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Synthesis of tris-, tetrakis-, and pentakisazo dyes and their application to guest–host liquid crystal displays

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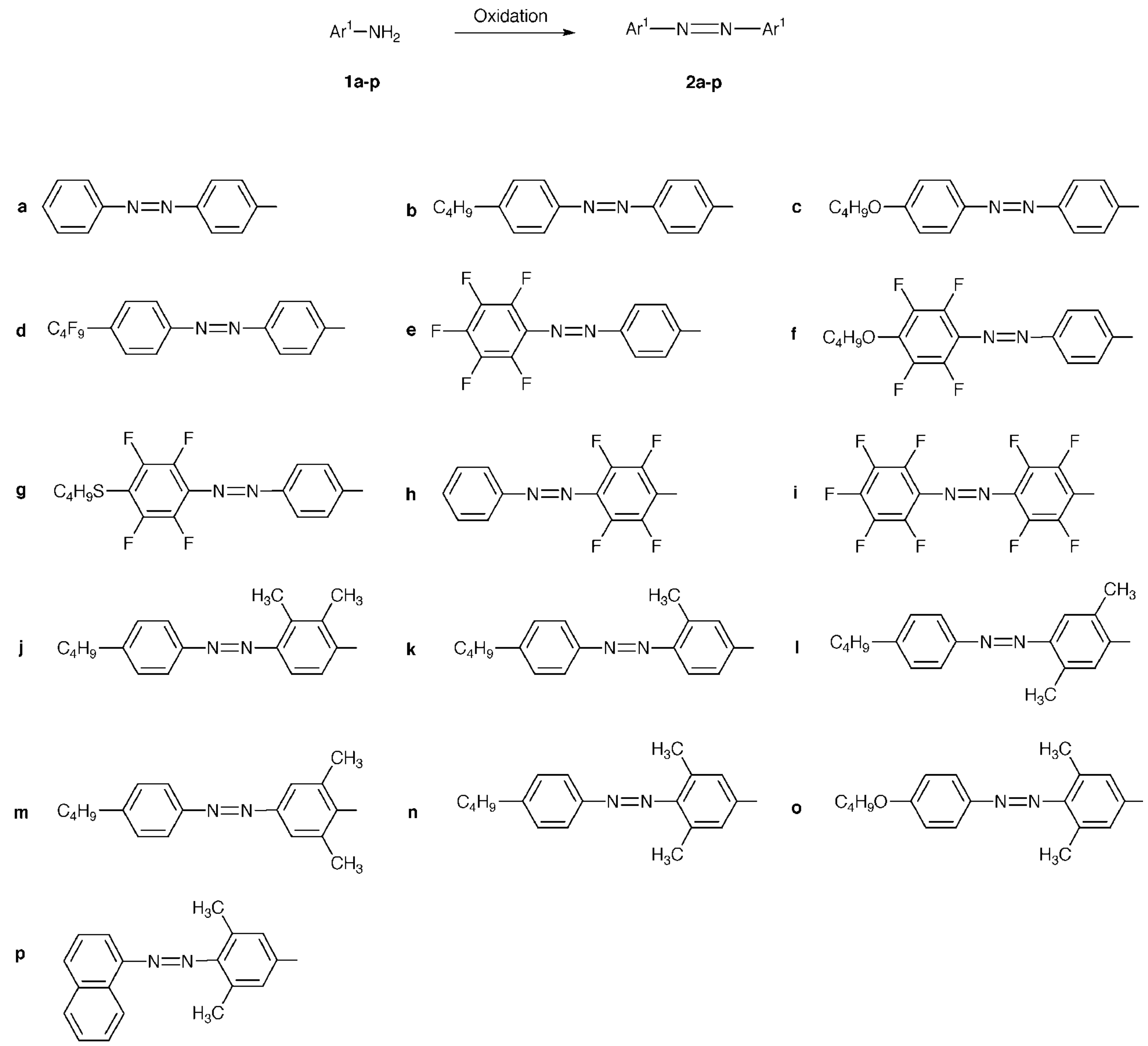
Tris-, tetrakis-, and pentakisazo dyes have been prepared by the oxidation of 4-(arylazo)arylamines. Iodobenzene diacetate was the preferred oxidant for preparation of 4,4′-bis(arylazo)azobenzenes and 4,4′-bis(arylazo)-2,2′,3,3′,5,5′,6,6′-octafluoroazobenzenes, whereas silver(II) oxide proved a satisfactory oxidant for synthesis of 4,4′-(arylazo)(methyl-substituted)azobenzenes. Unsymmetrical tris- and tetrakisazo dyes were also obtained by cross oxidation. The absorption bands of these azo dyes were observed in the range of 381–472 nm in liquid crystals. The solubility of the trisazo dyes in hexane was the highest, followed by the tetrakis- and pentakisazo dyes. The unsymmetrical derivative having methyl groups in the central *p*-phenylene moieties was most soluble among the trisazo dyes. The order parameters (*S*) of the tris-, tetrakis-, and pentakisazo derivatives were in the range 0.66–0.81, sufficiently high for the practical application of these dyes in liquid crystal displays.

The tris-,[1] tetrakis-,[2] and pentakisazo derivatives[3] have been proposed as positive dichroic dyes used in guest–host (GH) liquid crystal displays (LCD's). Recently, the reflection type GH-LCD has attracted much attention due to its brightness.[4] The chemical structures of all the dichroic azo dyes are limited to the derivatives with strong electron donor groups (*N*,*N*-dialkylamino- or hydroxy-), as these are necessary to facilitate the azo coupling reaction. One patent has reported the preparation of polyazo dyes by the reduction of 4-(arylazo)nitrobenzenes with lithium aluminum hydride.[5] However, no detailed information concerning the properties of the polyazo dyes has been presented. In order to form azo linkages, diazotisation-coupling, the condensation of amines with nitroso and nitro compounds, the reduction of aromatic nitro derivatives, and the oxidation of aromatic amines are useful reactions.[6] Among these reactions, the advantages of the oxidation method include fewer steps to prepare the polyazo dyes than the diazotisation-coupling and condensation reactions and product formation substituted with alkyl, alkylthio, and perfluoroalkyl groups at both terminal ends. These products are not obtained by the diazotisation-coupling reactions. Many kinds of oxidizing reagents such as lead(IV) acetate,[7] bleaching powder,[7a] silver(II) oxide,[8] silver(II) carbonate,[9] sodium hypochlorite,[10] manganese(IV) oxide,[11] *N*-chloroacetoanilide,[12] chromyl chloride,[13] 2,2′-bipyridylchromium(VI) peroxide,[14] iodobenzene diacetate,[15] copper salts,[16] barium salts,[17] potassium hexacyanoferrate(III),[18] and an oxygen molecule[19] have been reported to form azobenzenes. It has also been reported that the combination of the substrates and oxidizing reagents drastically changes the yields of the products. The syntheses of the tris-, tetrakis-, and pentakisazo dyes by the oxidation of (arylazo)arylamines have not been reported so far. The important properties that a dichroic dye should have for LC display application are high order parameter and good solubility in the LC host. In our previous paper, perfluoroalkyl- and (perfluoro-*p*-phenylene)-substituted bisazo dyes have been reported to show higher solubility than the corresponding fluorine-free derivatives.[20] Therefore, the synthesis and properties of the fluorine-containing polyazo dyes are also of interest. In this paper, we report the synthesis, absorption bands, solubility, and dichroism of the tris-, tetrakis-, and pentakisazo dyes obtained by the oxidation of the 4-(arylazo)arylamines.

Results and discussion

The oxidation of the 4-(arylazo)arylamines **1** to form symmetrical trisazo dyes **2** is shown in Scheme 1. In order to check the oxidation reaction of the 4-(arylazo)anilines, 4-aminoazobenzene (**1a**) was reacted with various oxidizing reagents. These results are summarized in Table 1. The type of oxidizing reagents drastically affected the reaction with **1a**. Among the reagents, iodobenzene diacetate easily prepared 4,4′-bis(phenylazo)azobenzene (**2a**). Unidentified products, which were not developed by the column chromatography (silica gel, acetone), were also formed in the reaction. 2,7-Bis(phenylazo)phenazine was not isolated in the reaction. No reaction was observed when azobenzene was treated with iodobenzene diacetate under the same conditions, suggesting that the azo linkage was not oxidized by the reagent. On the basis of these results, a series of 4-(4-arylazo)azobenzenes **2b–g** were synthesized in low to moderate yields using iodobenzene diacetate.

For the oxidation of 4-(arylazo)-2,3,5,6-tetrafluoroaniline (**1h**) to provide 4,4′-bis(phenylazo)-2,2′,3,3′,5,5′,6,6′-octafluoroazobenzene (**2h**), iodobenzene diacetate gave the best result among lead(IV) acetate, iodobenzene diacetate, and silver(II) oxide. Therefore, the perfluorotrisazo dye **2i** was also



Scheme 1

synthesized in moderate yield by the oxidation of **1i** with iodobenzene diacetate.

The oxidation of 4-(arylazo)(methyl-substituted)anilines was examined using 4-(4-butylphenylazo)-2,3-dimethylaniline (**1j**). In a series of reactions, silver(II) oxide showed a satisfactory result to prepare 4,4′-bis(4-butylphenylazo)-2,2′,3,3′-tetramethylazobenzene (**2j**). Therefore, the 4,4′-bis(arylazo)-(methyl-substituted)trisazo dyes **2k–p** were obtained in low to moderate yields using silver(II) oxide.

The oxidation reactions of 4-(4-butylphenylazo)-1-naphthylamine (**1q**) with iodobenzene diacetate, silver(II) oxide, and lead(IV) acetate to obtain 4,4′-bis(4-butylphenylazo)-1,1′-azonaphthalene were also examined. However, no formation of the desired product was observed.

Thus, the choice of oxidizing reagents for the 4-(arylazo)-arylamines **1** was very important in order to obtain the desired trisazo dyes **2**.

Scheme 2 shows the synthesis of the pentakisazo dyes. The bisazo amino derivatives **3a–c** were synthesized in moderate yields by the diazotization-coupling reaction of the monoazo amino derivatives **1b**, **1n**, and **1q** with 3,5-dimethylaniline. As the methyl-free pentakisazo dyes seemed to be less soluble in liquid crystals, these starting materials were prepared. Pentakisazo dyes **4a–c** were prepared by the oxidation of **3a–c** with silver(II) oxide which showed good results for the oxidation of 4-(arylazo)(methyl-substituted)anilines **1j–p** among the oxidizing reagents.

The synthesis of the unsymmetrical trisazo dye **5** is shown in Scheme 3. The cross oxidation of **1m** with **1n** afforded the unsymmetrical trisazo dye **5** in 5% yield together with the formation of the corresponding symmetrical trisazo dyes **2m** and **2n** in 13 and 32% yields respectively. The yield of 2,2′,6,6′-tetramethyl derivative **2m** was lower than that of the 3,3′,5,5′-tetramethyl derivative **2n**, probably due to steric hindrance of the methyl groups at the 2- and 6-positions in **1m**.

Scheme 4 indicates the synthesis of the unsymmetrical tetrakisazo dye **6**. The cross oxidation of the monoazo amino derivative **1n** with **3b** gave the tetrakisazo dye **6** in 7% yield. The symmetrical trisazo **2n** and pentakisazo dyes **4b** were also obtained in 7 and 12% yields, respectively.

Table 2 summarizes the physical properties of the azo dyes. The absorption maxima (λ_{max}) of the polyazo dyes in liquid crystals were more bathochromic than those in hexane due to the higher polarity of the liquid crystals. No remarkable differences in λ_{max} of the polyazo dyes in ZLI-1565 and ZLI-4792 were observed. The λ_{max} of the symmetrical trisazo dyes **2a–p** were observed in the range of 381–424 nm in the liquid crystals. That of the unsymmetrical trisazo dye **5** was observed at around 385 nm. The λ_{max} of the tetrakisazo dye **6** and pentakisazo dyes **4a–c** were observed at 400 and 403–472 nm,

Table 1 Synthesis of tris-, tetrakis-, and pentakisazo dyes

Starting materials	Oxidation conditions	Yield of **2**^{a}(%)
1a	$CuCl_2$ (0.5 equiv.), air, C_5H_5N, r.t., 5 h	0 (100)
	$Cu(OCOCH_3)$ (0.3 equiv.), air, CH_3OH, r.t., 2.5 h	0 (100)
	MnO_2 (6 equiv.), C_6H_6, reflux, 21 h	3 (77)
	NaOCl (6 equiv.), H_2O, r.t., 4 h	10 (7)
	$K_3Fe(CN)_6$ (7.6 equiv.), KOH, CH_3OH, 45 °C, 10 d	10
	CuCl (0.5 equiv.), air, C_5H_5N, r.t., 5 h	13
	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	18
	$NaBO_2$, H_2O_2, $3H_2O$ (1.4 equiv.), H_3BO_3, CH_3COOH, 50–60 °C, 6 h	19 (7)
	$Pb(OCOCH_3)_4$ (2 equiv.), C_6H_6, reflux, 1 h	27
	$C_6H_5I(OCOCH_3)_2$ (1 equiv.), C_6H_6, r.t., 1 h	8
	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, r.t., 1 h	22
	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	36
1b	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	46
1c	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	26
1d	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	16
1e	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	28
1f	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	32
1g	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	35
1h	$Pb(OCOCH_3)_4$ (2 equiv.), C_6H_6, reflux, 1 h	18
	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	43
	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	10
1i	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	54
1j	$Pb(OCOCH_3)_4$ (2 equiv.), C_6H_6, reflux, 1 h	26
	$C_6H_5I(OCOCH_3)_2$ (2 equiv.), C_6H_6, reflux, 1 h	20
	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	28
1k	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	37
1l	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	30
1m	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	21
1n	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	32
1o	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	34
1p	AgO (10 equiv.), $CHCl_3$, r.t., 3 h	9

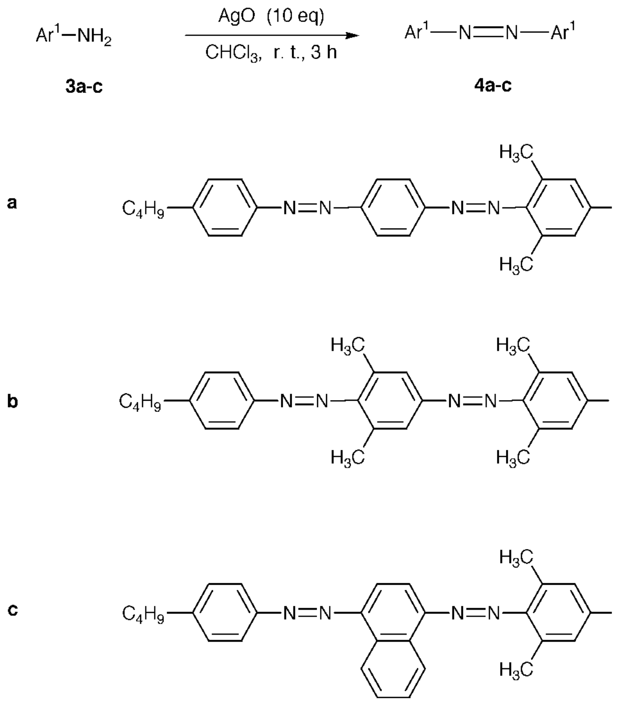
^{a}Isolated yield. Figures in parentheses indicate recovered starting material.

respectively. Thus, the color of these dyes was yellow to orange in the liquid crystals. The solubility of the azo dyes in hexane at 25 °C is summarized in Table 2.

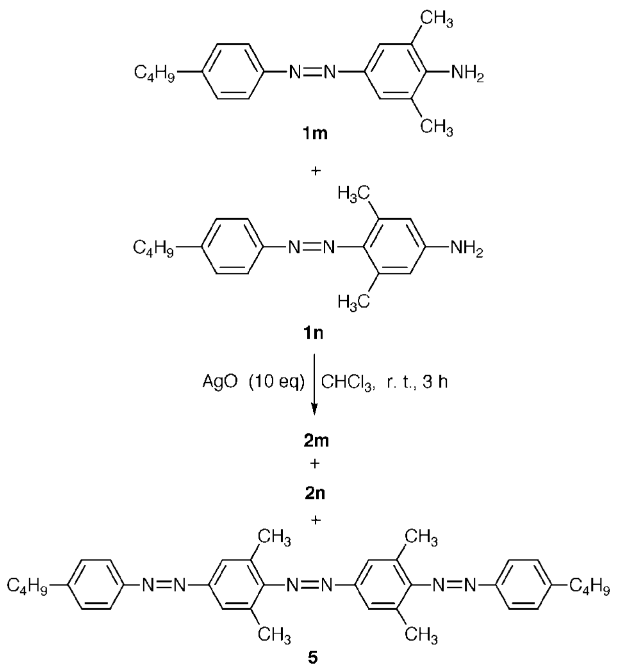
The first factor affecting the solubility was the dye skeleton. The solubility of the polyazo dyes was in the order of the dye skeleton: trisazo **2** > tetrakisazo **6** > pentakisazo **4**. For example, those of **2n**, **6**, and **4b** were observed to be 1.32, 0.367, and 0.055 mmol dm^{-3}, respectively.

The second factor was the presence of methyl groups on the central *p*-phenylene moieties. The solubility of the trisazo dyes increased in the order of the methyl derivatives: 3,3′,5,5′-tetramethyl **2n** (1.32) > 2,2′,6,6′-tetramethyl **2m** (0.902) > 3,3′-dimethyl **2k** (0.789) > 2,2′,3,3′-tetramethyl **2j** (0.248) > 2,2′,5,5′-tetramethyl **2l** (0.156) > methyl-free **2b** (0.123).

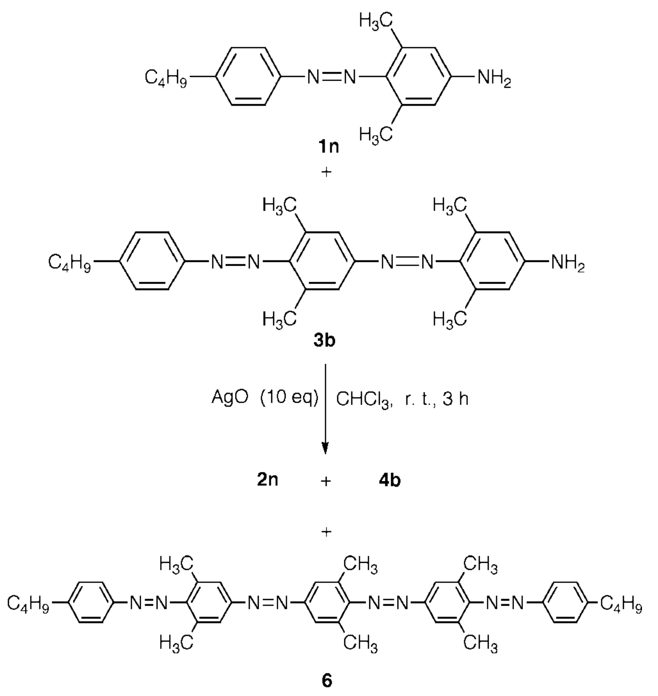
The third factor was the substituents at both terminal ends. The solubility of the trisazo dyes **2a–d** increased at both terminal substituents in the following order: butyl **2b** (0.123) > perfluorobutyl **2d** (0.077) > butoxy **2c** (0.029) and



Scheme 2



Scheme 3



Scheme 4

substituent-free **2a** (0.029). A similar tendency was observed in the trisazo dyes containing perfluoro-*p*-phenylene moieties: butoxy **2f** (0.157), butylthio **2g** (0.128) > substituent-free **2e** (0.028).

The fourth factor was the symmetry of the molecules. An unsymmetrical dye **5** (2.55) was much more soluble than the corresponding symmetrical ones **2m** (0.902) and **2n** (1.32).

In the case of the bisazo dyes, the perfluoroalkyl and perfluoro-*p*-phenylene derivatives have been reported to have a higher solubility than the corresponding fluorine-free ones.[20] Unfortunately, in the case of the trisazo dyes, the fluorine-containing derivatives **2e** (0.028), **2h** (0.021) and **2i** (insoluble) did not show a higher solubility than the fluorine-free trisazo dye **2a** (0.029).

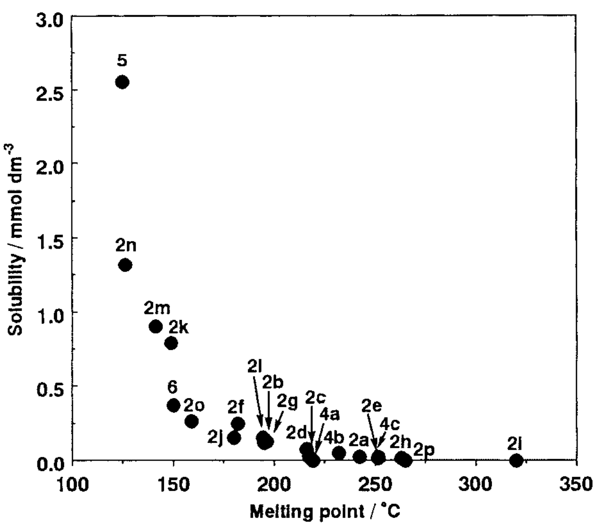


Fig. 1 Relationship between solubility and melting points.

The relationship between solubility and melting points of these azo dyes is indicated in Fig. 1. It is clear that the lower the melting points, the higher the solubility. The melting points of the pentakisazo **4** and (terminal butyl)- and (side methyl)-free trisazo dyes **2a**, **2e**, **2h**, **2i** were high (>220 °C). However, those of the methyl-substituted trisazo derivatives **2k**, **2m**, **2n**, and **5** were low (<150 °C). These results suggest that the weaker the intermolecular interactions, the higher the solubility. The introduction of steric methyl groups (steric factor $E_S = -1.24$) into the central *p*-phenylene moieties could decrease the intermolecular interactions between the aromatic rings.[21] The intermolecular interactions in the trisazo dyes were much stronger than those of the bisazo dyes. Therefore, the introduction of perfluoro-*p*-phenylene moieties ($E_S = -0.46$) could not affect the interactions, resulting in no solubility improvement in the fluorine-containing trisazo dyes.

The dichroism of the dyes was then measured. Dye (about 0.2 wt%) was dissolved in a liquid crystal. When the dye was not soluble in the liquid crystal, the suspension was filtered. The cell (thickness: about 50 μm) was prepared by filling the solution between two glass plates attached with transparent electrodes, on which polyimide was applied and rubbed. The

Table 2 Properties of tris-, tetrakis-, and pentakisazo dyes

			ZLI-1565		ZLI-4792			
Compd.	λ_{max}/nm (ε)[a]	Solubility[b]/mmol dm^{-3}	λ_{max}/nm	S	λ_{max}/nm	S	θ/°	l/d
2a	384 (44000)	0.029	396	0.74	394	0.74	−3.1	3.89
2b	392 (55000)	0.123	411	0.73	412	0.71	−2.6	5.21
2c	405 (19400)	0.029	421	0.78	418	0.77	−3.0	5.14
2d	389 (58000)	0.077	402	0.74	401	0.75	−8.0	4.41
2e	380 (51000)	0.028	391	0.71	391	0.71	−2.3	3.59
2f	388 (54000)	0.157	405	0.71	406	0.74	−2.7	5.02
2g	393 (41000)	0.128	410	0.73	411	0.75	−1.8	5.05
2h	360 (36000)	0.021	384	0.66	381	0.67	−2.2	3.47
2i	—[c]	—[c]	—[d]	—[d]	—[d]	—[d]	−2.6	3.60
2j	400 (56000)	0.248	416	0.75	416	0.74	−8.2	4.08
2k	399 (48000)	0.789	417	0.71	414	0.72	−9.9	4.17
2l	408 (53000)	0.156	423	0.71	424	0.70	−7.5	3.81
2m	372 (55000)	0.902	394	0.77	393	0.76	−2.5	4.04
2n	382 (59000)	1.32	396	0.70	403	0.68	−2.4	4.05
2o	387 (76000)	0.269	399	0.76	398	0.75	−2.5	4.29
2p	404 (32000)[e]	—[c]	—[d]	—[d]	—[d]	—[d]	−1.2	2.63
4a	397 (78000)	—[c]	410	0.81	412	0.81	−1.7	5.49
4b	393 (13000)	0.055	403	0.78	406	0.78	−2.8	5.41
4c	452 (7800)	0.021	472	0.79	470	0.79	−6.9	4.80
5	374 (54000)	2.55	385	0.74	388	0.73	−2.7	4.02
6	387 (64000)	0.367	400	0.75	399	0.75	−2.3	4.69

[a] Measured in hexane. [b] Measured in hexane at 25 °C. [c] Insoluble in hexane and chloroform at 25 °C. [d] Insoluble in liquid crystals. [e] Measured in chloroform (insoluble in hexane).

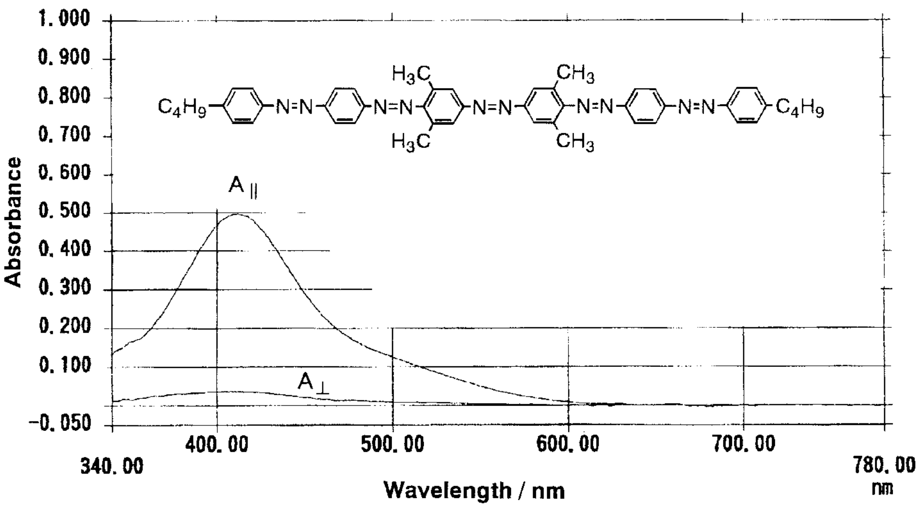


Fig. 2 Dichroism of pentakisazo dye **4a**.

glass plates attached with transparent electrodes were required to evaluate the cell as a device in a LC display. The cells were not heated. The polariser was placed in front of the cell. The order parameter (*S*) was calculated on the basis of the following equation: $S=(A_{\parallel}-A_{\perp})/(A_{\parallel}+2A_{\perp})$, where $A_{\parallel}$ and $A_{\perp}$ represent the absorbance of light polarized parallel and perpendicular to the direction of the alignment of the dye molecule in the liquid crystal medium, respectively. A typical absorption spectrum is shown in Fig. 2. The *S* value of **4a** in ZLI-1565 was calculated to be 0.81. The order parameter (*S*) of the azo dyes is summarized in Table 2. The *S* values were measured to be 0.66–0.81.

The dichroism could be analyzed by calculating the deviation of the angle (θ) between the direction of the transition moment and that of the long axis, and the *l*/*d* ratio, where *l* and *d* represent the length of the long axis and diameter of the circumscribed cylinders of the molecule, respectively.[22] The θ values and *l*/*d* ratios in the most stable conformation of the azo dyes were calculated using MOPAC93 with the MNDO-PM3 method. A typical example is depicted in Fig. 3. The calculated θ value of **4a** was −1.7°. The *l* and *d* values were calculated to be 48.8 and 8.89 Å respectively, the *l*/*d* ratio being 5.49. The calculated results are indicated in Table 2. Their θ values were very small (−1.2 to −9.9°), suggesting that the *l*/*d* ratio is the main factor affecting the dichroism.

The relationship between the *S* value and the *l*/*d* ratio is indicated in Fig. 4. Though the figure showed some scatter, the trend that the greater the *l*/*d* ratio, the higher the dichroism was observed. The *S* values of the polyazo dyes prepared in this study were measured to be 0.66–0.81. This shows that they can be used as practical dichroic dyes. In order to obtain a much higher dichroism ($S>0.85$), the synthesis of slimmer ($l/d>6.50$) derivatives seems to be required.

We have synthesized novel tris-, tetrakis-, and pentakisazo dyes by the oxidation of 4-(arylazo)arylamines. The color of these dyes was yellow to orange in liquid crystals. Iodobenzene diacetate and silver(II) oxide were good oxidizing reagents for preparing the polyazo dyes. The fluorine-containing trisazo dyes did not show a solubility higher than the fluorine-free derivatives. The dye skeleton, the presence of methyl groups in the central *p*-phenylene moieties, and terminal substituents could affect the solubility. The dichroism of these polyazo dyes was high enough for practical use.

Experimental

Instruments

Melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus and a Rigaku TAS-100 instrument. NMR spectra (**1h**, **1k**, **1o–q**, **2a–h**, **2j–p**, **3c**, **4a–c**, **5**, **6**: $CDCl_3$ solution; **1j**, **1l–n**, **3a**, **3b**: DMSO-d_6 solution) were recorded on a Jeol α-400 spectrometer using tetramethylsilane (^1H) and trifluoroacetic acid (^{19}F) as internal and external standards, respectively. Mass spectra (70 eV, EI) were taken on a Shimadzu QP-1000 spectrometer. UV spectra were measured with a Shimadzu UV-160A spectrometer.

Materials

4-Aminoazobenzene (**1a**), 3-methylaniline, 2,3-dimethylaniline, 3,5-dimethylaniline, 2,6-dimethylaniline, 1-naphthylamine, lead(IV) acetate, and iodobenzene diacetate were purchased from Tokyo Kasei Co., Ltd. 4-Nitrosonitrobenzene,[23] 4-(4-butylphenylazo)aniline (**1b**),[20e] 4-(4-butoxyphenylazo)aniline (**1c**),[20a] 4-[4-(perfluorobutyl)phenylazo]aniline (**1d**),[20e] 4-(pentafluorophenylazo)aniline (**1e**),[20a] 4-(4-butoxy-2,3,5,6-tetra-

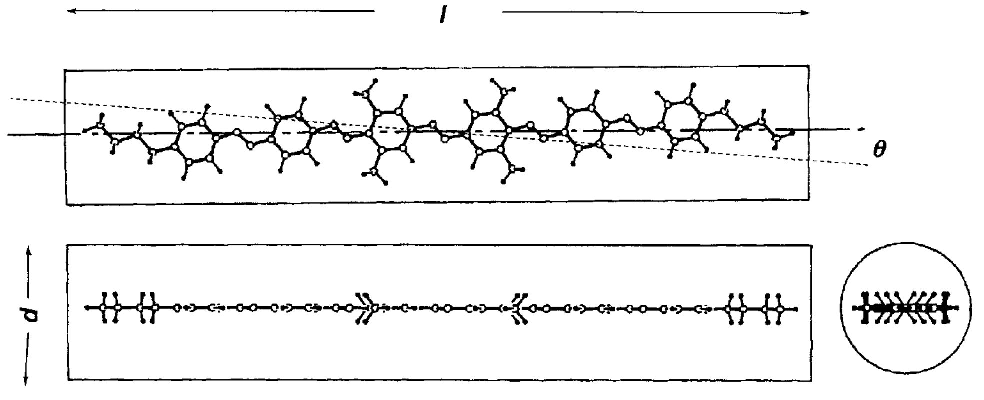


Fig. 3 Calculation of *l*/*d* ratio and θ value of pentakisazo dye **4a**.

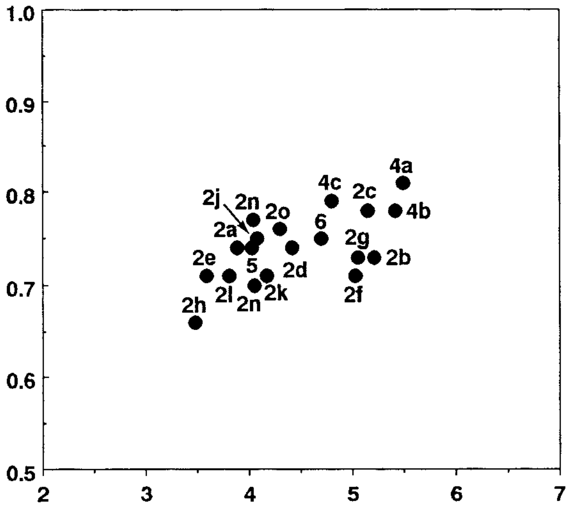


Fig. 4 Relationship between S and l/d ratio.

fluorophenylazo)aniline (**1f**),[20a] 4-(4-butylthio-2,3,5,6-tetrafluorophenylazo)aniline (**1g**),[20a] and 4-aminononafluoroazobenzene (**1i**)[7a] were prepared as described in the literature.

Preparation of silver(II) oxide

To an aqueous solution (500 mL) of sodium hydroxide (36 g) were added an aqueous suspension (100 mL) of potassium persulfate (37.5 g) and a saturated aqueous solution of silver nitrate (25.5 g) at 85 °C. The mixture was stirred at 90 °C for 15 min. The black precipitate was filtered, washed with a dilute aqueous solution of sodium hydroxide and dried *in vacuo*.

Synthesis of 2,3,4,5,6-pentafluoroazobenzene

To a stirring acetic acid solution (100 mL) of aniline (3.07 g, 33 mmol) at 60 °C was added an acetic acid solution (20 mL) of pentafluoronitrosobenzene (6.50 g, 33 mmol) and the mixture was stirred at room temperature for 3 h. After the reaction was completed, the mixture was poured into water. The resulting precipitate was filtered, washed with water, dried, purified by column chromatography (SiO_2, $CHCl_3$–C_6H_{14} = 1 : 1), and recrystallised from a chloroform–hexane mixed solution. Yield 42%; mp 94–95 °C; δ_H 7.54–7.58 (m, 3H), 7.93–7.95 (m, 2H); δ_F −84.4 (2F), −75.1 (1F), −72.6 (2F); *m/z* 272 (M^+; 14%), 167 (8), 105 (21), 77 (100).

Synthesis of 4-amino-2,3,5,6-tetrafluoroazobenzene (1h)

To an ethanol solution (50 mL) of 2,3,4,5,6-pentafluoroazobenzene (1.8 g, 6.6 mmol) was added 28% ammonia (4 mL). The tube was sealed and heated at 55 °C for 30 h. After the reaction was completed, the mixture was poured into water. The resulting precipitate was filtered, washed with water, dried, purified by column chromatography (SiO_2, $CHCl_3$–C_6H_{14} = 1 : 1), and recrystallised from a chloroform–hexane mixed solution. Yield 53%; mp 133–134 °C; δ_H 4.36 (2H, br s), 7.46–7.54 (3H, m), 7.88–7.90 (2H, m); δ_F −85.8 (2F), −73.4 (2F); *m/z* 269 (M^+; 30%), 164 (17), 105 (17), 77 (100).

Synthesis of 4-(arylazo)arylamines 1j–1q

To an acetone solution (5 mL) of arylamines (1.49 g, 10 mmol) were added concentrated hydrochloric acid (4 mL) and an aqueous solution (5 mL) of sodium nitrite (0.69 g, 10 mmol) at 0 °C and the mixture was stirred at 0 °C for 2 h. To the mixture was added coupling components (10 mmol). The mixture was stirred at 0–20 °C overnight. After the reaction was completed, the mixture was poured into water (200 mL). The resulting precipitate was filtered, washed with benzene, dried, purified by column chromatography (SiO_2, CH_2Cl_2), and recrystallised from a chloroform–hexane mixed solution.

4-(4-Butylphenylazo)-2,3-dimethylaniline 1j. Yield 14%; mp 156–158 °C; δ_H 0.90 (3H, t, J 7.5), 1.31 (2H, sextet, J 7.5), 1.58 (2H, quintet, J 7.5), 2.10 (3H, s), 2.59 (3H, s), 2.63 (2H, t, J 7.5), 3.39 (2H, br s), 6.68 (1H, d, J 8.9), 7.32 (2H, d, J 8.2), 7.47 (1H, d, J 8.9), 7.68 (2H, d, J 8.2); *m/z* 281 (M^+; 23%), 120 (100), 91 (21).

4-(4-Butylphenylazo)-3-methylaniline 1k. Yield 21%; mp 175–177 °C; δ_H 0.94 (3H, t, J 7.3), 1.38 (2H, sextet, J 7.3), 1.64 (2H, quintet, J 7.3), 2.65 (3H, s), 2.67 (2H, t, J 7.3), 3.95 (2H, br s), 6.59 (1H, dd, J 8.9 and 2.1), 6.64 (1H, d, J 2.1), 7.55 (2H, d, J 8.4), 7.63 (1H, d, J 8.9), 7.76 (2H, d, J 8.4); *m/z* 267 (M^+; 34%), 134 (20), 106 (100).

4-(4-Butylphenylazo)-2,5-dimethylaniline 1l. Yield 53%; mp 121–123 °C; δ_H 0.91 (3H, t, J 7.5), 1.33 (2H, sextet, J 7.5), 1.58 (2H, quintet, J 7.5), 2.15 (3H, s), 2.54 (3H, s), 2.64 (2H, t, J 7.5), 3.52 (2H, br s), 6.77 (1H, s), 7.34 (2H, d, J 8.4), 7.54 (1H, s), 7.70 (2H, d, J 8.4); *m/z* 281 (M^+; 35%), 120 (100), 119 (97).

4-(4-Butylphenylazo)-2,6-dimethylaniline 1m. Yield 11%; mp 123–124 °C; δ_H 0.90 (3H, t, J 7.5), 1.31 (2H, sextet, J 7.5), 1.57 (2H, quintet, J 7.5), 2.17 (6H, s), 2.62 (2H, t, J 7.5), 3.39 (2H, br s), 7.30 (2H, d, J 8.3), 7.45 (2H, s), 7.64 (2H, d, J 8.3); *m/z* 281 (M^+; 23%), 148 (12), 120 (100), 91 (18).

4-(4-Butylphenylazo)-3,5-dimethylaniline 1n. Yield 65%; mp 170–172 °C; δ_H 0.92 (3H, t, J 7.5), 1.34 (2H, sextet, J 7.5), 1.60 (2H, quintet, J 7.5), 2.37 (6H, s), 2.66 (2H, t, J 7.5), 3.43 (2H, br s), 6.67 (2H, s), 7.35 (2H, d, J 8.3), 7.69 (2H, d, J 8.3); *m/z* 281 (M^+; 26%), 224 (14), 120 (100), 91 (18).

4-(4-Butoxyphenylazo)-3,5-dimethylaniline 1o. Yield 46%; mp 181–182 °C; δ_H 0.95 (3H, t, J 7.1), 1.46 (2H, sextet, J 7.1), 1.73 (2H, quintet, J 7.1), 2.34 (6H, s), 3.45 (2H, br s), 4.07 (1H, t, J 7.1), 6.74 (2H, s), 7.09 (2H, d, J 8.9), 7.76 (2H, d, J 8.9); *m/z* 297 (M^+; 55%), 240 (35), 120 (100).

3,5-Dimethyl-4-(1-naphthylazo)aniline 1p. Yield 43%; mp 194–195 °C; δ_H 2.55 (6H, s), 3.45 (2H, br s), 6.58 (2H, s), 7.55–7.72 (4H, m), 7.98–8.07 (2H, m), 8.70 (1H, d, J 8.3); *m/z* 275 (M^+; 41%), 148 (12), 120 (100).

4-(4-Butylphenylazo)-1-naphthylamine 1q. Yield 90%; mp 70–71 °C; δ_H 0.96 (3H, t, J 7.5), 1.40 (2H, sextet, J 7.5), 1.66 (2H, quintet, J 7.5), 2.70 (2H, t, J 7.5), 4.57 (2H, br s), 6.83 (1H, d, J 8.3), 7.33 (2H, d, J 8.5), 7.55 (1H, t, J 8.0), 7.64 (1H, t, J 8.0), 7.83 (1H, d, J 8.0), 7.90 (1H, d, J 8.3), 7.91 (2H, d, J 8.5), 9.05 (1H, d, J 8.0); *m/z* 303 (M^+; 25%), 142 (100), 115 (57).

Synthesis of trisazo dyes 2

The oxidation reactions were carried out by the following procedures. The physical and spectral data of all the products are also given below.

Method A (with lead(IV) acetate)

To a benzene suspension (30 mL) of 4-(arylazo)arylamines **1** (1.0 mmol) was added lead(IV) acetate (886 mg, 2.0 mmol) and the mixture was refluxed for 1 h. After the reaction was completed, the suspension was filtered and washed with warm benzene. The benzene layer was washed with a 50% aqueous acetic acid solution, water, a saturated solution of sodium hydrogen carbonate, water, and finally concentrated *in vacuo*. The product was purified by silica gel column chromatography

(**2a**, **2h**: $CHCl_3$–$C_6H_{14} = 1:1$; **2j**: $CH_3C_6H_5$) and recrystallised (**2a**, **2h**: $CHCl_3$; **2j**: C_6H_{14}).

Method B (with iodobenzene diacetate)

To a benzene suspension (30 mL) of 4-(arylazo)arylamines **1** (1.0 mmol) was added iodobenzene diacetate (0.64 g, 2.0 mmol) and the mixture was refluxed for 1 h. After the reaction was completed, the mixture was filtered. The benzene layer was washed with water and concentrated *in vacuo*. The product was purified by silica gel column chromatography (**2a**, **2e**, **2f**, **2h** and **2i**: $CHCl_3$–$C_6H_{14} = 1:1$; **2b–d** and **2g**: CH_2Cl_2; **2j**: $CH_3C_6H_5$) and recrystallised (**2a** and **2e–i**: $CHCl_3$; **2b–d** and **2j**: C_6H_{14}).

Method C (with silver(II) oxide)

To a chloroform suspension (30 mL) of 4-(arylazo)arylamines **1** (1.0 mmol) was added silver(II) oxide (1.24 g, 10 mmol) and the mixture was stirred for 3 h at room temperature. After the reaction was completed, the mixture was filtered. After concentration of the filtrate, the product was purified by silica gel column chromatography (**2a**: $CHCl_3$–$C_6H_{14} = 1:1$; **2h**: CH_2Cl_2; **2j–p**: $CH_3C_6H_5$) and recrystallised (**2a**: $CHCl_3$; **2h**, **2j–p**: C_6H_{14}).

Method D (oxidation of 1a with other reagents)

To a solution (50 mL) of **1a** (179 mg, 1 mmol) was added an oxidizing reagent (catalyst). In the case of copper(I) chloride, copper(II) chloride, and copper(II) acetate, air (90 mL min^{-1}) was bubbled into the mixture. After the reaction, the mixture was filtered. The filtrate was extracted with ethyl acetate (200 mL × 3). The extract was then concentrated *in vacuo*. The product was isolated by column chromatography.

4,4′-Bis(phenylazo)azobenzene 2a. Mp 242 °C (Found: C, 74.32; H, 4.77; N, 21.56. $C_{24}H_{18}N_6$ requires C, 73.83; H, 4.65; N, 21.51%); δ_H 7.51–7.53 (6H, m), 7.97–7.99 (4H, m), 8.09 (4H, d, *J* 8.8), 8.13 (4H, d, *J* 8.8); *m/z* 390 (M$^+$; 31%), 285 (15), 181 (27), 105 (30), 77 (100).

4,4′-Bis(4-butylphenylazo)azobenzene 2b. Mp 195 °C (Found: C, 76.26; H, 6.81; N, 16.67. $C_{32}H_{34}N_6$ requires C, 76.46; H, 6.82; N, 16.72%); δ_H 0.96 (6H, t, *J* 7.5), 1.40 (4H, sextet, *J* 7.5), 1.67 (4H, quintet, *J* 7.5), 2.71 (4H, t, *J* 7.5), 7.35 (4H, d, *J* 8.3), 7.90 (4H, d, *J* 8.3), 8.05–8.12 (8H, m); *m/z* 502 (M$^+$; 39%), 341 (17), 237 (22), 133 (100).

4,4′-Bis(4-butoxyphenylazo)azobenzene 2c. Mp 217 °C (Found: C, 71.66; H, 6.27; N, 15.63. $C_{32}H_{34}N_6O_2$ requires C, 71.89; H, 6.41; N, 15.72%); δ_H 1.01 (6H, t, *J* 7.4), 1.56 (4H, sextet, *J* 7.4), 1.83 (4H, quintet, *J* 7.4), 4.07 (4H, t, *J* 7.4), 7.03 (4H, d, *J* 9.0), 7.96 (4H, d, *J* 9.0), 8.02–8.11 (8H, m); *m/z* 534 (M$^+$; 49%), 253 (23), 177 (30), 149 (100), 93 (34).

4,4′-Bis[4-(perfluorobutyl)phenylazo]azobenzene 2d. Mp 216 °C (Found: C, 46.51; H, 2.10; N, 10.55. $C_{32}H_{16}F_{18}N_6$ requires C, 46.50; H, 1.95; N, 10.17%); δ_H 7.79 (4H, d, *J* 8.5), 8.05–8.19 (12H, m); δ_F −47.7 (4F), −44.8 (4F), −33.1 (4F), −3.20 (6F); *m/z* 826 (M$^+$; 2%), 503 (14), 399 (64), 295 (67), 104 (59), 76 (100).

4,4′-Bis(pentafluorophenylazo)azobenzene 2e. Mp 251 °C (Found: C, 50.12; H, 1.56; N, 14.66. $C_{24}H_8F_{10}N_6$ requires C, 50.54; H, 1.41; N, 14.74%); δ_H 8.12 (4H, d, *J* 8.7), 8.15 (4H, d, *J* 8.7); δ_F −84.1 (4F), −73.7 (2F), −71.7 (4F); *m/z* 570 (M$^+$; 51%), 271 (100), 195 (22), 167 (55), 104 (42), 76 (97).

4,4′-Bis(4-butoxy-2,3,5,6-tetrafluorophenylazo)azobenzene 2f. Mp 180 °C (Found: C, 56.82; H, 3.92; N, 12.39. $C_{32}H_{26}F_8N_6O_2$ requires C 56.64; H, 3.86; N, 12.38%); δ_H 1.00 (6H, t, *J* 7.4), 1.54 (4H, sextet, *J* 7.4), 1.82 (4H, quintet, *J* 7.4), 4.37 (4H, t, *J* 6.5), 8.08–8.14 (8H, m); δ_F −80.5 to −80.6 (4F), −73.2 to −73.3 (4F); *m/z* 678 (M$^+$; 23%), 445 (56), 269 (69), 76 (100), 57 (67).

4,4′-Bis[4-(butylthio)-2,3,5,6-tetrafluorophenylazo]azobenzene 2g. Mp 196 °C (Found: C, 53.76; H, 3.35; N, 11.84. $C_{32}H_{26}F_8N_6S_2$ requires C 54.08; H, 3.69; N, 11.82%); δ_H 0.94 (6H, t, *J* 7.4), 1.48 (4H, sextet, *J* 7.4), 1.63 (4H, quintet, *J* 7.4), 3.06 (4H, t, *J* 7.4), 8.11–8.16 (8H, m); δ_F −72.9 to −73.0 (4F), −57.4 to −57.5 (4F); *m/z* 710 (M$^+$; 11%), 341 (42), 104 (46), 76 (100).

4,4′-Bis(phenylazo)-2,2′,3,3′,5,5′,6,6′-octafluoroazobenzene 2h. Mp 263 °C (Found: C, 53.68; H, 1.96; N, 15.71. $C_{24}H_8F_8N_6$ requires C, 53.94; H, 1.89; N, 15.73%); δ_H 7.56–7.62 (6H, m), 8.00 (4H, d, *J* 7.2); δ_F −73.2 (4F), −71.4 (4F); *m/z* 534 (M$^+$; 18%), 105 (24), 77 (100).

4,4′-Bis(pentafluorophenylazo)-2,2′,3,3′,5,5′,6,6′-octafluoroazobenzene 2i. Mp 320 °C (Found: C, 40.45; N, 12.44. $C_{24}H_8F_{18}N_6$ requires C, 40.36; N, 11.77%); *m/z* 714 (M$^+$; 18%), 343 (34), 195 (58), 176 (28), 167 (100), 148 (43).^{19}F-NMR spectra were not obtained due to low solubility of this compound in DMSO-d_6.

4,4′-Bis(4-butylphenylazo)-2,2′,3,3′-tetramethylazobenzene 2j. Mp 182 °C (Found: C, 77.12; H, 7.56; N, 14.85. $C_{36}H_{42}N_6$ requires C, 77.38; H, 7.58; N, 15.04%); δ_H 0.96 (6H, t, *J* 7.5), 1.40 (4H, sextet, *J* 7.5), 1.67 (4H, quintet, *J* 7.5), 2.71 (4H, t, *J* 7.5), 2.78 (6H, s), 2.82 (6H, s), 7.34 (4H, d, *J* 8.4), 7.58 (2H, d, *J* 9.0), 7.62 (2H, d, *J* 9.0), 7.89 (4H, d, *J* 8.4); *m/z* 558 (M$^+$; 38%), 265 (21), 161 (41), 133 (100).

4,4′-Bis(4-butylphenylazo)-3,3′-dimethylazobenzene 2k. Mp 149 °C (Found: C, 76.88; H, 7.17; N, 15.64. $C_{34}H_{38}N_6$ requires C, 76.95; H, 7.22; N, 15.84%); δ_H 1.00 (6H, t, *J* 7.5), 1.40 (4H, sextet, *J* 7.5), 1.67 (4H, quintet, *J* 7.5), 2.71 (4H, t, *J* 7.5), 2.82 (6H, s), 7.34 (4H, d, *J* 8.4), 7.78 (4H, d, *J* 8.4), 7.86 (2H, dd, *J* 8.6 and 2.1), 7.89 (2H, d, *J* 8.6), 7.93 (2H, d, *J* 2.1); *m/z* 530 (M$^+$; 40%), 251 (45), 133 (85), 91 (100).

4,4′-Bis(4-butylphenylazo)-2,2′,5,5′-tetramethylazobenzene 2l. Mp 194 °C (Found: C, 76.90; H, 7.66; N, 14.58. $C_{36}H_{42}N_6$ requires C, 77.38; H, 7.58; N, 15.04%); δ_H 0.96 (6H, t, *J* 7.6), 1.40 (4H, sextet, *J* 7.6), 1.67 (4H, quintet, *J* 7.6), 2.70 (4H, t, *J* 7.6), 2.73 (6H, s), 2.79 (6H, s), 7.34 (4H, d, *J* 8.4), 7.60 (4H, s), 7.89 (4H, d, *J* 8.4); *m/z* 558 (M$^+$; 27%), 265 (33), 209 (28), 91 (100).

4,4′-Bis(4-butylphenylazo)-2,2′,6,6′-tetramethylazobenzene 2m. Mp 141 °C (Found: C, 77.15; H, 7.76; N, 14.95. $C_{36}H_{42}N_6$ requires C, 77.38; H, 7.58; N, 15.04%); δ_H 0.96 (6H, t, *J* 7.5), 1.40 (4H, sextet, *J* 7.5), 1.66 (4H, quintet, *J* 7.5), 2.56 (12H, s), 2.72 (4H, t, *J* 7.5), 7.34 (4H, d, *J* 8.4), 7.73 (4H, s), 7.88 (4H, d, *J* 8.4); *m/z* 558 (M$^+$; 28%), 515 (33), 265 (16), 161 (58), 91 (100).

4,4′-Bis(4-butylphenylazo)-3,3′,5,5′-tetramethylazobenzene 2n. Mp 126 °C (Found: C, 77.20; H, 7.62; N, 14.79. $C_{36}H_{42}N_6$ requires C, 77.38; H, 7.58; N, 15.04%); δ_H 0.96 (6H, t, *J* 7.5), 1.41 (4H, sextet, *J* 7.5), 1.67 (4H, quintet, *J* 7.5), 2.43 (12H, s), 2.72 (4H, t, *J* 7.5), 7.36 (4H, d, *J* 8.2), 7.72 (4H, s), 7.86 (4H, d, *J* 8.2); *m/z* 558 (M$^+$; 45%), 265 (42), 133 (62), 104 (41), 91 (100).

4,4′-Bis(4-butoxyphenylazo)-3,3′,5,5′-tetramethylazobenzene 2o. Mp 159 °C (Found: C, 72.90; H, 7.08; N, 14.00.

$C_{36}H_{42}N_6O_2$ requires C, 73.19; H, 7.17; N, 14.23%); δ_H 1.01 (6H, t, J 7.1), 1.54 (4H, sextet, J 7.1), 1.83 (4H, quintet, J 7.1), 2.42 (12H, s), 4.08 (4H, t, J 7.1), 7.03 (4H, d, J 8.9), 7.71 (4H, s), 7.92 (4H, d, J 8.9); *m/z* 590 (M^+; 100%), 281 (51), 149 (73).

4,4′-Bis(1-naphthylazo)-3,3′,5,5′-tetramethylazobenzene 2p. Mp 265 °C (Found: C, 79.08; H, 5.49; N, 15.56. $C_{36}H_{30}N_6$ requires C, 79.10; H, 5.53; N, 15.37%); δ_H 2.62 (12H, s), 7.60–7.68 (6H, m), 7.81 (4H, s), 7.85 (2H, d, J 7.7), 7.97 (2H, d, J 7.7), 8.04 (2H, d, J 7.7), 8.86 (2H, d, J 7.7); *m/z* 546 (M^+; 32%), 259 (33), 127 (100), 104 (30).

Synthesis of 4-[4-(4-butylphenylazo)arylazo]-3,5-dimethylanilines 3

To an acetone solution (30 mL) of 4-(4-butylphenylazo)arylamines **1b**, **1n**, and **1q** (15 mmol) were added concentrated hydrochloric acid (6 mL) and an aqueous solution (20 mL) of sodium nitrite (1.04 g, 15 mmol) at 0 °C and the mixture was stirred at 0 °C for 2 h. To the mixture was added 3,5-dimethylaniline (1.82 g, 15 mmol). The mixture was stirred at 0–20 °C overnight. After the reaction was completed, the mixture was poured into water (200 mL). The resulting precipitate was filtered, washed with benzene, dried, and purified by column chromatography (SiO_2, $CH_3C_6H_5$). The physical and spectral data of **3** are given below.

4-[4-(4-Butylphenylazo)phenylazo]-3,5-dimethylaniline 3a. Yield 55%; mp 183–184 °C; δ_H 0.92 (3H, t, J 7.4), 1.35 (2H, sextet, J 7.4), 1.62 (2H, quintet, J 7.4), 2.48 (6H, s), 2.69 (2H, t, J 7.4), 3.52 (2H, br s), 6.52 (2H, s), 7.44 (2H, d, J 8.5), 7.86 (2H, d, J 8.5), 7.91 (2H, d, J 8.8), 8.02 (2H, d, J 8.8); *m/z* 385 (M^+; 52%), 148 (16), 120 (100).

4-[4-(4-Butylphenylazo)-3,5-dimethylphenylazo]-3,5-dimethylaniline 3b. Yield 56%; mp 189–190 °C; δ_H 0.93 (3H, t, J 7.5), 1.35 (2H, sextet, J 7.5), 1.62 (2H, quintet, J 7.5), 2.39 (6H, s), 2.43 (6H, s), 2.70 (2H, t, J 7.5), 3.46 (2H, br s), 6.63 (2H, s), 7.44 (2H, d, J 8.4), 7.57 (2H, s), 7.82 (2H, d, J 8.4); *m/z* 413 (M^+; 89%), 252 (13), 148 (18), 120 (100), 91 (24).

4-[4-(4-Butylphenylazo)naphthylazo]-3,5-dimethylaniline 3c. Yield 27%; mp 132–133 °C; δ_H 0.97 (3H, t, J 7.5), 1.41 (2H, sextet, J 7.5), 1.68 (2H, quintet, J 7.5), 2.69 (6H, s), 2.73 (2H, t, J 7.5), 3.99 (2H, br s), 6.50 (2H, s), 7.38 (2H, d, J 8.4), 7.69–7.73 (2H, m), 7.83 (1H, d, J 8.3), 7.92 (1H, d, J 8.3), 8.00 (2H, d, J 8.4), 8.89–8.93 (1H, m), 9.00–9.05 (1H, m); *m/z* 435 (M^+; 65%), 259 (35), 120 (100).

Synthesis of pentakisazo dyes 4

To a chloroform solution (30 mL) of 4-[4-(4-butylphenylazo)arylazo]-3,5-dimethylanilines **3** (1 mmol) was added silver(II) oxide (1.24 g, 10 mmol) and the mixture was stirred for 3 h at room temperature. After the reaction was completed, the resulting precipitate was filtered. The filtrate was concentrated *in vacuo*. The product was purified by column chromatography (SiO_2, $CHCl_3$–C_6H_{14} = 2 : 1) and recrystallised from hexane. The physical and spectral data of **4** are shown below.

4,4′-Bis[4-(4-butylphenylazo)phenylazo]-3,3′,5,5′-tetramethylazobenzene 4a. Yield 5%; mp 219 °C (Found: C, 75.00; H, 6.59; N, 18.10. $C_{48}H_{50}N_{10}$ requires C, 75.17; H, 6.57; N, 18.26%); δ_H 0.96 (6H, t, J 7.5), 1.40 (4H, sextet, J 7.5), 1.67 (4H, quintet, J 7.5), 2.52 (12H, s), 2.72 (4H, t, J 7.5), 7.36 (4H, d, J 8.4), 7.76 (4H, s), 7.91 (4H, d, J 8.4), 8.08 (8H, s). The EI mass spectrum could not be measured.

4,4′-Bis[4-(4-butylphenylazo)-3,5-dimethylphenylazo]-3,3′,5,5′-tetramethylazobenzene 4b. Yield 23%; mp 232 °C (Found: C, 75.87; H, 7.30; N, 17.29. $C_{52}H_{58}N_{10}$ requires C, 75.88; H, 7.10; N, 17.02%); δ_H 0.97 (6H, t, J 7.5), 1.41 (4H, sextet, J 7.5), 1.68 (4H, quintet, J 7.5), 2.44 (12H, s), 2.47 (12H, s), 2.73 (4H, t, J 7.5), 7.36 (4H, d, J 8.5), 7.71 (4H, s), 7.74 (4H, s), 7.87 (4H, d, J 8.5). The EI mass spectrum could not be measured.

4,4′-Bis[4-(4-butylphenylazo)naphthylazo]-3,3′,5,5′-tetramethylazobenzene 4c. Yield 8%; mp 251 °C (Found: C, 77.79; H, 6.21; N, 16.28. $C_{56}H_{54}N_{10}$ requires C, 77.57; H, 6.28; N, 16.15%); δ_H 0.98 (6H, t, J 7.5), 1.42 (4H, sextet, J 7.5), 1.69 (4H, quintet, J 7.5), 2.68 (12H, s), 2.75 (4H, t, J 7.5), 7.40 (4H, d, J 8.3), 7.75–7.80 (4H, m), 7.83 (4H, s), 7.94 (4H, s), 8.03 (4H, d, J 8.3), 8.93–8.98 (2H, m), 9.03–9.07 (2H, m). The EI mass spectrum could not be measured.

Synthesis of 4,4′-bis(4-butylphenylazo)-2,3′,5′,6-tetramethylazobenzene (5)

To a chloroform solution (30 mL) of 4-(4-butylphenylazo)-2,6-dimethylaniline **1m** (1 mmol, 0.281 g) and 4-(4-butylphenylazo)-3,5-dimethylaniline **1n** (1 mmol, 0.281 g) was added silver(II) oxide (2.48 g, 20 mmol) and the mixture was stirred for 3 h at room temperature. After the reaction was completed, the resulting precipitate was filtered. The filtrate was concentrated *in vacuo*. The products were isolated by column chromatography (SiO_2, $C_6H_5CH_3$–C_6H_{14} = 1 : 1) and recrystallised from hexane. 4,4′-Bis(4-butylphenylazo)-2,2′,6,6′-tetramethylazobenzene (**2m**) and 4,4′-bis(4-butylphenylazo)-3,3′,5,5′-tetramethylazobenzene (**2n**) were also obtained in 13 and 32% yields, respectively. 4,4′-Bis(4-butylphenylazo)-2,3′,5′,6-tetramethylazobenzene (**5**) was obtained in 5% yield. The physical and spectral data of **5** are given below. Mp 125 °C (Found: C, 77.09; H, 7.67; N, 15.11. $C_{36}H_{42}N_6$ requires C, 77.38; H, 7.58; N, 15.04%); δ_H 0.96 (3H, t, J 7.5), 0.97 (3H, t, J 7.5), 1.39 (2H, sextet, J 7.5), 1.41 (2H, sextet, J 7.5), 1.66 (2H, quintet, J 7.5), 1.68 (2H, quintet, J 7.5), 2.43 (6H, s), 2.46 (6H, s), 2.70 (2H, t, J 7.5), 2.72 (2H, t, J 7.5), 7.33 (2H, d, J 8.3), 7.36 (2H, d, J 8.3), 7.70 (4H, s), 7.86 (2H, d, J 8.3), 7.87 (2H, d, J 8.3); *m/z* 558 (M^+; 76%), 161 (31), 133 (76), 91 (100).

Synthesis of 4-(4-butylphenylazo)-3,3′,5′,5′-tetramethyl-4′-[4-(4-butylphenylazo)-3,5-dimethylphenylazo]azobenzene (6)

To a chloroform solution (30 mL) of 4-(4-butylphenylazo)-3,5-dimethylaniline **1n** (1 mmol, 0.281 g) and 4-[4-(4-butylphenylazo)-3,5-dimethylphenylazo]-3,5-dimethylaniline **3b** (1 mmol, 0.413 g) was added silver(II) oxide (2.48 g, 20 mmol) and the mixture was stirred for 3 h at room temperature. After the reaction was completed, the resulting precipitate was filtered. The filtrate was concentrated *in vacuo*. The products were isolated by column chromatography (SiO_2, $C_6H_5CH_3$–C_6H_{14} = 2 : 1) and recrystallised from hexane. 4,4′-Bis(4-butylphenylazo)-3,3′,5,5′-tetramethylazobenzene (**2n**) and 4,4′-bis[4-(4-butylphenylazo)-3,5-dimethylphenylazo]-3,3′,5,5′-tetramethylazobenzene (**4b**) were also obtained in 7 and 12% yields, respectively. 4-(4-Butylphenylazo)-3,3′,5,5′-tetramethyl-4′-[4-(4-butylphenylazo)-3,5-dimethylphenylazo]azobenzene (**6**) was obtained in 7% yield. The physical and spectral data of **6** are shown below. Mp 150 °C (Found: C, 76.55; H, 7.62; N, 16.22. $C_{44}H_{50}N_8$ requires C, 76.49; H, 7.29; N, 15.61%); δ_H 0.97 (6H, t, J 7.5), 1.41 (4H, sextet, J 7.5), 1.67 (4H, quintet, J 7.5), 2.43 (12H, s), 2.47 (6H, s), 2.72 (4H, t, J 7.5), 7.36 (4H, d, J 8.3), 7.71 (2H, s), 7.73 (2H, s), 7.74 (2H, s), 7.87 (4H, d, J 8.3); *m/z* 690 (M^+; 52%), 265 (44), 133 (57), 91 (100).

Measurement of solubility

A saturated hexane solution of an azo dye was prepared at 25 °C. After filtering the solution through a membrane filter (0.5 µm), the UV spectrum of the solution was measured. The solubility was calculated on the basis of the ε value of the respective azo dye.

MO Calculation

θ Values and l/d ratios were calculated from the geometry of the most stable conformer optimized by the MOPAC93 program[24] by the MNDO-PM3 method.[25] The heat of formation of any conformation of a molecule was calculated. On optimization of the conformers, the dye molecules were assumed to have *Cs* symmetry and azo linkages the *trans* form. The van der Waals radius was taken into account. The transition moments of the dyes were calculated by the CNDO/S method[26] (singlet excitation, Nishimoto–Mataga equation, and 60 CI) using the geometry obtained by MNDO-PM3 calculation.

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