Synthesis and Properties of Novel Dichroic Disazo Dyes Containing the Tetrafluoro-*p*-phenylene Moiety for Guest−Host Liquid Crystal Displays

Masaki Matsui,* Naoki Tanaka, Noboru Andoh, Kazumasa Funabiki, Katsuyoshi Shibata, and Hiroshige Muramatsu

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

Yoshinao Ishigure and Erina Kohyama

Gifu Prefectural Industrial Technology Research Center, Kitaoyobi 47, Kasamatsu, Hashima, Gifu 501-6064, Japan

Yasuo Abe

Research Institute for Advanced Science and Technology, Osaka Prefecture University, Gakuen-Cho 1-2, Sakai, Osaka 599-8570, Japan

Masaharu Kaneko

Yokohama Research Center, Mitsubishi Chemical Company, Kamoshida 1000, Aoba, Yokohama 227-8502, Japan

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Novel disazo dyes containing tetrafluoro-*p*-phenylene moiety(ies) have been synthesized. The absorption bands of these compounds were observed in the range of 432−555 nm in ZLI-4792. The introduction of tetrafluoro-*p*-phenylene moieties in both the terminal ends was very effective in increasing the solubility. The 4-butylthio derivative was most soluble among the 4-(butylthio)-, 4-(alkoxy)-, and 4-(butylamino)tetrafluoro-*p*-phenylene derivatives. The dichroisms of all the tetrafluoro-*p*-phenylene derivatives were similar ($S = 0.69-0.77$) to those of the *p*-phenylene derivatives (0.68−0.76). These results indicate that the novel fluorine-containing disazo dyes can be practically used as dichroic dyes in guest−host liquid crystal displays.

Introduction

Guest−host liquid crystal displays have been used in digital clocks and instrument panels in cars. Recently, reflection type guest−host liquid crystal display has been attracted much attention due to the brightness of the display.[1] Dichroic dyes used in the guest−host liquid crystal displays are required to have good solubility and dichroism in the liquid crystals. Polyazo,[2] anthraquinone,[3] and perylene dyes[4] have been proposed as positive dichroic dyes. In our previous paper, perfluoroalkyl-substituted disazo dyes have been reported to show higher solubility than the corresponding alkyl-substituted ones.[5] The introduction of fluorine atoms in organic molecules can change the properties of the compounds. Especially, perfluoroaromatic compounds could show interesting properties. Polyamides,[6] polycarbonates,[7] and polyurethanes[8] having perfluoro-*p*-phenylene moieties in their skeletons have been reported to be thermally stable. Biphenyl liquid crystals having a tetrafluoro-*p*-phenylene moiety show high

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polarity and less viscosity.[9] Perfluorinated poly(*p*-phenylene) deposited with rhodium has been reported to have appropriate redox potentials for water-splitting and enhanced stability under severe photocatalytic oxidation conditions.[10] Tetrafluoroterephthalic acid salts of group IIB have been reported to be very stable toward heating.[11] Palladium complexes having tetrafluoro-*p*-phenylene moieties have been reported to recognize electron-rich aromatic guests.[12] Thus, the tetrafluoro-*p*-phenylene moiety introduced in the core structure of a molecule can show unique properties. When the *p*-phenylene moieties of the disazo dyes are substituted with a tetrafluoro-*p*-phenylene group, the absorption bands, solubility, and dichroism may drastically change. Therefore, the novel disazo dyes having perfluoro-*p*-phenylene moiety(ies) have been synthesized. Their application to guest−host liquid crystal displays have also been examined in this study.

Experimental Section

Instruments. Melting points and decomposition temperature were measured with a Rigaku Thermoflex TAS 200 TG 8101G apparatus. NMR spectra were recorded on a JEOL α-400 spectrometer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer. UV spectra were measured with a Shimadzu UV-160A spectrometer.

Materials. Pentafluoroaniline (**1**) was purchased from Tokyo Kasei Co., Ltd. Decafluoroazobenzene (**12**),[13] perfluoronitrosobenzene,[14] and 4-nitrosonitrobenzene[15] were synthesized as described in the literature.

Synthesis of 4-(Pentafluorophenylazo)aniline (2). To an acetone solution (5 mL) of pentafluoroaniline **1** (1.83 g, 10 mmol) were added 70% sulfuric acid (7 mL) and an aqueous solution of sodium nitrite (0.7 g, 10 mmol) at 0 °C, and the mixture stirred for 1.5 h. To the mixture was added an aqueous solution (50 mL) of sodium anilinomethanesulfonate (2.1 g, 10 mmol). The pH value of the mixture was adjusted to 8.0 by dilute aqueous sodium hydroxide solution. The mixture was stirred at 5 °C overnight. After the reaction was completed, the mixture was poured into water. The resulting precipitate was filtered, dissolved in a 1% aqueous sodium hydroxide solution (70 mL), and stirred at 45 °C for 1.5 h. Product was extracted with dichloromethane, washed with water, and dried. After evaporation of the solvent, the product was purified by column chromatography (SiO_2, CH_2Cl_2): yield 19%; mp 155−156 °C; ^{1}H NMR ($CDCl_3$) δ = 4.24 (s, 2H), 6.73 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −73.8 (2F), −77.9 (1F), −85.2 (2F); EIMS (70 eV) *m*/*z* (rel intensity) 287 (M^+; 32), 120 (22), 92 (100).

Synthesis of 4-(4-Butoxytetrafluorophenylazo)aniline (2a). To a butanol solution (30 mL) of 4-(pentafluorophenylazo)aniline **2** (0.7 g, 2.4 mmol) was added a butanol solution (5 mL) of sodium butoxide (3.8 mmol) and the mixture stirred at 50 °C for 4 h. After the reaction was completed, the mixture was poured into water. The product was extracted with dichloromethane, washed with dilute hydrochloric acid and water, and dried. After concentrating the extract, the product was isolated by column chromatography (SiO_2, CH_2Cl_2): yield 87%; mp 72−73 °C; ^{1}H NMR ($CDCl_3$) δ = 0.98 (t, J = 7.2 Hz, 3H), 1.52 (sext, J = 7.2 Hz, 2H), 1.78 (quint, J = 7.2 Hz, 2H), 4.20 (br s, 2H), 4.28 (t, J = 7.2 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −75.1 (2F), −80.6 (2F); EIMS (70 eV) *m*/*z* (rel intensity) 341 (M^+; 23), 120 (38), 92 (100).

Synthesis of 4-[4-(Butylthio)tetrafluorophenylazo]-aniline (2e). To an ethanol solution (40 mL) of 4-(pentafluorophenylazo)aniline **2** (1.0 g, 3.5 mmol) was added a butanethiol solution (6 mL) of sodium butanethiolate (4 mmol) and the mixture stirred at room temperature for 20 h. After the reaction was completed, the mixture was poured into aqueous dilute sodium hydroxide solution. The product was extracted with dichloromethane, washed with a dilute sodium hydroxide solution, water, and dried. After concentrating the extract, the product was isolated by column chromatography (SiO_2, $CHCl_3$−C_6H_{14}): yield 88%; mp 131−133 °C; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.4 Hz, 3H), 1.44 (sext, J = 7.4 Hz, 2H), 1.58 (quint, J = 7.4 Hz, 2H), 2.97 (t, J = 7.4 Hz, 2H), 4.26 (br s, 2H), 6.73 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −57.4 (2F), −74.1 (2F); EIMS (70 eV) *m*/*z* (rel intensity) 357 (M^+; 27), 120 (38), 92 (100).

Synthesis of 4-[4-(Pentafluorophenylazo)phenylazo]-*N*,*N*-diethylaniline (3). To an acetone solution (15 mL) of 4-(pentafluorophenylazo)aniline **2** (0.29 g, 1 mmol) were added concentrated hydrochloric acid (0.5 mL, 6 mmol) and an aqueous solution (5 mL) of sodium nitrite (0.07 g, 1 mmol) at 0 °C, and the mixture stirred for 1.5 h. To the mixture were added *N*,*N*-diethylaniline (0.15 g, 1 mmol) and sodium acetate (2 g) and the mixture stirred at 5 °C overnight. After the reaction was completed, the mixture was poured into water. The resulting precipitate was filtered, purified by column chromatography (SiO_2, $CHCl_3$−C_6H_{14}), and recrystallized from chloroform−hexane: yield 83%; mp 178 °C; ^{1}H NMR ($CDCl_3$) δ = 1.25 (t, J = 7.1 Hz, 6H), 3.48 (q, J = 7.1 Hz, 4H), 6.74 (d, J = 9.4 Hz, 2H), 7.90 (d, J = 9.4 Hz, 2H), 7.97 (d, J = 8.9 Hz, 2H), 8.04 (d, J = 8.9 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −72.3 (2F), −75.2 (1F), −84.5 (2F); EIMS (70 eV) *m*/*z* (rel intensity) 447 (M^+; 100), 432 (41), 148 (58). Anal. Calcd for $C_{22}H_{18}F_5N_5$: C, 59.06; H, 4.06; N, 15.65. Found: C, 59.22; H, 4.00; N, 15.76.

Synthesis of 4-[4-(4-Alkoxytetrafluorophenylazo)-phenylazo]-*N*,*N*-diethylanilines (4a−c). To a solution [**4a**, butanol (30 mL); **4b**, THF (10 mL); **4c**, DMF (10 mL)] of 4-[4-(pentafluorophenylazo)phenylazo]-*N*,*N*-diethylaniline (**3**, 0.109 g, 0.24 mmol) was added the corresponding sodium alkoxide (0.24 mmol), and the mixture heated [**4a,** 40 °C (1 h); **4b**, 50 °C (1 h); **4c**, 50 °C (2 h)]. After the reaction was completed, the mixture was poured into water and extracted with dichloromethane. The extract was washed with water, dried over anhydrous sodium sulfate, purified by column chromatography (SiO_2, $CH_3C_6H_5$:C_6H_{14} = 1:1), and recrystallized from chloroform−hexane. The physical and spectral data are given below.

4-[4-(4-Butoxytetrafluorophenylazo)phenylazo]-*N*,*N*-diethylaniline (4a): yield 49%; mp 187 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 6.9 Hz, 6H), 1.54 (sext, J = 7.0 Hz, 2H), 1.81 (quint, J = 7.0 Hz, 2H), 3.48 (q, J = 6.9 Hz, 4H), 4.34 (t, J = 7.0 Hz, 2H), 6.74 (d, J = 9.1 Hz, 2H), 7.90 (d, J = 9.1 Hz, 2H), 7.96 (d, J = 8.7 Hz, 2H), 8.03 (d, J = 8.7 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −73.6 (2F), −80.4 (2F); EIMS (70 eV) *m*/*z* (rel intensity) 501 (M^+; 68), 486 (32), 148 (100), 133 (32). Anal. Calcd for $C_{26}H_{27}F_4N_5O$: C, 62.27; H, 5.43; N, 13.96. Found: C, 62.28; H, 5.38; N, 14.01.

4-[4-[4-(1*H*,1*H*-Perfluorobutyloxy)tetrafluorophenylazo]-phenylazo]-*N*,*N*-diethylaniline (4b): yield 46%; mp 155 °C; ^{1}H NMR ($CDCl_3$) δ = 1.26 (t, J = 7.1 Hz, 6H), 3.48 (q, J = 7.1 Hz, 4H), 4.74 (t, J = 12.8 Hz, 2H), 6.74 (d, J = 9.2 Hz, 2H),

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7.90 (d, J = 9.2 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H), 8.04 (d, J = 8.7 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −3.03 (3F), −43.8 (2F), −49.6 (2F), −72.6 (2F), −79.3 (2F); EIMS (70 eV) m/z (rel intensity) 627 (M^+, 46), 612 (27), 148 (100), 133 (34). Anal. Calcd for $C_{26}H_{20}F_{11}N_5O$: C, 49.77; H, 3.21; N, 11.16. Found: C, 49.47; H, 3.20; N, 11.15.

4-[4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyloxy)tetrafluorophenylazo]phenylazo]-*N*,*N*-diethylaniline (4c): yield 51%; mp 173 °C; ^{1}H NMR ($CDCl_3$) δ = 1.25 (t, J = 7.1 Hz, 6H), 2.65−2.77 (m, 2H), 3.48 (q, J = 7.1 Hz, 4H), 4.61 (t, J = 6.6 Hz, 2H), 6.74 (d, J = 9.3 Hz, 2H), 7.90 (d, J = 9.3 Hz, 2H), 7.97 (d, J = 9.0 Hz, 2H), 8.04 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −3.2 (3F), −35.9 (2F), −46.7 (2F), −48.2 (2F), −73.0 (2F), −79.9 (2F); EIMS (70 eV) m/z (rel intensity) 691 (M^+; 19), 676 (12), 237 (17), 148 (100), 133 (34). Anal. Calcd for $C_{28}H_{22}F_{13}N_5O$: C, 48.64; H, 3.21; N, 10.13. Found: C, 48.34; H, 3.01; N, 10.17.

Synthesis of 4-[4-[4-(Butylamino)tetrafluorophenylazo]phenylazo]-*N*,*N*-diethylaniline (4d). To an ethanol solution (20 mL) of 4-[4-(pentafluorophenylazo)phenylazo]-*N*,*N*-diethylaniline (**3**, 270 mg, 0.6 mmol) was added butylamine (73 mg, 1 mmol) and the mixture refluxed for 4 h. After the reaction was completed, the mixture was poured into water and extracted with dichloromethane. The extract was purified by column chromatography (SiO_2, $CH_3C_6H_5$:C_6H_{14} = 1:1) and recrystallized from chloroform−hexane. The physical and spectral data are given below. Yield 36%; mp 206 °C; ^{1}H NMR ($CDCl_3$) δ = 0.98 (t, J = 7.4 Hz, 3H), 1.24 (t, J = 7.1 Hz, 6H), 1.45 (sext, J = 7.4 Hz, 2H), 1.65 (quint, J = 7.4 Hz, 2H), 3.45−3.55 (m, 6H), 4.17 (br s, 1H), 6.74 (d, J = 9.2 Hz, 2H), 7.89 (d, J = 9.2 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −73.0 (2F), −85.3 (2F); EIMS (70 eV) m/z (rel intensity) 500 (M^+; 61), 485 (33), 148 (100), 133 (37). Anal. Calcd for $C_{26}H_{28}F_4N_6$: C, 62.39; H, 5.64; N, 16.79. Found: C, 61.60; H, 5.71; N, 16.48.

Synthesis of 4-[4-[4-(Butylthio)tetrafluorophenylazo]phenylazo]-*N*,*N*-diethylaniline (4e). To an 1,4-dioxane solution (12 mL) of 4-[4-(pentafluorophenylazo)phenylazo]-*N*,*N*-diethylaniline (**3**, 310 mg, 0.7 mmol) were added butanethiol (63 mg, 0.7 mmol) and potassium carbonate (100 mg, 0.7 mmol). The mixture was refluxed for 21 h. After the reaction was completed, the mixture was poured into water and extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, purified by column chromatography (SiO_2, $CHCl_3$), and recrystallized from chloroform−hexane: yield 69%; mp 158 °C; ^{1}H NMR ($CDCl_3$) δ = 0.93 (t, J = 7.4 Hz, 3H), 1.26 (t, J = 6.9 Hz, 6H), 1.47 (sext, J = 7.4 Hz, 2H), 1.59 (quint, J = 7.4 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 3.48 (q, J = 6.9 Hz, 4H), 6.75 (d, J = 8.9 Hz, 2H), 7.91 (d, J = 8.9 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −57.2 (2F), −73.0 (2F); EIMS (70 eV) m/z (rel intensity) 517 (M^+; 73), 502 (40), 148 (100), 133 (35). Anal. Calcd for $C_{26}H_{27}F_4N_5S$: C, 60.33; H, 5.26; N, 13.53. Found: C, 60.56; H, 5.02; N, 15.15.

Synthesis of 4-Substituted Pentafluoroazobenzenes (5). To an acetic acid solution (20 mL) of aniline **1** (5.1 mmol) was added an acetic acid solution (15 mL) of pentafluoronitrosobenzene (1.0 g, 5.1 mmol) at 60 °C and the mixture stirred for 2 h. After the reaction was completed, the mixture was poured into water and extracted with dichloromethane. The extract was washed with water and purified by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} = 1:2). The physical and spectral data are given below.

4-Butoxypentafluoroazobenzene (5a): yield 55%; mp 80−82 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.1 Hz, 3H), 1.52 (sext, J = 7.1 Hz, 2H), 1.82 (quint, J = 7.1 Hz, 2H), 4.07 (t, J = 7.1 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −73.3 (2F), −76.7 (1F), −84.8 (2F); EIMS (70 eV) m/z (rel intensity) 344 (M^+; 37), 177 (19), 167 (16), 149 (100).

4-Butylthiopentafluoroazobenzene (5e): yield 32%; mp 67−68 °C; ^{1}H NMR ($CDCl_3$) δ = 0.97 (t, J = 7.4 Hz, 3H), 1.50 (sext, J = 7.4 Hz, 2H), 1.72 (quint, J = 7.4 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −72.7 (2F), −75.6 (1F), −84.6 (2F); EIMS (70 eV) m/z (rel intensity) 360 (M^+; 44), 165 (100).

Reaction of 4-Substituted Pentafluoroazobenzenes (5) with 25% Aqueous Ammonia. To an ethanol solution (12 mL) of 4-substituted pentafluoroazobenzenes **5** (1.02 mmol) was added 25% aqueous ammonia (1 mL). The tube was sealed and heated at 75 °C for 40 h. After the reaction was completed, the mixture was poured into water and extracted with dichloromethane. The products were washed with water and purified by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} = 1:1). The physical and spectral data are given below.

4-(4-Butoxyphenylazo)tetrafluoroaniline (6a): yield 51%; mp 100−101 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.1 Hz, 3H), 1.52 (sext, J = 7.1 Hz, 2H), 1.81 (quint, J = 7.1 Hz, 2H), 4.05 (t, J = 7.1 Hz, 2H), 4.27 (br s, 2H), 6.99 (d, J = 9.0 Hz, 2H), 7.87 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −74.3 (2F), −85.9 (2F); EIMS (70 eV) m/z (rel intensity) 341 (M^+; 44), 164 (19), 149 (100).

2-(4-Butoxyphenylazo)tetrafluoroaniline (6′a): yield 43%; mp 100−101 °C; ^{1}H NMR ($CDCl_3$) δ =1.00 (t, J = 7.1 Hz, 3H), 1.53 (sext, J = 7.1 Hz, 2H), 1.81 (quint, J = 7.1 Hz, 2H), 4.05 (t, J = 7.1 Hz, 2H), 6.55 (br s, 2H), 6.99 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −70.7 (1F), −76.1 (1F), −88.6 (1F), −98.1 (1F); EIMS (70 eV) m/z (rel intensity) 341 (M^+; 29), 149 (100).

4-(4-Butylthiophenylazo)tetrafluoroaniline (6e): yield 40%; mp 81−83 °C; ^{1}H NMR ($CDCl_3$) δ = 0.95 (t, J = 7.4 Hz, 3H), 1.49 (sext, J = 7.4 Hz, 2H), 1.70 (quint, J = 7.4 Hz, 2H), 3.01 (t, J = 7.4 Hz, 2H), 4.36 (br s, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −73.6 (d, J = 12.2 Hz, 2F), −85.9 (dd, J = 19.8 and 8.5 Hz, 2F); EIMS (70 eV) m/z (rel intensity) 357 (M^+; 100), 165 (75), 109 (41).

4-(4-Butylthiophenylazo)-2,5,6-trifluoro-1,3-phenylenediamine (6′e): yield 40%; mp 100−102 °C; ^{1}H NMR ($CDCl_3$) δ = 0.94 (t, J = 7.4 Hz, 3H), 1.48 (sext, J = 7.4 Hz, 2H), 1.68 (quint, J = 7.4 Hz, 2H), 2.99 (t, J = 7.4 Hz, 2H), 4.27 (br s, 2H), 6.57 (br s, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −73.5 (1F), −89.3 (1F), −96.1 (1F); EIMS (70 eV) m/z (rel intensity) 354 (M^+; 100), 165 (79), 109 (54).

Synthesis of 4-[4-(4-Substituted-phenylazo)tetrafluorophenylazo]-*N*,*N*-diethylanilines (7). To 70% sulfuric acid (1.03 mL) was added sodium nitrite (0.06 g, 0.88 mmol) and the mixture was heated to 70 °C and then cooled to 0 °C. To the solution was added an acetic acid−propionic acid mixed solution (1:5, 3.5 mL) of 4-(4-substituted phenylazo)tetrafluoroaniline (**6**, 0.88 mmol) and the mixture stirred at 0 °C for 2.5 h. The mixture was added to a 70% ethanol suspension (30 mL) of *N*,*N*-diethylaniline (0.88 mmol), propionic acid (1.8 mL), acetic acid (8.2 mL), and sodium acetate (3 g) at 0 °C. The mixture was stirred overnight at 0−20 °C. After the reaction was completed, the mixture was poured into water. Product was extracted with dichloromethane, washed with water, purified by column chromatography (SiO_2, $CHCl_3$), and recrystallized from chloroform−hexane. The physical and spectral data are given below.

4-[4-(4-Butoxyphenylazo)tetrafluorophenylazo]-*N*,*N*-diethylaniline (7a): yield 64%; mp 188 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 6H), 1.54 (sext, J = 7.1 Hz, 2H), 1.83 (quint, J = 7.1 Hz, 2H), 3.50 (q, J = 7.1 Hz, 4H), 4.08 (t, J = 7.1 Hz, 2H), 6.73 (d, J = 9.3 Hz, 2H), 7.02 (d, J = 8.9 Hz, 2H), 7.90 (d, J = 9.3 Hz, 2H), 7.95 (d, J = 8.9 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −89.9 (2F), −90.4 (2F); EIMS (70 eV) m/z (rel intensity) 501 (M^+; 48), 177 (18), 148 (100), 133 (36). Anal. Calcd for $C_{26}H_{27}F_4N_5O$: C, 62.27; H, 5.43; N, 13.96. Found: C, 62.20; H, 5.52; N, 13.95.

4-[4-(4-Butylthiophenylazo)tetrafluorophenylazo]-*N*,*N*-diethylaniline (7e): yield 34%; mp 157 °C; ^{1}H NMR ($CDCl_3$) δ = 0.97 (t, J = 7.4 Hz, 3H), 1.26 (t, J = 7.1 Hz, 6H), 1.51 (sext, J = 7.4 Hz, 2H), 1.72 (quint, J = 7.4 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H), 3.50 (t, J = 7.1 Hz, 4H), 6.73 (d, J = 9.3 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.90 (d,

J = 9.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −74.3 (2F), −75.2 (2F); EIMS (70 eV) *m/z* (rel intensity) 517 (M^+; 16), 165 (52), 148 (100), 133 (47). Anal. Calcd for $C_{26}H_{27}F_4N_5S$: C, 60.33; H, 5.26; N, 13.53. Found: C, 60.07; H, 5.10; N, 13.67.

Synthesis of 4-Substituted 4′-Nitroazobenzenes (8). To an acetic acid solution (20 mL) of aniline **1** (5 mmol) was added an acetic acid suspension of nitrosonitrobenzene (5 mmol) and the mixture stirred at 60 °C for 1 h. After the reaction was completed, the mixture was poured into water (200 mL). The resulting precipitate was filtered, washed with water, dried, and purified by column chromatography (SiO_2, $CHCl_3$). The physical and spectral data are given below.

4-Butoxy-4′-nitroazobenzene (8a): yield 80%; mp 117−118 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.2 Hz, 3H), 1.53 (sext, J = 7.2 Hz, 2H), 1.83 (quint, J = 7.2 Hz, 2H), 4.08 (t, J = 7.2 Hz, 2H), 7.03 (d, J = 8.9 Hz, 2H), 7.96 (d, J = 7.6 Hz, 2H), 7.98 (d, J = 7.6 Hz, 2H), 8.36 (d, J = 8.9 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 299 (M^+; 40), 177 (25), 149 (100).

4-Butythio-4′-nitroazobenzene (8e): yield 56%; mp 87−89 °C; ^{1}H NMR ($CDCl_3$) δ = 0.97 (t, J = 7.3 Hz, 3H), 1.53−1.55 (m, 2H), 1.67−1.76 (m, 2H), 3.04 (t, J = 7.3 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 8.01 (d, J = 9.2 Hz, 2H), 8.37 (d, J = 9.2 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 315 (M^+; 82), 193 (15), 165 (100).

Synthesis of 4-(4-Substituted-phenylazo)anilines (9). To an 85% ethanol solution (100 mL) of 4-substituted 4′-nitroazobenzene **8** (2 mmol) was added an aqueous solution (5 mL) of sodium sulfide nonahydrate (4 mmol) and the mixture refluxed for 15 min. After the reaction was completed, the mixture was poured into water (150 mL). The resulting precipitate was filtered, washed with water, dried, and purified by column chromatography (SiO_2, $CHCl_3$). The physical and spectral data are given below.

4-(4-Butoxyphenylazo)aniline (9a): yield 87%; mp 105−106 °C; ^{1}H NMR ($CDCl_3$) δ = 0.99 (t, J = 7.2 Hz, 3H), 1.51 (sext, J = 7.2 Hz, 2H), 1.80 (quint, J = 7.2 Hz, 2H), 3.98 (br s, 2H), 4.03 (t, J = 7.2 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 9.0 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 269 (M^+; 64), 149 (23), 120 (49), 92 (100).

4-(4-Butylthiophenylazo)aniline (9e): yield 56%; mp 87−90 °C; ^{1}H NMR ($CDCl_3$) δ = 0.94 (t, J = 7.1 Hz, 3H), 1.41−1.54 (m, 2H), 1.63−1.74 (m, 2H), 2.99 (t, J = 7.1 Hz, 2H), 4.03 (br s, 2H), 6.73 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H); EIMS (70 eV) *m/z* (rel intensity) 285 (M^+; 42), 92 (100).

Synthesis of 4-Substituted 4′-(Pentafluorophenylazo)-azobenzenes (10). To an acetic acid solution (20 mL) of 4-(4-substituted-phenylazo)aniline **9** (1.9 mmol) was added an acetic acid solution (8 mL) of pentafluoronitrosobenzene (1.9 mmol) and the mixture stirred at 70 °C for 1.5 h. After the reaction was completed, the mixture was poured into water (100 mL). Product was extracted with chloroform, washed with water, dried, and purified by column chromatography (SiO_2, $CHCl_3$). The physical and spectral data are given below.

4-Butoxy-4′-(pentafluorophenylazo)azobenzene (10a): yield 48%; mp 154−155 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.0 Hz, 3H), 1.53 (sext, J = 7.0 Hz, 2H), 1.83 (quint, J = 7.0 Hz, 2H), 4.07 (t, J = 7.0 Hz, 2H), 7.03 (d, J = 9.1 Hz, 2H), 7.97 (d, J = 9.1 Hz, 2H), 8.03 (d, J = 9.0 Hz, 2H), 8.08 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −72.5 (2F), −74.9 (1F), −84.8 (2F); EIMS (70 eV) *m/z* (rel intensity) 448 (M^+; 21), 177 (22), 149 (100).

4-Butylthio-4′-(pentafluorophenylazo)azobenzene (10e): yield 44%; mp 125−127 °C; ^{1}H NMR ($CDCl_3$) δ = 0.97 (t, J = 7.4 Hz, 3H), 1.50 (sext, J = 7.4 Hz, 2H), 1.72 (quint, J = 7.4 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.90 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 9.2 Hz, 2H), 8.09 (d, J = 9.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −71.9 (2F), −74.2 (1F), −84.2 (2F); EIMS (70 eV) *m/z* (rel intensity) 464 (M^+; 40), 165 (100).

Synthesis of 4-[4-(4-Substituted-phenylazo)phenylazo]-*N,N*-diethyltetrafluoroanilines (11). To an ethanol solution (20 mL) of 4-substituted 4′-(pentafluorophenylazo)-azobenzene **10** (1 mmol) was added diethylamine (4 mmol) andthe mixture was heated at 75 °C in a sealed tube for 24 h. After the reaction was completed, the mixture was poured into water (100 mL). Product was extracted with chloroform, washed with water, dried, purified by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} = 1:1), and recrystallized from chloroform−hexane. The physical and spectral data are given below.

4-[4-(4-Butoxyphenylazo)phenylazo]-*N,N*-diethyltetrafluoroaniline (11a): yield 22%; mp 138 °C; ^{1}H NMR ($CDCl_3$) δ = 1.01 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.0 Hz, 6H), 1.54 (sext, J = 7.1 Hz, 2H), 1.82 (quint, J = 7.1 Hz, 2H), 3.37 (q, J = 7.0 Hz, 4H), 4.07 (t, J = 7.1 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 8.01 (d, J = 8.7 Hz, 2H), 8.04 (d, J = 8.7 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −73.4 (2F), −74.1 (2F); EIMS (70 eV) *m/z* (rel intensity) 501 (M^+, 28), 253 (70), 177 (55), 149 (100). Anal. Calcd for $C_{26}H_{27}F_4N_5O$: C, 62.27; H, 5.43; N, 13.96. Found: C, 62.35; H, 5.46; N, 14.12.

4-[4-(4-Butylthiophenylazo)phenylazo]-*N,N*-diethyltetrafluoroaniline (11e): yield 32%; mp 111 °C; ^{1}H NMR ($CDCl_3$) δ = 0.97 (t, J = 7.4 Hz, 3H), 1.19 (t, J = 7.1 Hz, 6H), 1.51 (sext, J = 7.4 Hz, 2H), 1.72 (quint, J = 7.4 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 3.38 (q, J = 7.1 Hz, 4H), 7.40 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 4H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −73.2 (2F), −74.2 (2F); EIMS (70 eV) *m/z* (rel intensity) 517 (M^+, 48), 269 (87), 165 (100). Anal. Calcd for $C_{26}H_{27}F_4N_5S$: C, 60.33; H, 5.26; N, 13.53. Found: C, 60.76; H, 5.18; N, 13.43.

Reaction of Decafluoroazobenzene (12) with 25% Aqueous Ammonia. To an ethanol solution (75 mL) of decafluoroazobenzene **12** (2.0 g, 5.5 mmol) was added 25% aqueous ammonia (10 mL), and the mixture refluxed for 3 h. After the reaction was completed, the mixture was poured into a saturated solution of ammonium chloride, extracted with ether, and dried over anhydrous sodium sulfate. The products were isolated by column chromatography (SiO_2, $CH_3C_6H_5$). The physical and spectral data are given below.

4-Aminononafluoroazobenzene (13): yield 53%; mp 136−137 °C (lit.[9] mp 133 °C).

2-Aminononafluoroazobenzene (13′): yield 32%; mp 149−151 °C; ^{1}H NMR ($CDCl_3$) δ = 6.70 (br s, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −67.96 (1F), −70.5 (1F), −72.5 (2F), −74.4 (1F), −84.1 (2F), −87.87 (1F), −96.9 (1F); EIMS (70 eV) *m/z* (rel intensity) 359 (M^+; 39), 192 (16), 164 (100).

Synthesis of 4-[4-(Butylthio)tetrafluorophenylazo]-tetrafluoroaniline (13e). To an ethanol solution (20 mL) of 4-aminononafluoroazobenzene (**13**, 0.3 g, 0.8 mmol) was added a butanethiol solution (2 mL) of sodium butanethiolate (0.8 mmol) and the mixture stirred at 0−20 °C overnight. After the reaction was completed, the mixture was poured into an aqueous dilute sodium hydroxide solution. The product was extracted with dichloromethane, washed with an aqueous dilute sodium hydroxide solution and water, and dried. After concentrating the extract, the product was isolated by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} = 1:1): yield 88%; mp 111−113 °C; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.3 Hz, 3H), 1.45 (sext, J = 7.3 Hz, 2H), 1.59 (quint, J = 7.3 Hz, 2H), 3.01 (t, J = 7.3 Hz, 2H), 4,57 (br s, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = -57.0 (2F), −71.0 (2F), −73.3 (2F), −85.7 (2F); EIMS (70 eV) *m/z* (rel intensity) 429 (M^+; 89), 192 (51), 164 (100).

Synthesis of 4-[4-(Pentafluorophenylazo)tetrafluorophenylazo]-*N,N*-diethylaniline (14). To 70% sulfuric acid (1.7 mL) was added sodium nitrite (96 mg, 1.4 mmol). The mixture was stirred upon warming until the sodium nitrite dissolved completely (70 °C). Then, the mixture was cooled to 0 °C. To the solution was added a propionic acid−acetic acid mixed solution (1:5, 3 mL) of 4-aminononafluoroazobenzene (**13**, 500 mg, 1.4 mmol) and the reaction stirred at 0 °C for 2.5 h. The mixture was added to a 70% ethanol suspension (40 mL) of *N,N*-diethylaniline (210 mg, 1.4 mmol), propionic acid (0.5 mL), acetic acid (2.5 mL), and sodium acetate (3 g) at 0 °C. The mixture was stirred overnight at 0−20 °C. After the reaction was completed, the mixture was poured into water. The resulting precipitate was filtered,

purified by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} = 1:1), and recrystallized from chloroform−hexane: yield 33%; mp 225 °C; ^{1}H NMR ($CDCl_3$) δ = 1.27 (t, J = 7.1 Hz, 6H), 3.51 (q, J = 7.1 Hz, 4H), 6.74 (d, J = 8.9 Hz, 2H), 7.91 (d, J = 8.9 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −70.8 (2F), −71.9 (1F), −72.2 (2F), −74.5 (2F), −83.8 (2F); EIMS (70 eV) *m/z* (rel intensity) 519 (M^+; 43), 504 (32), 195 (83), 167 (100), 148 (66), 71 (39), 57 (57). Anal. Calcd for $C_{22}H_{14}F_9N_5$: C, 50.88; H, 2.72; N, 13.48. Found: C, 50.71; H, 2.48; N, 13.38.

Synthesis of 4-(4-Butoxytetrafluorophenylazo)tetrafluorophenylazo-*N,N*-diethylaniline (15a). To a butanol solution (30 mL) of 4-[4-(pentafluorophenylazo)tetrafluorophenylazo]-*N,N*-diethylaniline (**14**, 110 mg, 0.21 mmol) was added sodium butoxide (0.24 mmol). The mixture was heated at 50 °C for 1 h. After the reaction was completed, the mixture was poured into water and extracted with dichloromethane. The extract was washed with water, dried, purified by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} =1:1), and recrystallized from chloroform−hexane: yield 42%; mp 173 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.4 Hz, 3H), 1.26 (t, J = 7.1 Hz, 6H), 1.53 (sext, J = 7.4 Hz, 2H), 1.81 (quint, J = 7.4 Hz, 2H), 3.50 (q, J = 7.1 Hz, 4H), 4.39 (t, J = 7.4 Hz, 2H), 6.73 (d, J = 9.2 Hz, 2H), 7.90 (d, J = 9.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −72.0 (2F), −73.1 (2F), −74.8 (2F), −80.1 (2F); EIMS (70 eV) *m/z* (rel intensity) 573 (M^+; 82), 558 (30), 148 (100). Anal. Calcd for $C_{26}H_{23}F_8N_5O$: C, 54.45; H, 4.04; N, 12.21. Found: C, 54.45; H, 4.01; N, 11.95.

Synthesis of 4-[4-[4-(Butylamino)tetrafluorophenylazo]tetrafluorophenylazo]-*N,N*-diethylaniline (15d). To an ethanol solution (20 mL) of 4-[4-(pentafluorophenylazo)-tetrafluorophenylazo]-*N,N*-diethylaniline (**14**, 200 mg, 0.4 mmol) was added butylamine (30 mg, 0.4 mmol) and the mixture refluxed for 4 h. After the reaction was completed, the mixture was poured into saturated aqueous ammonium chloride solution (20 mL) and extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, purified by column chromatography (SiO_2, $CH_3C_6H_5$:C_6H_{14} =1:1), and recrystallized from chloroform−hexane: yield 30%; mp 187 °C; ^{1}H NMR ($CDCl_3$) δ = 0.98 (t, J = 7.3 Hz, 3H), 1.26 (t, J = 6.9 Hz, 6H), 1.45 (sext, J = 7.3 Hz, 2H), 1.66 (quint, J = 7.3 Hz, 2H), 3.50 (q, J = 6.9 Hz, 4H), 3.56 (t, J = 7.3 Hz, 2H), 4.41 (br s, 1H), 6.73 (d, J = 9.1 Hz, 2H), 7.89 (d, J = 9.1 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −71.0 (2F), −74.5 (2F), −75.2 (2F), −85.6 (2F); EIMS (70 eV) *m/z* (rel intensity) 572 (M^+; 27), 148 (100), 133 (33). Anal. Calcd for $C_{26}H_{24}F_8N_6$: C, 54.55; H, 4.23; N, 14.68. Found: C, 54.73; H, 3.99; N, 14.42.

Synthesis of 4-[4-[4-(Butylthio)tetrafluorophenylazo]-tetrafluorophenylazo]-*N,N*-diethylaniline (15e). To 70% sulfuric acid (1.2 mL) was added sodium nitrite (0.07 g, 1.0 mmol) and the mixture was heated to 70 °C and then cooled to 0 °C. To the solution was added an acetic acid−propionic acid mixed solution (1:5, 3.5 mL) of 4-[4-(butylthio)tetrafluorophenylazo]tetrafluoroaniline (**13e**, 0.43 g, 1.0 mmol) and the mixture stirred at 0 °C for 3 h. The mixture was added to a 70% ethanol suspension (20 mL) of *N,N*-diethylaniline (0.2 g, 1.3 mmol), propionic acid (2.5 mL), acetic acid (12.5 mL), and sodium acetate (3 g) at 0 °C. The mixture was stirred overnight at 0−20 °C. After the reaction was completed, the mixture was poured into water. Product was extracted with dichloromethane, washed with water, purified by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} = 1:1), and recrystallized from chloroform−hexane: yield 36%; mp 168 °C; ^{1}H NMR ($CDCl_3$) δ = 0.94 (t, J = 7.4 Hz, 3H), 1.27 (t, J = 7.1 Hz, 6H), 1.47 (sext, J = 7.4 Hz, 2H), 1.62 (quint, J = 7.4 Hz, 2H), 3.07 (t, J = 7.4 Hz, 2H), 3.51 (q, J = 7.1 Hz, 4H), 6.74 (d, J = 9.3 Hz, 2H), 7.91 (d, J = 9.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −57.0 (2F), −71.9 (2F), −72.3 (2F), −74.5 (2F); EIMS (70 eV) *m/z* (rel intensity) 589 (M^+; 22), 574 (15), 148 (100). Anal. Calcd for $C_{26}H_{23}F_8N_5S$: C, 52.96; H, 3.93; N, 11.88. Found: C, 52.92; H, 4.37; N, 11.86.

Synthesis of 4-(4-Substituted-tetrafluorophenylazo)-pentafluoroazobenzenes (16). To an acetic acid solution (20 mL) of 4-(pentafluorophenylazo)aniline (**2**, 2.8 mmol) was added an acetic acid solution (10 mL) of pentafluoronitrosobenzene (1.0 g, 5.1 mmol) and the mixture stirred at 60 °C for 3 h. After the reaction was completed, the mixture was poured into water (100 mL). The resulting precipitate was filtered, washed with water, dried, and purified by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} = 2:1). The physical and spectral data are given below.

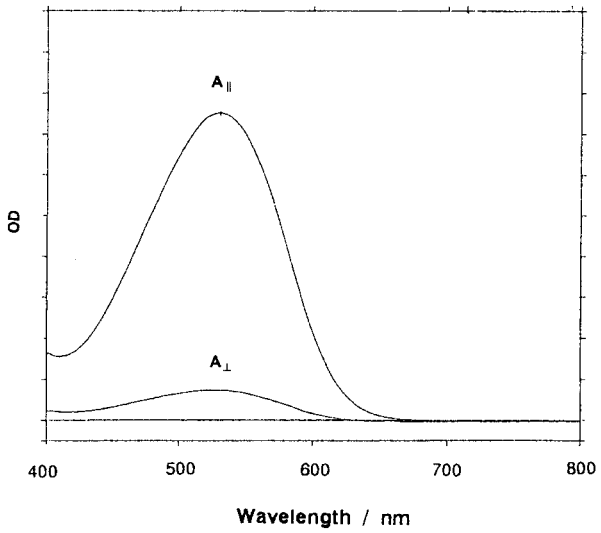


Figure 1. Dichroism of compound **4e** measured in ZLI-1565.

4-(4-Butoxytetrafluorophenylazo)pentafluoroazobenzene (16a): yield 43%; mp 134−136 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.2 Hz, 3H), 1.53 (sext, J = 7.2 Hz, 2H), 1.82 (quint, J = 7.2 Hz, 2H), 4.38 (t, J = 7.2 Hz, 2H), 8.01−8.11 (m, 4H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −71.6 (2F), −72.6 (2F), −73.6 (1F), −80.2 (2F), −84.1 (2F); EIMS (70 eV) *m/z* (rel intensity) 520 (M^+; 38), 271 (67), 167 (35), 104 (48), 76 (100).

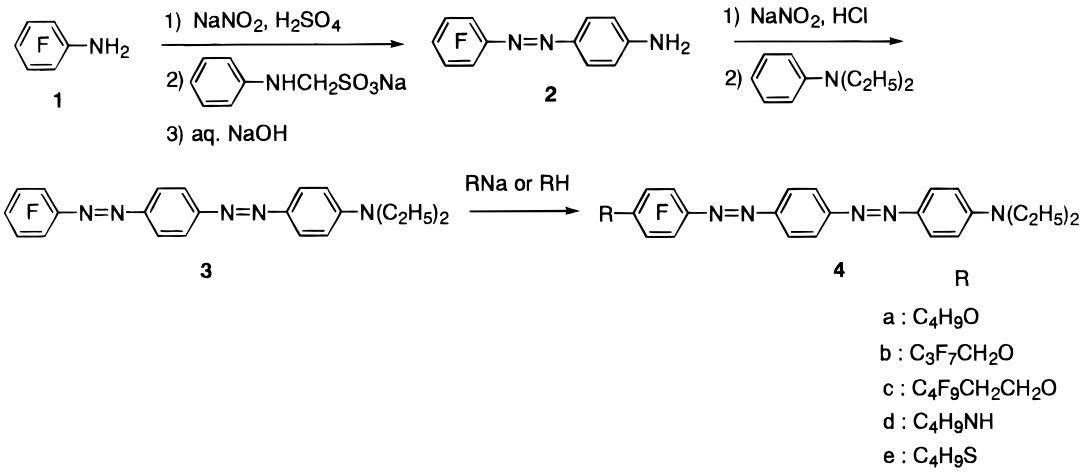
4-(4-Butylthiotetrafluorophenylazo)pentafluoroazobenzene (16e): yield 47%; mp 116−119 °C; ^{1}H NMR ($CDCl_3$) δ = 0.94 (t, J = 7.3 Hz, 3H), 1.47 (sext, J = 7.3 Hz, 2H), 1.62 (quint, J = 7.3 Hz, 2H), 3.06 (t, J = 7.3 Hz, 2H), 8.11 (s, 4H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −57.0 (2F), −71.4 (2F), −72.3 (2F), −73.3 (1F), −84.0 (2F); EIMS (70 eV) *m/z* (rel intensity) 536 (M^+; 44), 271 (71), 167 (32), 104 (52), 76 (100).

Synthesis of 4-[4-(4-Substituted-tetrafluorophenylazo)phenylazo]-*N,N*-diethyltetrafluoroanilines (17). To an ethanol solution (17 mL) of azobenzene **16** (1.2 mmol) was added diethylamine (4 mmol) and the mixture was heated at 65 °C in a sealed tube for 7 h. After the reaction was completed, the mixture was poured into water (100 mL). Product was extracted with chloroform, washed with water, dried, purified by column chromatography (SiO_2, $CHCl_3$:C_6H_{14} = 1:1), and recrystallized from chloroform−hexane. The physical and spectral data are given below.

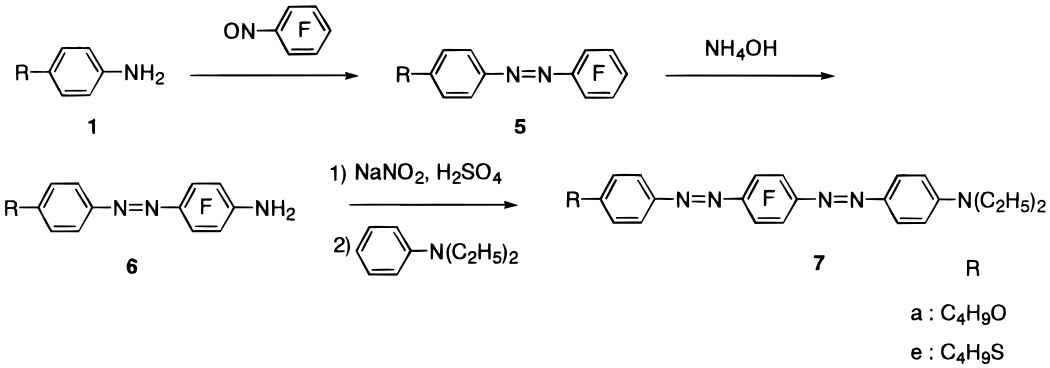
4-[4-(4-Butoxytetrafluorophenylazo)phenylazo]-*N,N*-diethyltetrafluoroaniline (17a): yield 18%; mp 113 °C; ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, J = 7.0 Hz, 3H), 1.19 (t, J = 7.1 Hz, 6H), 1.52 (sext, J = 7.0 Hz, 2H), 1.81 (quint, J = 7.0 Hz, 2H), 3.39 (q, J = 7.1 Hz, 4H), 4.36 (t, J = 7.0 Hz, 2H), 8.03−8.07 (m, 4H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −72.8 (2F), −73.0 (2F), −74.3 (2F), −80.2 (2F); EIMS (70 eV) *m/z* (rel intensity) 573 (M^+; 57), 325 (85), 104 (57), 76 (100). Anal. Calcd for $C_{26}H_{23}F_8N_5O$: C, 54.45; H, 4.04; N, 12.21. Found: C, 54.10; H, 4.17; N, 11.97.

4-[4-[4-(Butylthio)tetrafluorophenylazo]phenylazo]-*N,N*-diethyltetrafluoroaniline (17e): yield 21%; mp 85 °C; ^{1}H NMR ($CDCl_3$) δ = 0.94 (t, J = 7.3 Hz, 3H), 1.20 (t, J = 7.1 Hz, 6H), 1.47 (sext, J = 7.3 Hz, 2H), 1.62 (quint, J = 7.3 Hz, 2H), 3.05 (t, J = 7.3 Hz, 2H), 3.40 (q, J = 7.1 Hz, 4H), 8.04−8.10 (m, 4H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ = −57.0 (2F), −72.5 (4F), −74.4 (2F); EIMS (70 eV) *m/z* (rel intensity) 589 (M^+; 31), 574 (17), 341 (73), 104 (67), 76 (100). Anal. Calcd

Scheme 1



Scheme 2



for $C_{26}H_{23}F_8N_5S$: C, 52.96; H, 3.93; N, 11.88. Found: C, 52.84; H, 4.10; N, 11.79.

Measurement of Dichroism. Dye (about 1 wt %) was dissolved in liquid crystal. The cell (thickness about 9 μm) was prepared by filling the solution between two glass plates attached with transparent electrodes, on which polyimide was applied and rubbed. The absorption of the solution was measured. The order parameter (S) is 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 spectra is shown in Figure 1. The S value of **4e** in ZLI-1565 was calculated to be 0.74.

MO Calculation. The θ values and l/d ratio were calculated from the geometry of the most stable conformer optimized by the MOPAC93 program[16] by the MNDO−PM3 method.[17] The heat of formation of any conformations of a molecule was calculated. On optimization of conformers, the dye molecules were assumed to have C_s symmetry, azo linkages being the trans form. van der Waals radius was taken into account. Transition moments of dyes were calculated by the CNDO/S method[18] (singlet excitation, Nishimoto−Mataga equation, and 60 CI) using the geometry obtained by MNDO−PM3 calculation.

Results and Discussion

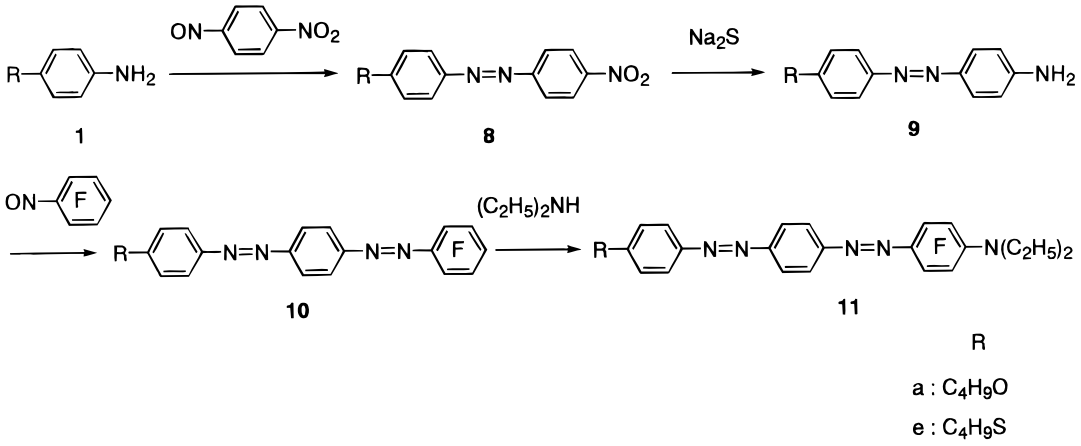
The synthesis of 4-[4-(4-substituted-tetrafluorophenylazo)phenylazo]-*N*,*N*-diethylanilines **4** is shown in Scheme 1. 4-(Pentafluorophenylazo)aniline (**2**) was obtained by the diazotization−coupling reaction of pentafluoroaniline with sodium anilinomethanesulfonate followed by deprotection under alkaline conditions. One more diazotization−coupling reaction of **2** with *N*,*N*-diethylaniline produced 4-[4-(pentafluorophenylazo)-phenylazo]-*N*,*N*-diethylaniline (**3**) in good yield. The alkoxy derivatives **4a**−**c** were obtained by treating **3** with the corresponding sodium alkoxides in moderate yields. The butylamino derivative **4d** was prepared by refluxing **3** with butylamine in ethanol. The butylthio derivative **4e** was obtained by the reaction of **3** with butanethiol in the presence of potassium carbonate in good yield.

The 4-[4-(4-substituted-phenylazo)tetrafluorophenylazo]-*N*,*N*-diethylanilines **7** were prepared as depicted in Scheme 2. The condensation reaction of 4-substituted anilines **1** with pentafluoronitrosobenzene afforded **5** in moderate yields. The amination reaction of **5a** with aqueous ammonia afforded the 2- and 4-amino derivatives in 43 and 51% yields, respectively, while that of **5e** gave the 4-amino and 2,4-diamino derivatives both in 40% yields. The diazotization−coupling reaction of the 4-amino derivatives **6** with *N*,*N*-diethylaniline provided **7** in moderate yields.

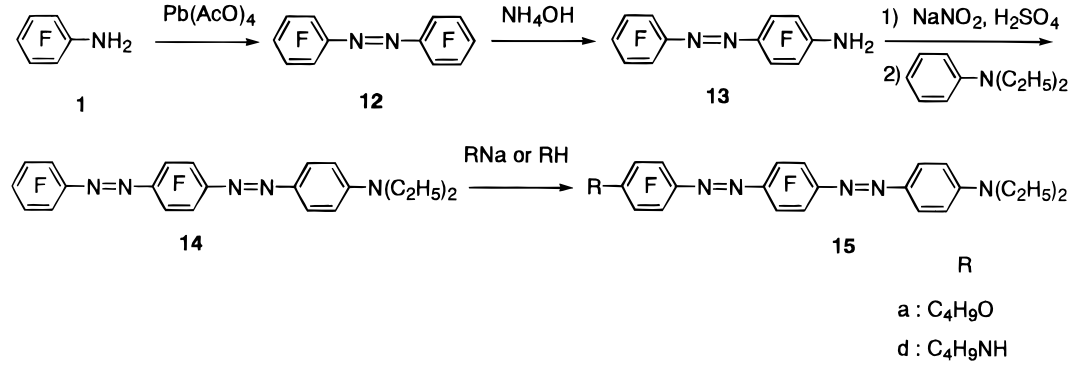
The 4-[4-(4-substituted-phenylazo)phenylazo]-*N*,*N*-diethyltetrafluoroanilines **11** were obtained as indicated in Scheme 3. The condensation reaction of anilines **1** with 4-nitrosonitrobenzene gave the 4-nitroazobenzenes **8**, followed by the reduction of the nitro group to afford the 4-(4-substituted-phenylazo)anilines **9**. The conden-

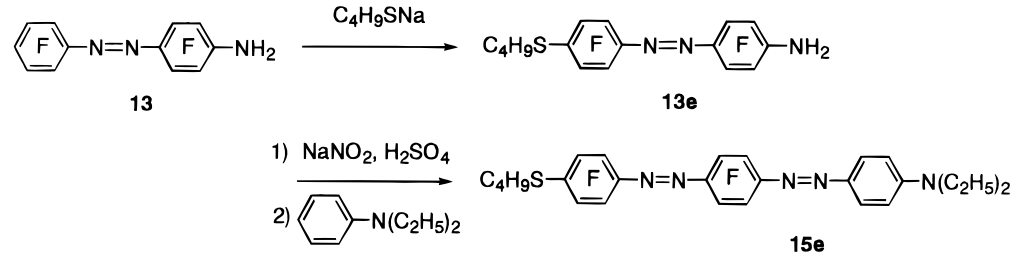
(16) MOPAC93, JCPE No. P081, JCPE Office, 1-7-12, Nishinenishi, Thuchiura 300, Japan.
(17) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.
(18) Tanaka, S.; Y. Ono, Y.; Ueda, Y. *Chem. Pharm. Bull.* **1985**, *33*, 3077.

Scheme 3

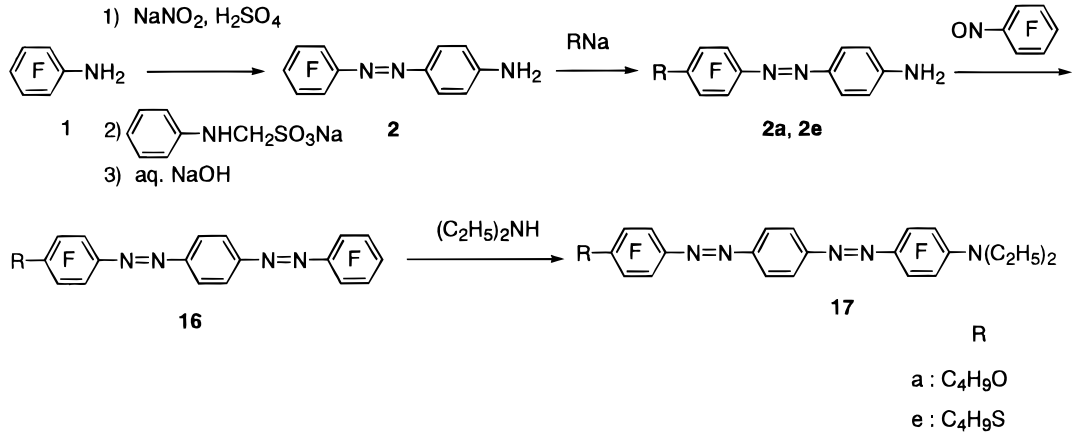


Scheme 4





Scheme 5



sation of **9** with pentafluoronitrosobenzene gave the 4-substituted 4′-(pentafluorophenylazo)azobenzenes **10**. The nucleophilic substitution reaction of **10** with diethylamine provided the desired products **11** in low yield, accompanied by several unisolated byproducts.

Scheme 4 shows the synthesis of the 4-[4-(4-substituted-tetrafluorophenylazo)tetrafluorophenylazo]-*N*,*N*-diethylanilines **15**. The reaction of **12** with aqueous ammonia produced the 2- and 4-aminononafluoroazobenzenes in 32 and 53% yields, respectively. The 4-amino derivative **13** was diazotized and then coupled with *N*,*N*-diethylaniline to give 4-[4-(pentafluorophenylazo)tetrafluorophenylazo]-*N*,*N*-diethylaniline (**14**), which was further treated with sodium butoxide and

Table 1. Properties of Disazo Dyes

R—Ar^1—N=N—Ar^2—N=N—Ar^3

Compd	R	Ar^1	Ar^2	Ar^3	λ_{max} [a] nm	ε [a]	Half [a] wavelength nm	*Td* [b] °C	Solubility [c] mg / 100 ml (mmol dm^{-3})	ZLI-1565 [d] λ_{max} nm	S	ZLI-4792 [d] λ_{max} nm	S	θ / °	*l/d*
3	F	F		$N(C_2H_5)_2$	480	43100	108	291	45 (1.00)	525	0.72	521	0.74	0.1	2.90
4a	C_4H_9O	F		$N(C_2H_5)_2$	472	40900	110	295	18 (0.36)	519	0.73	514	0.76	0.4	3.49
4b	$C_3F_7CH_2O$	F		$N(C_2H_5)_2$	481	38400	103	293	45 (0.71)	525	0.75	521	0.76	2.2	3.43
4c	$C_4F_9CH_2CH_2O$	F		$N(C_2H_5)_2$	478	38200	110	292	28 (0.40)	521	0.75	518	0.77	3.9	3.61
4d	C_4H_9NH	F		$N(C_2H_5)_2$	468	36600	119	300	4 (0.07)	512	0.74	508	0.76	1.0	3.42
4e	C_4H_9S	F		$N(C_2H_5)_2$	482	36500	116	286	70 (1.35)	529	0.74	524	0.75	0.6	3.63
7a	C_4H_9O		F	$N(C_2H_5)_2$	460	28600	140	309	9 (0.18)	517	0.72	515	0.75	1.8	3.36
7e	C_4H_9S		F	$N(C_2H_5)_2$	469	32900	162	296	17 (0.32)	526	0.73	524	0.75	5.4	3.15
11a	C_4H_9O			F $N(C_2H_5)_2$	404	32400	90	320	105 (2.11)	429	0.72	432	0.73	3.1	3.51
11e	C_4H_9S			F $N(C_2H_5)_2$	411	36600	90	305	226 (4.37)	442	0.72	442	0.73	6.8	3.21
14	F	F	F	$N(C_2H_5)_2$	502	30500	132	274	8 (0.16)	558	0.71	553	0.73	0.0	2.86
15a	C_4H_9O	F	F	$N(C_2H_5)_2$	490	30300	132	272	24 (0.42)	549	0.73	543	0.75	0.9	3.48
15d	C_4H_9NH	F	F	$N(C_2H_5)_2$	481	35500	160	285	3 (0.06)	539	0.72	534	0.75	1.4	3.43
15e	C_4H_9S	F	F	$N(C_2H_5)_2$	505	24400	135	269	57 (0.98)	565	0.73	555	0.76	0.6	3.59
17a	C_4H_9O	F		F $N(C_2H_5)_2$	395	30900	133	312	212 (3.71)	435	0.69	435	0.72	1.8	3.63
17e	C_4H_9S	F		F $N(C_2H_5)_2$	409	28700	133	277	395 (6.70)	446	0.69	445	0.72	4.3	3.25
18a [e]	C_4H_9O			$N(C_2H_5)_2$	451	42200	106	311	7 (0.17)	492	0.72	487	0.74	2.2	3.49
18e [e]	C_4H_9S			$N(C_2H_5)_2$	463	36900	115	287	14 (0.32)	499	0.73	499	0.76	1.5	3.16
18f [e]	C_4F_9S			$N(C_2H_5)_2$	475	40700	110	242	56 (0.92)	515	0.70	509	0.76	1.9	3.19

[a] In hexane. [b] Measured by TG-DTA analysis (heated at 10 °C min^{-1} under an air atmosphere). [c] In hexane at 25 °C. [d] Liquid crystal from Merck Co., Ltd. [e] Reference 5.

butylamine to afford **15a** and **15d**, respectively. A similar nucleophilic substitution reaction of **14** with sodium butanethiolate gave the unseparable mixture of mono-, bis-, and tris(butylthio) derivatives in low yields. Therefore, the butylthio derivative **15e** was obtained by the nucleophilic substitution reaction of **13** with sodium butanethiolate to give **13e**, followed by the diazotization−coupling reaction with *N,N*-diethylaniline in good yield.

The synthesis of the 4-[4-(4-substituted-tetrafluorophenylazo)phenylazo]-*N,N*-diethyltetrafluoroanilines **17** is summarized in Scheme 5. Sodium butoxide and butylthiolate reacted with 4-(pentafluorophenylazo)-aniline (**2**) to give the corresponding 4-(substituted-tetrafluorophenylazo)anilines **2a** and **2e**, followed by the condensation reaction with pentafluoronitrosobenzene to give the 4-(4-substituted-tetrafluorophenylazo)pentafluoroazobenzenes **16**. The nucleophilic substitution reaction of **16** with diethylamine yielded **17** in low yields, accompanied by unseparable several by-products.

The preparation of the tris(perfluoro-*p*-phenylene) derivatives has been also tried. However, 4-aminononafluoroazobenzene (**13**) did not react with pentafluoronitrosobenzene, due to the low nucleophilicity of the amino moiety.

Azobenzenes are intramolecular push−pull chromophores, indicating that an electronic effect at both terminal moieties is very important. The diethylamino group is most electron-donating among the butylamino, butoxy, butylthio, and diethylamino substituents. Therefore, the terminal aromatic ring substituted with the diethylamino group can act as an electron-donating moiety. In a series of 4-[4-(4-substituted-tetrafluoro-

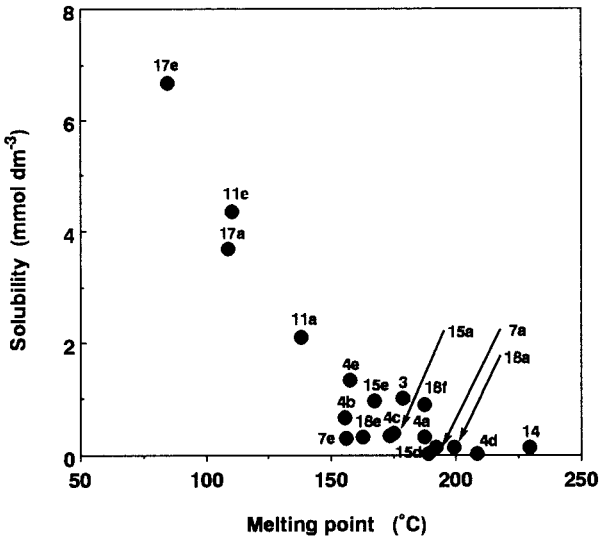


Figure 2. Relationship between solubility and melting point.

phenylazo)phenylazo]-*N*,*N*-diethylanilines **3** and **4**, the bathochromicity was in the order of the substituent: butylthio, 1*H*,1*H*-perfluorobutoxy, fluoro, 1*H*,1*H*,2*H*,2*H*-perfluorohexyloxy > butoxy > butylamino. This indicated that a larger electron-donating substituent could produce less bathochromic derivatives. The bathochromicity of the butylthio derivatives was in the order of the dye skeleton, **15e** ≫ **4e** > **7e**, **18e** ≫ **11e**, **17e**, suggesting that both terminal phenylene moieties could mainly affect the absorption maximum, followed by the central phenylene moiety. The 4-(butylthio)tetrafluoro-*p*-phenyl derivative **4e** was more bathochromic than the 4-(perfluorobutylthio)phenyl one **18f**. This showed that the 4-(butylthio)tetrafluoro-*p*-phenyl moiety is more electron-withdrawing than the 4-(perfluorobutylthio)-phenyl moiety.

The effect of fluorine atoms in the disazo dyes on the solubility in hexane at 25 °C was examined. In a series of 4-[4-(4-substituted-tetrafluorophenylazo)phenylazo]-*N*,*N*-diethylanilines **4**, the butylthio derivative **4e** was most soluble, followed by alkoxy derivative **4a**−**c**. The butylamino derivative **4d** was least soluble among them.

The 4-(butylthio)tetrafluorophenyl derivatives **4e** was more soluble than the 4-(perfluorobutylthio)phenyl derivative **18f**.

The solubility changed much more drastically by the introduction of perfluoro-*p*-phenylene moiety(ies). For the mono perfluoro-*p*-phenylene derivatives, the solubility was in the order **11e** > **4e** > **7e**. The introducton of a perfluoro-*p*-phenylene moiety adjacent to the more polar diethylamino site was the most effective way to increase the solubility, followed by the less polar butylthio site. The solubility of **7e** was similar to that of **18e**, indicating no significacant effect of the central perfluoro-*p*-phenylene moiety on the solubility. In the case of bis(perfluoro-*p*-phenylene) derivatives, the compound **17e**, in which perfluoro-*p*-phenylene moieties were introduce to both the terminal ends, was more soluble than compound **15e**. The same tendency was observed in the case of the 4-(butoxy)perfluoro-*p*-phenyl derivatives **4a**, **7a**, **11a**, **15a**, **17a**, and **18a**. Thus, the introduction of perfluoro-*p*-phenylene moieties, especially to both the terminal ends, was very effective in increasing the solubility.

The relationship between solubility and the melting point of the disazo dyes is shown in Figure 2. When the melting points of the azo dyes were above 150 °C, no remarkable difference in their solubility was observed. However, below 150 °C, the solubility increased as the melting point decreased. In the case of the 4-[4-(4-substituted-tetrafluorophenylazo)phenylazo]-*N*,*N*-diethylanilines **4a**, **4d**, and **4e**, the lower the electron-withdrawing nature of the terminal substituent, the lower the melting point, thus resulting in a higher solubility. In the series **4e**, **7e**, **11e**, **15e**, **17e**, **18e** and **18f**, the less polar the molecule, the lower the melting point. It is concluded that the less polar disazo dyes could decrease the intermolecular interactions between the substrates to increase the solubility.

The decomposition temperatures (T_ds) of the selected disazo dyes are also summarized in Table 1. In a series of 4-substituted tetrafluoro-*p*-phenylene derivatives **4**, the T_d of the butylthio derivative **4e** was lower than those of the other derivatives (**4a**, **4b**, **4c**, and **4d**). Bis-

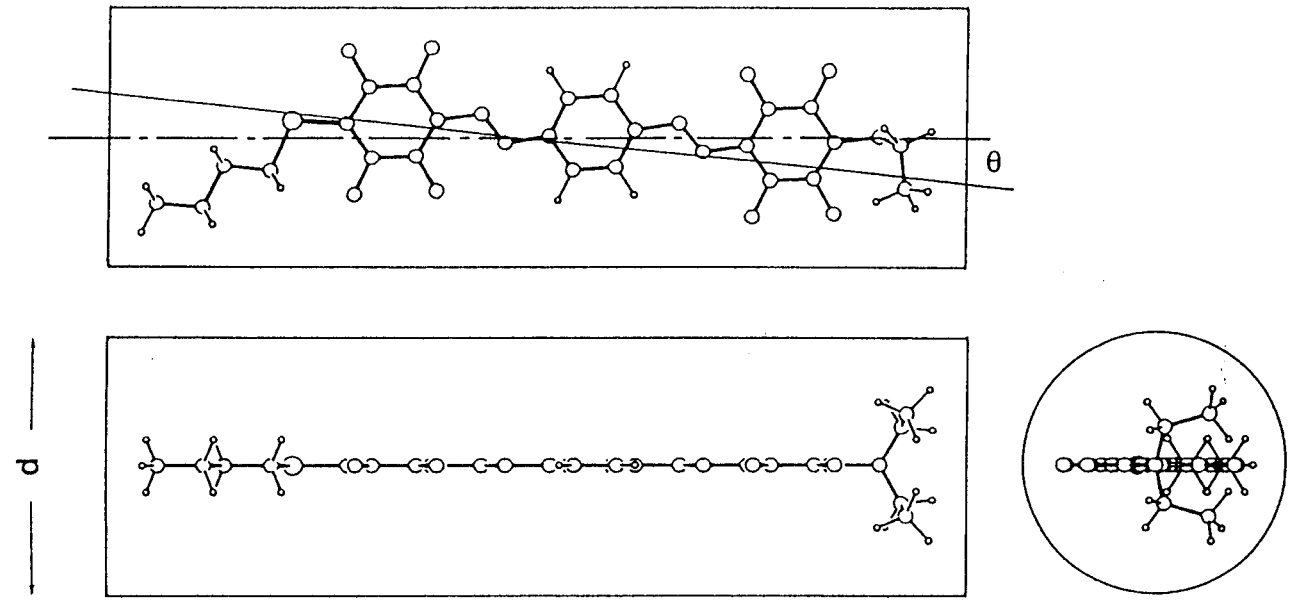


Figure 3. Calculation of l/d ratio and θ value of azo dye **17e**.

(tetrafluoro-*p*-phenylene) derivatives **15e** and **17e** showed lower T_d than the mono(tetrafluoro-*p*-phenylene) derivatives **4e**, **7e**, and **11e**. The T_ds of the butylthio derivatives **4e**, **7e**, **11e**, **15e**, and **17e** (269−305 °C) were higher than that of the 4-(perfluoroalkylthio)phenyl derivative **18f** (242 °C).

No remarkable difference in the dichroism between the disazo dyes having tetrafluoro-*p*-phenylene moiety(ies) **3**, **4**, **7**, **11**, **14**, **15**, and **17** and *p*-phenylene derivatives **18** was observed. The dichroism could be examined by calculating both the deviation of 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. 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 Figure 3. The calculated θ value of **17e** was 4.38. The l and d values were calculated to be 27.7 and 8.5 Å, respectively, the l/d ratio being 3.25. The calculated results are indicated in Table 1. The θ values of the tetrafluoro-*p*-phenylene derivatives were very small (<6.8°). Their l/d ratios were in the range of 2.86−3.61. These values are similar to those of *p*-phenylene derivatives **18**. These calculations could demonstrate that the tetrafluoro-*p*-phenylene derivatives showed similar dichroism as the *p*-phenylene derivatives. The S values of the tetrafluoro-*p*-phenylene derivatives were in the range of 0.69−0.77, being higher than the practically required value 0.70.

Conclusions

Novel dichroic disazo dyes containing tetrafluoro-*p*-phenylene moiety(ies) for guest−host liquid crystal displays have been synthesized. They showed higher solubility than the non-fluorine-containing derivatives. Especially when tetrafluoro-*p*-phenylene moieties were introduce to both the terminal ends, the solubility of the disazo dyes increased remarkably. The dichroism of tetrafluoro-*p*-phenylene disazo dyes (S > 0.70) was similar to that of non-fluorine-containing derivatives. These results indicate that these new tetrafluoro-*p*-phenylene derivatives can be used as practical dichroic dyes.

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