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5-Arylazoimidazo[2,I-b]-1,3,4-Thiadiazoles—New Dichroic T-Dyes For LCD

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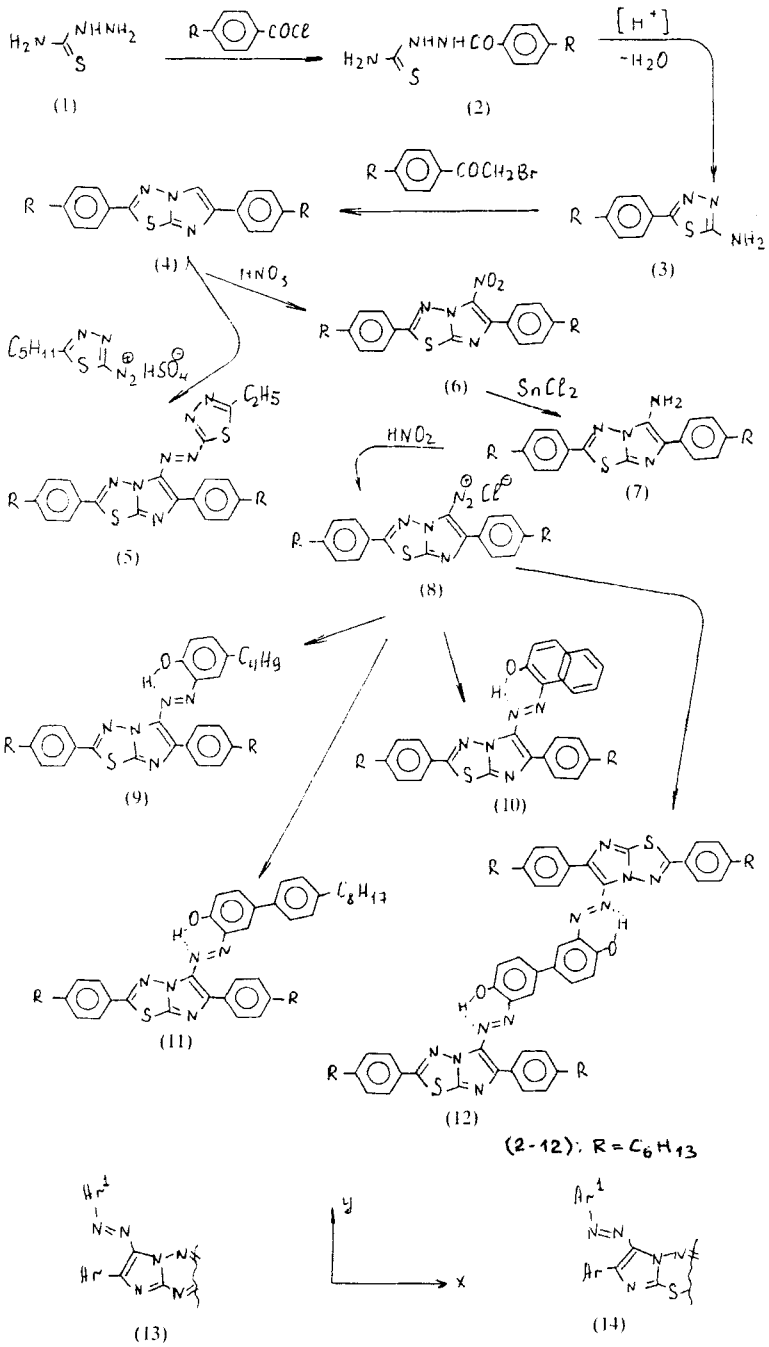
INTRODUCTION

Continuing research of dichroic *T*-dyes[1–4] we have obtained new 5-arylazo-2,6-diarylimidazo[2,I-b]-1,3,4-thiadiazoles (5,9-12). The compounds (2–5) have been synthesized by known methods.[5,6]

The distinctive feature of these *T*-dyes is their sufficiently high geometric anisotropy and more symmetrical arrangement of the arylazogroup in comparison to the substituted 4-aryl-5-arylazo-1,2-diaminoimidazoles earlier described by us.[4] Quantum-chemical calculations of the latter[7] and dichroism data of their long-wave absorption band (LAB) in liquid crystals[4] showed that oscillator of electron transition (which is responsible for LAB) is nearly perpendicular to their long geometric axis. It was supposed for this reason that oscillator of long-wave electron transition in new *T*-dyes (5,9-12) would be also nearly perpendicular to their long geometric axis because 4-aryl-5-arylazo-1,2-diaminoimidazoles and their derivatives as well as *T*-dyes (5,9-12) contain fragments (13,14 respectively) which are similar by electron structure and are responsible for LAB.

Consequently it was possible to expect that *T*-dyes (5,9-12) in liquid crystals exhibit a high value of negative dichroism.



(2-12): R = C_6H_{13}

EXPERIMENTAL

The compounds (2-12) were synthesized by known methods. Data of elemental analysis were satisfactory. Individuality of synthesized compounds was checked by TLC. Polarized spectra of *T*-dye solutions (5,9-12) in liquid crystalline mixture of 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls with clearing point equal to 60°C were measured at 20°C by an earlier described method.[8] Dichroism values were calculated on the base of $D_{\parallel}$ and $D_{\perp}$ values by formula $S = (D_{\parallel} - D_{\perp}/(D_{\parallel} + 2D_{\perp})$

DISCUSSION

T-dyes (5,9-12) have LAB at 460–530 nm and $S = -0.23 + -0.31$ (Table).

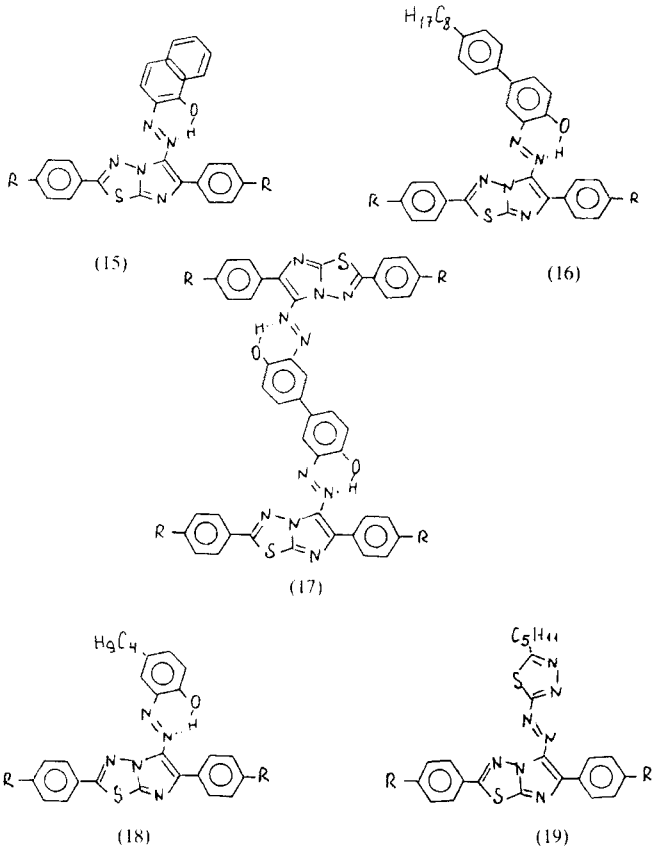
As follows from the Table, the *T*-dye (10) with 2-hydroxynaphthylazogroup and the bis-azodye (12) have the longest absorption band that correlates with well-known data. It is necessary to note that the azodye (12) is the first representative of a bis-azodye of the *T*-type. Sufficiently high value of negative dichroism testifies that obtained *T*-dyes (5,9-12) have the structure proposed on the scheme but not alternative structures (15-19). The structures (15-19) have a lower geometric anisotropy (ratio of the length of *T*-dye molecule to its width) in comparison with the structures (5,9-12); in the case of realization of structures (15-19) lower values of negative dichroism would be expected.

It is necessary to note that the *T*-dye (11) having two rod-like fragments similar to LC molecules binded with a "cross" azogroup

TABLE I

Position of long-wave absorption band and dichoroism of *T*-dyes (5,9-12)

Comp. N	M.p., °C	λ_{max}, nm	S
5	133–135	460	−0.23
9	131–133	465, 486	−0.29, −0.29
10	175–177	488, 510	−0.27, −0.27
11	162–164	476	−0.31
12	291–293	499, 530	−0.27, −0.28



(15) (16) (17) (18) (19)

has a higher S value (-0.31) than the T-dye (9) that has only one rod-like fragment for which $S = -0.29$. The T-dye (12) has a geometrical anisotropy about twice less than the T-dye (9). Nevertheless values of their negative dichroic ratios are approximately equal. We explain this by the fact that the bis-azodye (12) has three rod-like fragments bound with azogroups. Analogous dependence of a negative dichroic ratio value on the structure of T-dyes was observed by us earlier for anthraquinone[1–3] and aryazoazole[4] T-dyes. In our opinion the presence of two or more rod-like fragments in the T-dye molecule which are bound with azogroup or other fragment permitting an electron cross transition of π-π^* type stimulates a dye molecular packing in the liquid crystal (Figure).

This fact as well as our earlier idea of dichroic dye design is confirmed by experimental data of this and previous works.[1,4,10,11]

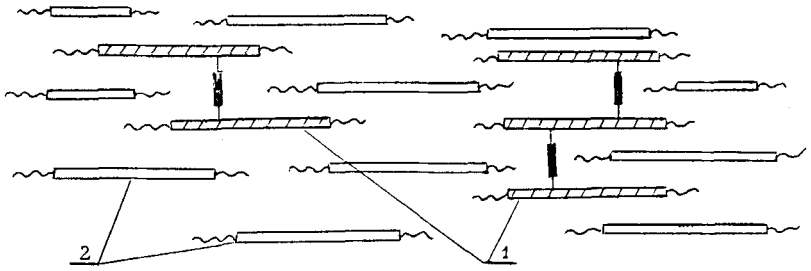


FIGURE Packing of *T*-dye molecules (1) including several rod-like fragments bound with transversal chromophore systems in a liquid crystal (2).

References

1. A. V. Ivashchenko, V. T. Lazareva, E. K. Prudnikova, V. G. Rumyantsev and V. V. Titov. *Mol. Cryst. Liq. Cryst.*, **129**, 259 (1985).
2. A. V. Ivashchenko, V. T. Lazareva, E. K. Prudnikova, V. G. Rumyantsev and V. V. Titov, *Mol. Cryst. Liq. Cryst.*, **129**, 267 (1985).
3. A. V. Ivashchenko, V. T. Lazareva, E. K. Prudnikova, V. G. Rumyantsev and V. V. Titov, *Mol. Cryst. Liq. Cryst.*, **129**, 277 (1985).
4. A. V. Ivashchenko, O. S. Petrova and V. V. Titov, *Mol. Cryst. Liq. Cryst.*, **108**, 51 (1984).
5. Pat. US 3 804 823 (1974).
6. Z. Pentimally, G. Milani and F. Biavati, *Gazz. Chim. Ital.*, **105**, 777 (1975).
7. A. V. Ivashchenko, O. S. Petrova, V. T. Grachev, 5th All-Union Conf. "*Liquid Crystals and their Practical Application*," Ivanovo, 1985; Abstracts, v. I, book I, p. 74, (1985).
8. L. M. Blinov, V. A. Kizel, V. G. Rumyantsev and V. V. Titov, *J. Phys.*, (Paris), **36**, 69 (1975).
9. A. V. Ivashchenko, V. G. Rumyantsev, V. T. Lazareva, E. K. Prudnikova, V. V. Titov and L. M. Blinov. *4th Intern. Liquid Cryst. Conf. of Socialist Countries*, Tbilisi (1981). Abstr., **1**, 253 (1981).
10. V. G. Rumyantsev, A. V. Ivashchenko, V. M. Muratov, V. T. Lazareva, E. K. Prudnikova and L. M. Blinov, *Mol. Cryst. Liq. Cryst.*, **94**, 205 (1983).
11. Pat. CH 651844 (1985); pat. Fr. 2487830 (1983); pat. Ger. 3152228 (1985); pat. US 4457859 (1984); pat. GB 2095273 (1984); pat. Canad 1183532 (1985).