [1, 4); no systematic studies have been pursued in this area. In [4, 5], among a large number of aromatic azo derivatives, data are reported on individual compounds of the 2-azophenylpyrimidine series, in which the azo group is separated from the pyrimidine ring by a benzene ring. The compounds are classed as yellow-orange dyes, and they have values of S in the 0.75-0.79 interval.

Research and development work in the synthesis of arylazopyrimidines has been quite limited in scope. Apart from the most numerous group of dihydroxy, trihydroxy, amino, and methyl derivatives of 5-phenylazopyrimidines [6], only one example of the preparation of a 4,6-unsubstituted 5-phenylazopyrimidine is known — by condensation of 5-aminopyrimidine with nitrosobenzene in acetic acid [7]. Of the several versions of the synthesis of 2-arylazopyrimidines [8, 9, 10], the one that appears to be convenient in practice is based on condensation of derivatives of 2-hydrazinopyrimidine with quinones [11].

We obtained 5-arylazopyrimidines IIIa,b by direct synthesis [6] — by condensation of an arylhydrazone of methyl mesoxalate (arylazomalonic ester) IV with the benzamidines Va,b. The reaction gave good yields, but this route is somewhat inconvenient in terms of varying the substituents in the benzene fragment of the molecule. In the example of 2-(*p*-cyanophenyl)-4,6-dihydroxypyrimidine (VI), we checked out the possibility of coupling 2-arylpyrimidines with diazonium salts. By interaction of the pyrimidine VI with *p*-butoxyphenyldiazonium chloride, we obtained the azopyrimidine IIIc, on which we performed modifications of the side substituents. The dihydroxy derivatives IIIa-c were converted by the action of $POCl_3$ to the dichloro derivatives Ia-c, and then to the corresponding methoxy derivatives.

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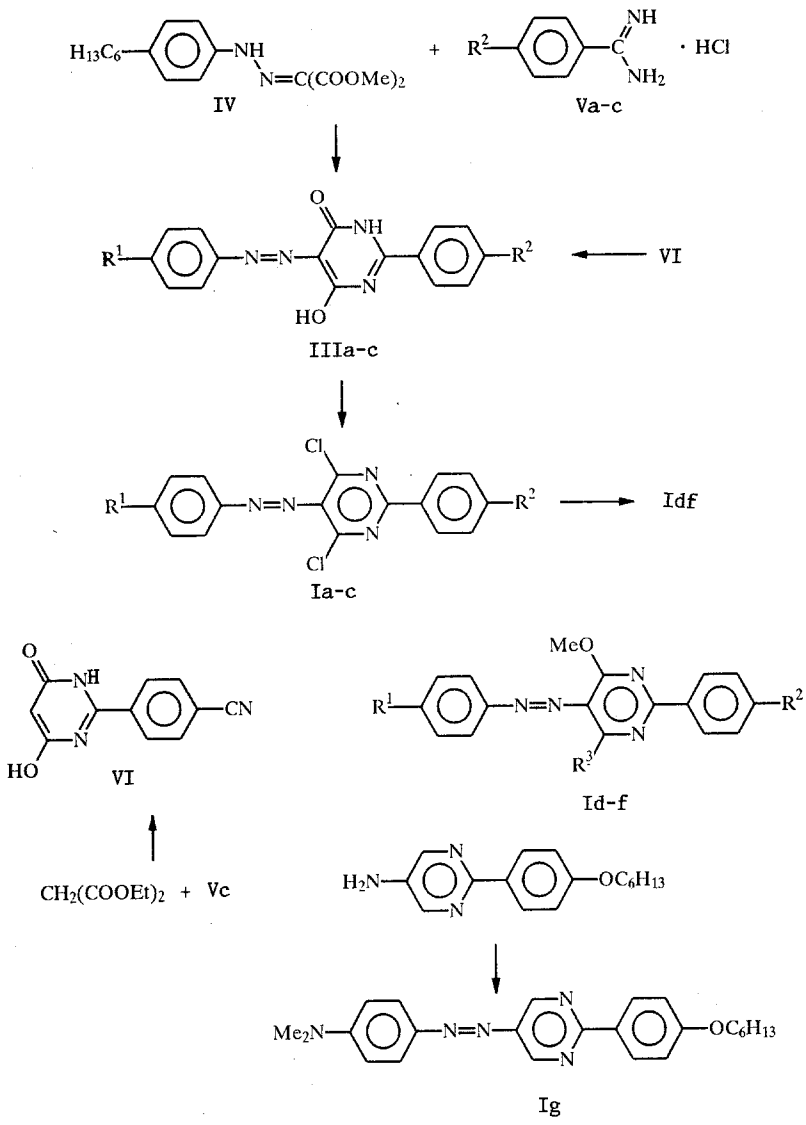
Scheme 1



Ia,b,d,e, IIIa,b) $R^1 = C_6H_{13}$; Ic,f, IIIc) R^1 = OBu; Ia,d, IIIa, IVa) R^2 = OBu; Ib,e, IIIb, Vb) $R^2 = OC_6H_{13}$; Ic,f, IIIc, Vc) R^2 = CN; Id) R^3 = Cl; Ie,f) R^3 = OMe.

The performance of dichroic dyes and particularly the order parameter S depend on the *l/d* ratio of the molecular structure, i.e., the length-to diameter ratio of the cylinder described around the molecule [12]. Therefore, the introduction of side substituents may have an adverse effect on the properties of the dye [3]. For the synthesis of 2-aryl-5-arylazopyrimidines that do not contain any substituents in position 4 or 6 of the pyrimidine ring, starting from 2-aryl-5-aminopyrimidines in which the coupling reaction cannot be carried out because of the low basicity of the amino group, we made use of the known conditions of synthesis of azo compounds from aromatic amino and nitroso compounds. However, we were not successful in carrying out the condensation of 2-aryl-5-aminopyrimidines with *p*-nitroso-N,N-dimethylaniline, either in acetic acid [7] or, by analogy with aminopyridines [13], in an alkaline medium.

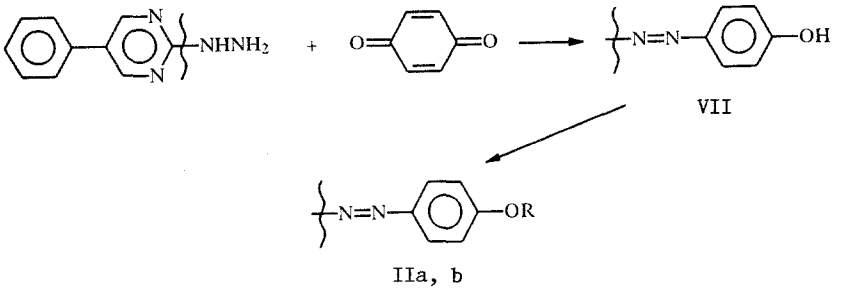
On the assumption that the mechanism of condensation of aromatic amines with nitroso compounds includes nucleophilic attack of the amino-group nitrogen atom at the positively charged nitrogen atom of the nitroso group [14], we used a superbasic medium [15] to accomplish deprotonation of the weakly basic 5-aminopyrimidine. And in fact, in a KOH/DMSO medium, we were successful in condensing 5-amino-2-(*p*-hexylphenyl)pyrimidine with *p*-nitroso-N,N-dimethylaniline, obtaining the azo derivative Ig.

TABLE 1. Characteristics of Dichroic Dyes I and II

Compound	Ic	Id	Ie	If	Ig	IIa	IIb	VIII
λ_{max}, nm	372	470	412	372	474	368	368	420
S	0,53	0,38	0,57	0,55	0,71	0,63	0,61	0,68

The 2-arylazopyrimidines II were synthesized by interaction of the corresponding 2-hydrazinopyrimidine with benzoquinone, followed by alkylation of the *p*-hydroxyphenylazo derivative VII that is formed as an intermediate.

Scheme 2



IIa, b

IIa) R = C_5H_{11}; IIb) R = C_7H_{15}

The azo compounds obtained in these syntheses were tested as dichroic dyes for liquid crystals, in the form of 0.5% solutions in LC-807 liquid crystal matrix, which is a mixture of *p*-alkyl- and *p*-alkoxycyanobiphenyls [16]. Also included for comparison was the previously obtained 5-[2-(*p*-butoxyphenyl)azopyrimidine (VIII) [17], as it has a favorable structure, without any side substituents.

From the values that are listed in Table 1 it can be seen that the presence of the rather bulky Cl or OCH_3 groups as side substituents in the pyrimidines Ic-f has a significant adverse effect on their order parameters in comparison with the other compounds. For the 2-azopyrimidines II, the values are somewhat higher, and probably can be improved still more by optimizing the structure (for example, by introducing additional end-substituents); however, the prospects for compounds of this series are doubtful, in view of the low position of the long-wave transition band.

The four-ring symmetric azopyrimidine VIII has even better indexes, but its solubility in the LC mixture is inadequate (0.125%). The best characteristics are exhibited by the azopyrimidine Ig, which, apart from its favorable geometry, also has a more favorable position of the donor and acceptor fragments in the molecule, giving a significant bathochromic shift of the long-wave absorption band.

Thus, on the basis of an examination of the properties of arylazopyrimidines differing in structure, we have found a promising type of azo dyes of the 2-aryl-5-(arylazo)pyrimidine series as dichroic dyes for liquid crystals, and we are proposing a method for their synthesis by the condensation of 5-aminopyrimidines with nitrosobenzenes in a superbasic medium.

EXPERIMENTAL

Polarization absorption spectra of oriented solutions of the dyes in LC-807, in the visible region, were measured in a PU-8800 spectrophotometer. The course of the reaction and the individuality of the substances were monitored chromatographically on Silufol UV-254 plates in a $CHCl_3$–alcohol system, 20:1.

The elemental analyses for C, H, Cl, and N were in agreement with the calculated compositions.

4,6-Dichloro-2-(*p*-hexyloxyphenyl)-5-(*p*-hexylphenylazo)pyrimidine (Ib, $C_{28}H_{34}Cl_2N_4O$). A mixture of 1 g (2 mmoles) of 4,6-dihydroxypyrimidine IIIb in 10 ml of $POCl_3$ was refluxed with stirring for 6 h. The excess $POCl_3$ was removed under vacuum; the residue was triturated with water and extracted with ether (3 × 30 ml); the extract was washed with water, dried with $MgSO_4$, and evaporated under vacuum. Obtained 0.45 g (50%) of the dichloroazopyrimidine Ib, mp 92-96°C (from alcohol).

4,6-Dichloro-2-(*p*-cyanophenyl)-5-(*p*-butoxyphenylazo)pyrimidine (Ic, $C_{21}H_{17}Cl_2N_5O$). A mixture of 0.5 g (1.3 mmoles) of the dihydroxypyrimidine IIIc in 14 mo of $POCl_3$ was refluxed for 3 h. The $POCl_3$ was removed under vacuum; the dry residue was diluted with 20 ml of water and extracted with chloroform (5 × 40 ml); the extract was washed with water and dried with $MgSO_4$. This chloroform solution was passed through a bed of aluminum oxide (d = 35 mm, l = 50 mm), and then evaporated under vacuum. Obtained 0.36 g (66%) of the dichloroazopyrimidine Ic, mp 125-130°C.

4-Chloro-6-methoxy-2-(*p*-butoxyphenyl)-5-(*p*-hexylphenylazo)pyrimidine (Id, $C_{27}H_{33}ClN_4O_2$). A mixture of 1.3 g (2.9 mmoles) of the dihydroxyazopyrimidine IIIa and 17 ml of $POCl_3$ was refluxed for 2 h. The $POCl_3$ was removed under vacuum, 20 ml of water was added, and the mixture was extracted with chloroform (3 × 40 ml); the extract was washed with water, dried with $MgSO_4$, and evaporated under vacuum. Obtained 0.33 g of the azopyrimidine Ia (24%), mp 101-103.5°C. To this product, 0.11 g (2 mmoles) of sodium methylate in 15 ml of absolute methanol was added, and the mixture was refluxed for 30 h. After cooling to 20°C, the precipitate was filtered off, washed with 5 ml of methanol, and dried in air. Obtained 0.22 g (67%) of the azopyrimidine Id, mp 63-65°C (from alcohol).

4,6-Dimethoxy-2-(*p*-hexyloxyphenyl)-5-(*p*-hexylphenylazo)pyrimidine (Ie, $C_{30}H_{40}N_4O_3$). A mixture of 0.5 g (1 mmole) of the dichloropyrimidine Ib and 0.22 g (4 mmoles) of sodium methylate in 20 ml of absolute methanol was refluxed for 30 h. After cooling to 20°C, the precipitate was filtered off and partitioned in a column with aluminum oxide (chloroform eluent), obtaining 0.2 g (40%) of the dimethoxyazopyrimidine Ie, mp 103-104°C.

4,6-Dimethoxy-2-(*p*-cyanophenyl)-5-(*p*-butoxyphenylazo)pyrimidine (If, $C_{23}H_{23}N_5O_3$). A mixture of 0.21 g (0.5 mmole) of the dichloropyrimidine Ic and 0.08 g (1.5 mmoles) of sodium methylate in 15 ml of absolute methanol was refluxed for 16.5 h. The reaction mixture was evaporated down, and the residue was dissolved in chloroform and passed through a bed of aluminum oxide (d = 30 mm, l = 100 mm). Obtained 0.2 g (99%) of the dimethoxypyrimidine If, mp 142-146°C (from benzene).

2-(Hexyloxyphenyl)-5-(*p*-dimethylaminophenylazo)pyrimidine (Ig, $C_{24}H_{29}N_5O$). To a mixture of 0.27 g (l mmole) of 5-amino-2-(*p*-hexyloxyphenyl)pyrimidine and 0.15 g (l mmole) of *p*-nitroso-N,N-dimethylaniline, 3 ml of a 40% NaOH solution and 2 ml of DMSO were added, and the mixture was heated for 30 min at 110-120°C. After cooling to 20°C, 20 ml of water was added and the mixture was extracted with chloroform; the extract was washed with water and dried with $MgSO_4$, after which the solvent was removed under vacuum. Obtained 0.6 g (15%) of the azopyrimidine Ig, mp 172-175°C (from alcohol).

2-(*p*-Amyloxyphenylazo)-5-phenylpyrimidine (IIa, $C_{21}H_{22}N_4O$). A solution of 1 g (3.6 mmoles) of the azopyrimidine VII in 30 ml of absolute benzene, plus 0.09 g (3.6 mmoles) of metallic sodium, was mixed for 40 min at 20°C on a magnetic stirrer. The solvent was removed under vacuum; 25 ml of DMF and 0.72 g (3.6 mmoles) of amyl iodide were added to the residue, and the mixture was held 4 h at 50°C. The reaction mixture was poured into 30 ml of water and extracted with chloroform (3 × 80 ml); the extract was washed with water, dried with $MgSO_4$, and evaporated under vacuum; the residue was partitioned in a column with silica gel (50/100 μm) with benzene as the eluent. Obtained 0.15 g (12%) of the azopyrimidine IIa, mp 135-138°C.

2-(*p*-Heptyloxyphenylazo)-5-phenylpyridimine (IIb, $C_{23}H_{26}N_4O$). To a solution of 0.1 g (3.6 mmoles) of the azopyrimidine VII in 22 ml of DMF, 0.2 g (4 mmoles) of a 50% suspension of NaH in oil was added, along with 1.1 g (6 mmoles) of heptyl bromide; the mixture was stirred for 2 h at 60°C. The reaction mixture, after cooling, was poured into 100 ml of water and extracted with chloroform (3 × 40 ml); the extract was dried with $MgSO_4$, evaporated under vacuum, and partitioned in an aluminum oxide column with chloroform eluent. Obtained 0.91 g (67%) of the azopyrimidine IIb, mp 128-130°C.

4,6-Dihydroxy-2-(*p*-butoxyphenyl)-5-(*p*-hexylphenylazo)pyrimidine (IIIa, $C_{26}H_{32}N_4O_3$). A mixture of 3.2 g (10 mmoles) of the arylazomalonic ester IV, 2.2 g (10 mmoles) of the amidine Va, and 1.62 g (30 mmoles) of sodium methylate in 50 ml of absolute methanol was stirred for 8 h at 20°C; the precipitate was filtered off and washed with water, obtaining 2.46 g (55%) of the azopyrimidine IIIa, mp > 350°C.

4,6-Dihydroxy-2-(*p*-hexyloxyphenyl)-5-(*p*-hexylphenylazo)pyrimidine (IIIb, $C_{28}H_{36}N_4O_3$). To a solution of 1.2 g (2.35 mmoles) of sodium methylate in 20 ml of absolute methanol, 1.9 g (7.45 mmoles) of the amidine Vb was added, the mixture was stirred for 20 min at 20°C, and the precipitate was filtered off. To the filtrate, 2.34 g (7.45 mmoles) of the arylazomalonic ester IV was added, and the mixture was stirred for 2 days at 20°C. The precipitate was filtered off and washed with ether. Obtained 2 g (56%) of the azopyrimidine IIIb, mp > 260°C (from ethanol).

4,6-Dihydroxy-2-(*p*-cyanophenyl)-5-(*p*-butoxyphenylazo)pyrimidine (IIIc, $C_{21}H_{19}N_5O_3$). A 0.28-g quantity (1.7 mmoles) of *p*-butoxyaniline was dissolved in 0.8 ml of 20% HCl, and 0.13 g (1.7 mmoles) of $NaNO_2$ was added. This freshly

prepared solution of the diazonium salt was added dropwise to a well-stirred suspension of 0.35 g (1.7 mmoles) of the dihydroxypyrimidine VI in 1.5 ml of a 10% NaOH solution. After holding this mixture for 16 h at 20°C, the precipitate was filtered off, washed with water, and air-dried. Obtained 0.61 g (92%) of the azopyrimidine IIIc, mp 292-294°C (from alcohol).

***p*-Hexylphenylhydrazone of Methyl Mesoxalate (IV, $C_{17}H_{24}N_2O_4$).** A diazonium salt solution freshly prepared from 21.1 g (0.12 mole) of *p*-hexylaniline, 10 g (0.15 mole) of $NaNO_2$, 20 ml of 36% HCl, and 150 ml of an ice–water mixture was poured into a prechilled (0°C) solution of dimethyl malonate in 127 ml of ethanol. Then 20 ml of a saturated aqueous solution of sodium acetate was added slowly (dropwise), and the reaction mixture was held for 12 h at 5°C. The precipitate was filtered off, washed with water, and air-dried. Obtained 17.6 g (46%) of the arylazomalonic ester IV, mp 40-41°C (from alcohol).

4,6-Dihydroxy-2-(*p*-cyanophenyl)pyrimidine (VI, $C_{11}H_7N_2O_2$). A mixture of 1.82 g (10 mmoles) of the amidine Vc, 1.6 g (10 mmoles) of malonic ester, and 0.54 g (10 mmoles) of sodium methylate in 10 ml of absolute ethanol was stirred for 2 days at 20°C. The suspension was diluted with 20 ml of water and acidified with concentrated HCl to pH ~7; the precipitate was filtered off and dried. Obtained 0.73 g (74%) of the dihydroxypyrimidine VI, mp 305-308°C.

2-(*p*-Hydroxyphenylazo)-5-phenylpyrimidine (VII, $C_{16}H_{12}N_4O$). To a stirred solution of 1.62 g (15 mmoles) of *p*-benzoquinone in 100 ml of 50% aqueous methanol, a solution of 0.93 g (5 mmoles) of 5-phenyl-2-hydrazinopyrimidine in 38 ml of 75% aqueous methanol was added dropwise. The reaction mixture was then diluted to 300 ml with water and stirred for 10 min at 20°C; the precipitate was filtered off and air-dried. Obtained 1.13 g (83%) of the azopyrimidine VII, mp 267-269°C.

REFERENCES

1. A. V. Ivashchenko and V. G. Rumyantsev, Mol. Cryst. Liq. Cryst. A., **150**, 1 (1987).
2. V. V. Titov and A. V. Ivashchenko, Zh. Vses. Khim. Ova., **28**, 176 (1983)/
3. "Dichroic dyes for liquid-crystal displays," in series: The Aniline Dye Industry [in Russian], Review Information of MNPO "NIOPiK," NIITÉKhM, Moscow (1987).
4. M. Kaneko, T. Ozawa, T. Yoneyama, S. Imazeki, A. Mucoh, and M. Sato, Eur. Pat. 76633; Chem. Abstr., **99**, 46062 (1983).
5. M. Kaneko, T. Yoneyama, J. Iwanami, S. Imazeki, A. Muhoo, and M. Sato, Eur. Pat. 98522; Chem. Abstr., **100**, 148633 (1984).
6. D. J. Brown, The Pyrimidines, Supplement 2, Wiley, New York (1985), p. 153.
7. N. Whittaker, J. Chem. Soc., No. 6, 1565 (1951).
8. S. B. Gashev and L. D. Smirnov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 678 (1979).
9. R. Huisgen and K. von Fraunberg, Tetrahedron Lett., No. 30, 2595 (1969).
10. G. G. Moskalenko, V. F. Sedova, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 7, 962 (1989).
11. R. G. Anderson and G. Nickless, Analyst, **93**, No. 1102, 20 (1968).
12. H. Seki, T. Uchida, and Y. Shibata, Mol. Cryst. Liq. Cryst., **138**, 349 (1986).
13. E. V. Brown and G. R. Granneman, J. Am. Chem. Soc., **97**, 621 (1975).
14. Houben–Weyl Methoden der Organischen Chemie, Vol. 10/3 (1985), p. 332.
15. B. A. Trofimov, Zh. Org. Khim., **22**, 1991 (1986).
16. E. I. Kovshov and V. P. Sevost'yanov, Élektron. Promst., No. 5-6, 7 (1982).
17. M. A. Mikhaleva, V. T. Lazareva, M. F. Grebenkin, V. A. Savelev, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 11, 1545 (1982).