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Liquid azo dyes

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ABSTRACT

Any liquid azo dyes, in which auxochrome such as dialkylamino, alkoxy, and amino group is attached in a molecule, were produced. In a series of 2-alkyl-4'-(dimethylamino)azobenzenes, the butyl, hexyl, octyl, and dodecyl derivatives were liquid at room temperature, whereas the propyl, 1-methylethyl, 1-methylpropyl, 1,1-dimethylethyl, and octadecyl derivatives were solid. Thus, it is essential for liquid azo dyes to have a medium *n*-alkyl group at the 2-position. In a series of 2-butyl-4'-(dialkylamino) azobenzenes, the dimethylamino, diethylamino, dibutylamino, dioctylamino, and didodecylamino derivatives were liquid. 2-Butyl-4'-methoxyazobenzene and 4-amino-3,5-dimethyl-2'-butylazobenenzne were also liquid, whereas 2-butyl-4'-hydroxyazobenznene, 4-amino-2'-butylazobenzene, and 2-butyl-4'-(methylamino)azobenzene were solid. The prevention of π/π stacking, alkyl–alkyl interactions, and intermolecular hydrogen bond could produce liquid azo dyes.

1. Introduction

Azo dyes are well-known important compounds [1,2] and have been used not only for dyeing [3–5] but also for high-technology applications [6–8]. As organic dyes have auxochromes such as amino, alkylamino, dialkylamino, hydroxy, alkoxy, and nitro groups in a molecule, they are usually solid. These auxochromes can give strong polarity to the molecule to increase intermolecular interactions. Furthermore, dye molecule is usually large and has π-electrons to produce strong disperse forces and π–π interactions. In the course of our study on the solid-state fluorescent dyes, we could serendipitously find that a few coumarins [9] and (dialkylamino)perfluorophenazines [10] were liquid. These results motivated us to find new liquid azo dyes. Some azo compounds without auxochrome such as 2-ethyl- [11], 2,6-dimethyl- [12], and 2,2'-dibutylazobenzenes [13] are liquid. However, no liquid azo dyes which have the auxochrome in a molecule have been reported so far. We report herein the survey of a series of liquid azo dyes.

2. Experimental

2.1. Instruments

NMR spectra were recorded on a Varian Inova 400 spectrometer. Mass spectra were taken on a Jeol MStation 700 instrument. Elemental analysis was performed with a Yanaco MT-6 CHN corder. Thermal analysis was performed with SII Nanotechnology, DSC 6200 instruments.

2.2. Materials

2-Propylaniline, 2-(1-methylethyl)aniline, 2-butylaniline, 2-(1-methylpropyl)aniline, 2-(1,1-dimethylethyl)aniline, 2-butoxyaniline, 2-butylthioaniline, *N*-methylaniline, *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline, phenol, methyl iodide, ethyl iodide, propyl iodide, butyl iodide, octyl iodide, dodecyl iodide, octadecy iodide, and dioctadecylamine were purchased from market. 2-[3,3,4,4,5,5,5-Heptafluoro-2,2-bis(trifluoromethyl)pentyl]aniline and sodium anilinomethanesulfonates were supplied from NEOS Co., Ltd and Sumitomo Chemical Co., Ltd, respectively. 2-Hexylaniline [14], 2-octylaniline [14], 2-dodecylaniline [14], 2-(perfluorobutyl)aniline [15] and 4-nitronitrosobenene [16] were prepared as described in

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literature. *N*,*N*-Dibutylaniline, *N*,*N*-dioctylaniline, *N*,*N*-didodecylaniline were prepared by the *N*-alkylation reaction of aniline.

2.3. Synthesis of 4-arylazo-N,N-dialkylanilines **6**–**18**, **23**–**27**, and **29**

An aniline **A** (2 mmol) and aqueous hydrochloric acid (0.5 mol dm^{-3}, 0.6 ml, 6 mmol) were dissolved in water-DMF (1:3) mixed solvent (4 mL). The mixture was stirred for 30 min. To this solution were added water (3 mL), ice (*ca*. 3 g), and a 20% aqueous solution of sodium nitrite (140 mg, 2 mmol). The mixture was stirred at 0 °C for 1 h. Then, to the solution was added a DMF solution (5 mL) of coupling component **B** (2 mmol). The mixture was stirred at 0 °C overnight. After the reaction was completed, the mixture was poured into water (50 mL). The product was extracted with dichloromethane (20 mL × 2), washed with aqueous sodium carbonate (20 mL × 2), water (20 mL × 2), and purified by column chromatography.

2.3.1. 4-Dimethylamino-2'-propylazobenzene (**6**)

Yield 21%; ^{1}H NMR ($CDCl_3$) δ = 0.96 (t, J = 7.3 Hz, 3H), 1.70 (sex, J = 7.3 Hz, 2H), 3.08 (t, J = 7.3 Hz, 2H), 3.08 (s, 6H), 6.86 (d, J = 9.2 Hz, 2H), 7.25–7.37 (m, 3H), 7.63 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.2, 25.3, 33.7, 40.4 (2C), 111.7 (2C), 115.4, 125.0 (2C), 126.5, 129.4, 130.4, 141.4, 144.4, 151.0, 152.3; EIMS (70 eV) *m/z* (rel intensity) 267 (M^+; 34), 120 (100); Anal. Found: C, 75.98; H, 7.99; N, 15.54%. Calcd for $C_{17}H_{21}N_3$: C, 76.37; H, 7.92; N, 15.72%.

2.3.2. 4-Dimethylamino-2'-(1-methylethyl)azobenzene (**7**)

Yield 26%; ^{1}H NMR ($CDCl_3$) δ = 1.32 (d, J = 7.2 Hz, 6H), 3.10 (s, 6H), 4.09 (sep, J = 7.2 Hz, 1H), 6.85 (d, J = 9.2 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 7.4 Hz, 1H), 7.59 (d, J = 7.4 Hz, 1H), 7.84 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 23.9 (2C), 27.9, 40.4 (2C), 111.6 (2C), 115.4, 125.0 (2C), 126.1, 126.3, 129.7, 144.4, 146.7, 150.3, 152.3; EIMS (70 eV) *m/z* (rel intensity) 267 (M^+; 19), 252 (21), 135 (100), 120 (16); Anal. Found: C, 75.92; H, 7.99; N, 15.40%. Calcd for $C_{17}H_{21}N_3$: C, 76.37; H, 7.92; N, 15.72%.

2.3.3. 2-Butyl-4'-(dimethylamino)azobenzene (**8**)

Yield 21%; ^{1}H NMR ($CDCl_3$) δ = 0.93 (t, J = 7.5 Hz, 3H), 1.40 (sex, J = 7.5 Hz, 2H), 1.66 (quin, J = 7.5 Hz, 2H), 3.11 (s, 6H), 3.13 (t, J = 7.5 Hz, 2H), 6.86 (d, J = 9.2 Hz, 2H), 7.24–7.37 (m, 3H), 7.63 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.2, 22.7, 31.4, 34.4, 40.4 (2C), 111.7 (2C), 115.5, 125.1 (2C), 126.5, 129.5, 130.4, 141.7, 144.4, 151.0, 152.3; EIMS (70 eV) *m/z* (rel intensity) 281 (M^+; 18), 238 (31), 135 (100), 120 (43); Anal. Found: C, 76.91; H, 8.47; N, 14.76%. Calcd for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24; N, 14.93%.

2.3.4. 4-Dimethylamino-2'-(1-methylpropyl)azobenzene (**9**)

Yield 46%; ^{1}H NMR ($CDCl_3$) δ = 0.84 (t, J = 7.5 Hz, 3H), 1.31 (d, J = 7.5 Hz, 3H), 1.62–1.76 (m, 2H), 3.07 (s, 6H), 3.81 (sex, J = 7.5 Hz, 1H), 6.76 (d, J = 9.2 Hz, 2H), 7.21–7.35 (m, 3H), 7.56 (d, J = 7.5 Hz, 1H), 7.87 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) $^{\delta}$ = 12.4, 21.5, 31.2, 34.7, 40.4 (2C), 111.6 (2C), 115.4, 125.0 (2C), 126.2, 126.9, 129.6, 144.4, 145.7, 150.8, 152.3; EIMS (70 eV) *m/z* (rel intensity) 281 (M^+24), 135 (100); Anal. Found: C, 76.65; H, 8.48; N, 15.13%. Calcd for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24; N, 14.93%.

2.3.5. 4-Dimethylamino-2'-(2,2-dimethylethyl)azobenzene (**10**)

Yield 6%; ^{1}H NMR ($CDCl_3$) δ = 1.52 (s, 9H), 3.08 (s, 6H), 6.78 (d, J = 9.2 Hz, 2H), 7.25 (t, J = 8.2 Hz, 1H), 7.29 (t, J = 8.2 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 31.9 (3C), 36.1, 40.4 (2C), 111.7 (2C), 116.7, 125.3 (2C), 126.3, 126.7, 129.0, 144.3, 146.8, 152.3, 152.4; EIMS (70 eV) *m/z* (rel intensity) 281 (M^+; 23), 134 (100); Anal. Found: C, 76.54; H, 8.41; N, 15.12%. Calcd for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24; N, 14.93%.

2.3.6. 4-Dimethylamino-2'-(perfluorobutyl)azobenzene (**11**)

Yield 8%; ^{1}H NMR ($CDCl_3$) δ = 3.14 (s, 6H), 6.88 (d, J = 9.2 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.77–7.83 (m, 3H), 7.86 (d, J = 9.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext $CFCl_3$) δ = −80.6 (3F), −103.6 (2F), −120.7 (2F), −125.7 (2F); EIMS (70 eV) *m/z* (rel intensity) 443 (M^+; 65), 120 (100); Anal. Found: C, 48.72; H, 3.29; N, 9.45%. Calcd for $C_{18}H_{14}F_9N_3$: C, 48.77; H, 3.18; N, 9.48%.

2.3.7. 2-Butoxy-4'-(dimethylamino)azobenzene (**12**)

Yield 43%; ^{1}H NMR ($CDCl_3$) δ = 0.99 (t, J = 7.3 Hz, 3H), 1.52 (sex, J = 7.3 Hz, 2H), 1.87 (quin, J = 7.3 Hz, 2H), 3.08 (s, 6H), 4.16 (t, J = 7.3 Hz, 2H), 6.75 (d, J = 7.0 Hz, 2H), 6.98 (t, J = 8.1 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 7.30 (t, J = 8.1 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.1, 19.4, 31.5, 40.4 (2C), 69.8, 111.6 (2C), 114.8, 117.1, 121.1, 125.2 (2C), 130.6, 143.4, 144.4, 152.3, 156.0; EIMS (70 eV) *m/z* (rel intensity) 297 (M^+; 25), 190 (72), 162 (57), 135 (100); Anal. Found: C, 72.88; H, 7.63; N, 14.08%. Calcd for $C_{18}H_{23}N_3O$: C, 72.70; H, 7.80; N, 14.13%.

2.3.8. 2-Butylthio-4'-(dimethylamino)azobenzene (**13**)

Yield 79%; ^{1}H NMR ($CDCl_3$) δ = 0.96 (t, J = 7.4 Hz, 3H), 1.55 (sex, J = 7.4 Hz, 2H), 1.75 (quin, J = 7.4 Hz, 2H), 2.99 (t, J = 7.4 Hz, 2H), 3.10 (s, 6H), 6.76 (d, J = 9.2 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 13.8, 22.4, 31.0, 31.8, 40.4 (2C), 111.6 (2C), 116.3, 125.1, 125.3 (2C), 126.4, 129.6, 138.3, 144.2, 150.2, 152.6; EIMS (70 eV) *m/z* (rel intensity) 313 (M^+; 4), 256 (100), 184 (24), 77 (68); Anal. Found: C, 69.11; H, 7.38; N, 13.63%. Calcd for $C_{18}H_{23}N_3S$: C, 68.97; H, 7.40; N, 13.41%.

2.3.9. 4-Dimethylamino-2'-hexylazobenzene (**14**)

Yield 27%; ^{1}H NMR ($CDCl_3$) δ = 0.86 (t, J = 7.3 Hz, 3H), 1.27–1.37 (m, 6H), 1.67 (quin, J = 7.3 Hz, 2H), 3.08 (s, 6H), 3.08 (t, J = 7.3 Hz, 2H), 6.76 (d, J = 9.2 Hz, 2H), 7.21–7.29 (m, 3H), 7.59 (d, J = 7.4 Hz, 1H), 7.87 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.2, 22.7, 29.3, 31.6, 31.8, 32.1, 40.4 (2C), 111.6 (2C), 115.4, 125.0 (2C), 126.5, 129.4, 130.3, 141.7, 144.4, 151.0, 152.3; EIMS (70 eV) *m/z* (rel intensity) 309 (M^+; 25), 238 (23), 135 (100), 120 (12); Anal. Found: C, 77.82; H, 8.77; N, 13.60%. Calcd for $C_{20}H_{27}N_3$: C, 77.63; H, 8.79; N, 13.58%.

2.3.10. 4-Dimethylamino-2'-octylazobenzene (**15**)

Yield 34%; ^{1}H NMR ($CDCl_3$) δ = 0.86 (t, J = 6.9 Hz, 3H), 1.25–1.36 (m, 10H), 1.66 (quin, J = 7.6 Hz, 2H), 3.08 (s, 6H), 3.09 (t, J = 7.6 Hz, 2H), 6.77 (d, J = 9.2 Hz, 2H), 7.21–7.29 (m, 3H), 7.59 (d, J = 7.3 Hz, 1H), 7.88 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.2, 22.8, 29.4, 29.6, 29.7, 31.6, 32.0, 32.2, 40.4 (2C), 111.6 (2C), 115.4, 125.0 (2C), 126.5, 129.4, 130.3, 141.7, 144.4, 151.0, 152.3; EIMS (70 eV) *m/z* (rel intensity) 337 (M^+; 7), 238 (15), 135 (100); Anal. Found: C, 78.47; H, 9.53; N, 12.29%. Calcd for $C_{22}H_{31}N_3$: C, 78.29; H, 9.26; N, 12.45%.

2.3.11. 4-Dimethylamino-2'-dodecylazobenzene (**16**)

Yield 23%; ^{1}H NMR ($CDCl_3$) δ = 0.87 (t, J = 7.5 Hz, 3H), 1.25–1.36 (m, 18H), 1.65 (quin, J = 7.5 Hz, 2H), 3.07 (s, 6H), 3.07 (t, J = 7.5 Hz, 2H), 6.76 (d, J = 9.2 Hz, 2H), 7.21–7.28 (m, 3H), 7.58 (d, J = 7.4 Hz, 1H), 7.87 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.1, 22.8, 29.4, 29.55, 29.58, 29.69 (4C), 31.6, 31.9, 32.1, 40.4 (2C), 111.5 (2C), 115.4, 124.9 (2C), 126.5, 129.4, 130.3, 141.7, 144.3, 151.0, 152.3; EIMS (70 eV) *m/z* (rel intensity) 393 (M^+; 41), 365 (73), 238 (27), 135 (100), 120 (14); Anal. Found: C, 79.36; H, 10.32; N, 10.56%. Calcd for $C_{26}H_{39}N_3$: C, 79.34; H, 9.99; N, 10.6%.

*2.3.12. 4-Dimethylamino-2'-octadecylazobenzene (**17**)*

Yield 17%; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, J = 7.5 Hz, 3H), 1.23–1.36 (m, 30H), 1.66 (quin, J = 7.5 Hz, 2H), 3.08 (s, 6H), 3.08 (t, J = 7.5 Hz, 2H), 6.76 (d, J = 9.2 Hz, 2H), 7.21–7.29 (m, 3H), 7.59 (d, J = 7.3 Hz, 1H), 7.87 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.1, 22.7, 29.4, 29.51, 29.55, 29.72 (10C), 31.5, 31.9, 32.1, 40.3, 111.5 (2C), 115.3, 124.9 (2C), 126.4, 129.3, 130.2, 141.6, 144.2, 150.9, 152.2; EIMS (70 eV) *m/z* (rel intensity) 477 (M^+; 3), 345 (13), 238 (11), 135 (100), 120 (21); Anal. Found: C, 80.63; H, 11.14; N, 8.74%. Calcd for $C_{32}H_{51}N_3$: C, 80.45; H, 10.76; N, 8.80%.

*2.3.13. 4-Dimethylamino-2'-[3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl]- azobenzene (**18**)*

Yield 11%; ^{1}H NMR ($CDCl_3$) δ = 3.13 (s, 6H), 4.43 (s, 2H), 6.88 (d, J = 9.5 Hz, 2H), 7.41–7.48 (m, 2H), 7.58 (d, J = 7.7 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.87 (d, J = 9.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext $CFCl_3$) δ = −61.1 (6F), −79.9 (3F), −107.2 (2F), −122.1 (2F); EIMS (70 eV) *m/z* (rel intensity) 557 (M^+; 60), 388 (26), 120 (100); Anal. Found: C, 44.59; H, 2.95; N, 7.46%. Calcd for $C_{21}H_{16}F_{13}N_3$: C, 45.25; H, 2.89; N, 7.54%.

*2.3.14. 2-Butyl-4'-(methylamino)azobenzene (**23**)*

Yield 8%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.4 Hz, 3H), 1.34–1.42 (m, 2H), 1.61–1.68 (m, 2H), 2.92 (s, 3H), 3.10 (t, J = 7.4 Hz, 2H), 4.17 (br, 1H), 6.66 (d, J = 8.8 Hz, 2H), 7.21–7.32 (m, 3H), 7.59 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 22.5, 30.4, 31.1, 34.2, 111.8 (2C), 115.3, 125.2 (2C), 126.4, 129.4, 130.2, 141.6, 145.1, 150.7, 151.6; EIMS (70 eV) *m/z* (rel intensity) 267 (M^+, 14), 224 (31), 209 (8), 162 (14), 147 (39), 121 (100), 106 (65), 91 (54), 77 (80) 65 (64); Anal. Found: C, 76.46; H, 7.97; N, 15.53%. Calcd for $C_{17}H_{21}N_3$: C, 76.37; H, 7.92; N, 15.72%.

*2.3.15. 2-Butyl-4'-(diethylamino)azobenzene (**24**)*

Yield 18%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.3 Hz, 3H), 1.22 (t, J = 6.9 Hz, 6H), 1.38 (sex, J = 7.3 Hz, 2H), 1.65 (quin, J = 7.3 Hz, 2H), 3.09 (t, J = 7.3 Hz, 2H), 3.43 (q, J = 6.9 Hz, 4H), 6.72 (d, J = 9.2 Hz, 2H), 7.21–7.28 (m, 3H), 7.59 (d, J = 7.4 Hz, 1H), 7.85 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 12.6, 14.0, 22.6, 31.2, 34.2, 44.6, 110.9 (2C), 115.3, 125.2 (2C), 126.4, 129.1, 130.2, 141.3, 143.6, 149.8, 150.9; EIMS (70 eV) *m/z* (rel intensity) 309 (M^+; 57), 163 (100); Anal. Found: C, 77.81; H, 9.03; N, 13.71%. Calcd for $C_{20}H_{27}N_3$: C, 77.63; H, 8.79; N, 13.58%.

*2.3.16. 2-Butyl-4'-(dibutylamino)azobenzene (**25**)*

Yield 10%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.3 Hz, 3H), 0.98 (t, J = 7.3 Hz, 6H), 1.38 (sex, J = 7.3 Hz, 2H), 1.38 (sex, J = 7.3 Hz, 4H), 1.63 (quin, J = 7.3 Hz, 2H), 1.63 (quin, J = 7.3 Hz, 4H), 3.08 (t, J = 7.3 Hz, 2H), 3.36 (t, J = 7.3 Hz, 4H), 6.89 (d, J = 9.2 Hz, 2H), 7.25–7.29 (m, 3H), 7.58 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.06, 14.11, 20.3, 22.6, 29.4, 31.2, 34.2, 50.9, 110.9 (2C), 115.3, 125.2 (2C), 126.4, 129.1, 130.1, 141.3, 143.5, 150.2, 150.9; EIMS (70 eV) *m/z* (rel intensity) 365 (M^+; 76), 219 (100); Anal. Found C, 78.96; H, 9.83; N, 11.21%. Calcd for $C_{24}H_{35}N_3$: C, 78.85; H, 9.65; N, 11.49%.

*2.3.17. 2-Butyl-4'-(dioctylamino)azobenzene (**26**)*

Yield 15%; ^{1}H NMR ($CDCl_3$) δ = 0.89 (t, J = 7.3 Hz, 6H), 0.92 (t, J = 7.2 Hz, 3H), 1.29–1.65 (m, 28H), 3.08 (t, J = 7.2 Hz, 2H), 3.45 (t, J = 7.3 Hz, 4H), 6.68 (d, J = 9.2 Hz, 2H), 7.25–7.28 (m, 3H), 7.58 (d, J = 7.4 Hz, 1H), 7.84 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.06, 14.13, 22.6, 22.7, 27.1, 27.3, 29.3, 29.5, 31.2, 31.8, 34.2, 51.2, 110.9 (2C), 115.3, 125.2 (2C), 126.4, 129.1, 130.2, 141.3, 143.5, 150.2, 151.0; EIMS (70 eV) *m/z* (rel intensity) 477 (M^+; 67), 331 (100). Anal. Found: C, 80.63; H, 10.82; N, 8.55%. Calcd for $C_{32}H_{51}N_3$: C, 80.45; H, 10.76; N, 8.70%.

*2.3.18. 2-Butyl-4'-(didodecylamino)azobenzene (**27**)*

Yield 12%; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, J = 7.1 Hz, 6H), 0.92 (t, J = 7.3 Hz, 3H), 1.27–1.45 (m, 38H), 1.63–1.68 (m, 6H), 3.07 (t, J = 7.3 Hz, 2H), 3.34 (t, J = 7.1 Hz, 4H), 6.68 (d, J = 9.2 Hz, 2H), 7.19–7.29 (m, 3H), 7.58 (d, J = 7.4 Hz, 1H), 7.84 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.06, 14.13, 22.6, 22.7, 27.1, 27.3, 29.3, 29.5, 29.5, 29.7, 29.7, 29.7, 31.2, 31.9, 34.2, 51.2, 110.9 (2C), 115.3, 125.2 (2C), 126.4, 129.0, 130.1, 141.3, 143.5, 150.2, 151.0; EIMS (70 eV) *m/z* (rel intensity) 589 (M^+; 60), 443 (100); Anal. Found: C, 81.76; H, 11.51; N, 6.73%. Calcd for $C_{40}H_{67}N_3$: C, 81.43; H, 11.45; N, 7.12%.

*2.3.19. 2-Butyl-4'-hydroxyazobenzene (**29**)*

Yield 20%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.5 Hz, 3H), 1.38 (sex, J = 7.5 Hz, 2H), 1.64 (quin, J = 7.5 Hz, 2H), 3.10 (t, J = 7.5 Hz, 2H), 5.13 (s, 1H), 6.94 (d, J = 8.6 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 22.5, 31.1, 34.3, 115.3, 115.8 (2C), 125.0 (2C), 126.5, 130.4, 130.5, 142.3, 147.5, 150.3, 158.0; EIMS (70 eV) *m/z* (rel intensity) 254 (M^+; 100), 118 (69); Anal. Found: C, 75.84; H, 7.10; N, 10.81%. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01%.

*2.4. Synthesis of 4-bromo-2'-butylazobenzene (**28′**)*

To a dichloromethane solution (7 mL) of 4-bromonitrosobenzene (**C**, 0.44 g, 2.37 mmol) were added 2-butylaniline (**A(2-Bu)**, 0.289 g, 1.9 mmol) and acetic acid (3 mL). The mixture was stirred for 15 h. After the reaction was completed, to the reaction mixture was added ethyl acetate (100 mL). The organic layer was washed with aq. 1 M sodium hydroxide, aq. saturated sodium hydrogencarbonate, and brine. The organic layer was dried over anhydrous sodium sulfate and evaporated to give an oily compound, which was purified by column chromatography (SiO_2, $CHCl_3$: C_6H_{14} = 1: 1). Yield 67%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.6 Hz, 3H), 1.38 (sex, J = 7.6 Hz, 2H), 1.64 (quin, J = 7.6 Hz, 2H), 3.12 (t, J = 7.6 Hz, 2H), 7.22–7.27 (m, 1H), 7.33–7.40 (m, 2H), 7.62–7.64 (m, 3H), 7.78 (d, J = 8.9 Hz 2H); ^{13}C NMR ($CDCl_3$) δ = 13.9, 22.6, 31.1, 34.4, 115.0, 124.4 (2C), 125.0, 126.5, 130.6, 131.4, 132.3 (2C), 143.2, 150.1, 151.7; EIMS (70 eV) *m/z* 316 (M^+, 100);

*2.5. Synthesis of 2-butyl-4'-(dioctadecylamino)azobenzene (**28**)*

The a toluene solution (7 mL) of 4-bromo-2'-butylazobenznene (**28′**, 155 mg, 0.49 mmol) were added dioctadecylamine (**D**, 333 mg, 0.64 mmol), tris(dibenzylacetone)dipaladium (0) ($Pd_2(dba)_3$, 9 mg, 2 mol%), sodium *tert*.-butoxide (70 mg, 0.74 mmol), and 2-dicyclohexylphosphino-2′,4′,6'-triisopropylbiphenyl (XPhos) (6 mg, 2 mol%). The mixture was heated at 80 °C for 12 h under an argon atmosphere. After the reaction was completed, the mixture was diluted with diethyl ether and filtered. The filtrate was evaporated to give an oliy product, which was purified by silica gel column chromatography ($CHCl_3$: C_6H_{14} = 1: 9) to afford orange solid. Yield 27%; mp 33 °C; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, J 6.9 Hz, 6H), 0.92 (t, J = 7.3 Hz, 3H), 1.26–1.43 (m, 62H), 1.61–1.67 (m, 6H), 3.08 (t, J = 7.8 Hz, 2H), 3.34 (t, J = 7.8 Hz, 4H), 6.69 (d, J = 9.2 Hz, 2H), 7.22–7.29 (m, 3H) 7.58 (d, J = 7.3 Hz, 1H), 7.85 (d, J = 9.2 Hz 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 14.1 (2C), 22.6, 22.7 (2C), 27.2 (2C), 27.4 (2C), 29.4 (2C), 29.5 (2C), 29.6 (2C), 29.68 (6C), 29.71 (12C), 31.2, 31.9 (2C), 34.2, 51.4 (2C), 111.0 (2C), 115.3, 125.2 (2C), 126.4, 129.1, 130.1, 141.3, 143.6, 150.3, 151.0; FABMS (NPOE) *m/z* 759 (M^+); Anal. Found: C, 82.44; H, 12.41; N, 5.49%. Calcd for $C_{52}H_{91}N_3$: C, 82.36; H, 12.10; N, 5.54%.

2.6. Synthesis of 4-amino-2'-butylazobenzenes **19**–**22**

To water-DMF 1:3 mixed solvent (10 mL) were added 2-butylaniline (**A(2-Bu)**, 300 mg, 2.0 mmol) and conc. hydrochloric acid (0.6 mL, 6.0 mmol). The mixture was stirred at 0 °C for 10 min. To the mixture was added sodium nitrite (140 mg, 2.0 mmol) and stirred at 0 °C for 1 h. To the mixture was added a sodium anilinomethanesulfonate (**E**, 2.0 mmol) and stirred at 0 °C overnight. After the reaction was completed, the resulting precipitate was washed with water and heated in 10% aqueous sodium hydroxide solution (50 mL) at 60 °C for 2 h. The product was extracted with ethyl acetate and purified by column chromatography (SiO_2, AcOEt: C_6H_{14} = 1: 30).

2.6.1. 4-Amino-2'-butylazobenzene (**19**)

Yield 8%; ^{1}H NMR ($CDCl_3$) δ = 0.91 (t, J = 7.3 Hz, 3H), 1.38 (sex, J = 7.3 Hz, 2H), 1.65 (quin, J = 7.3 Hz, 2H), 3.10 (t, J = 7.3 Hz, 2H), 4.01 (s, 2H), 6.74 (d, J = 9.2 Hz, 2H), 7.21–7.31 (m, 3H), 7.59 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 22.6, 31.1, 34.2, 114.6 (2C), 115.3, 125.1 (2C), 126.4, 129.8, 130.3, 141.8, 146.1, 149.3, 150.6; EIMS (70 eV) *m/z* (rel intensity) 253 (M^+; 24), 148 (51), 107 (83), 92 (100); Anal. Found: C, 75.98; H, 7.70; N, 16.32%. Calcd for $C_{16}H_{19}N_3$: C, 75.85; H, 7.56; N, 16.59%.

2.6.2. 4-Amino-2'-butyl-2-methylazobenzene (**20**)

Yield 52%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.8 Hz, 3H), 1.38 (sex, J = 7.8 Hz, 2H), 1.66 (quin, J = 7.8 Hz, 2H), 2.67 (s, 3H), 3.11 (t, J = 7.8 Hz, 2H), 3.94 (s, 2H), 6.52 (d, J = 8.7 Hz, 1H), 6.58 (d, J = 8.7 Hz, 1H), 7.21–7.31 (m, 3H), 7.60 (d, J = 8.7 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 17.8, 22.6, 31.2, 34.3, 112.9, 115.6, 115.9, 117.5, 126.3, 129.5, 130.3, 141.0, 141.9, 144.1, 149.1, 150.9; EIMS(70 eV) *m/z* (rel intensity) 267 (M^+; 37), 149 (39), 120 (54), 106 (100); Anal. Found: C, 76.52; H, 8.13; N, 15.35%. Calcd for $C_{17}H_{21}N_3$: C, 76.37; H, 7.92; N, 15.72%.

2.6.3. 4-Amino-2'-butyl-2,5-dimethylazobenzene (**21**)

Yield 56%; ^{1}H NMR ($CDCl_3$) δ = 0.95 (t, J = 7.6 Hz, 3H), 1.41 (sex, J = 7.6 Hz, 2H), 1.67 (quin, J = 7.6 Hz, 2H), 2.17 (s, 3H), 2.65 (s, 3H), 3.12 (t, J = 7.6 Hz, 2H), 3.86 (s, 2H), 6.56 (s, 1H), 7.23–7.30 (m, 3H), 7.54 (s, 1H), 7.59 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 17.1, 17.3, 22.6, 31.2, 34.3, 115.6, 115.7, 118.1, 120.0, 126.3, 129.4, 130.2, 138.7, 141.7, 143.8, 147.6, 151.0; EIMS(70 eV) *m/z* (rel intensity) 281 (M^+; 4), 135 (22), 134 (24), 120 (100); Anal. Found: C, 77.14; H, 8.37; N, 15.14%. Calcd for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24; N, 14.93%.

2.6.4. 4-Amino-2'-butyl-3,5-dimethylazobenzene (**22**)

Yield 49%; ^{1}H NMR ($CDCl_3$) δ = 0.91 (t, J = 7.6 Hz, 3H), 1.39 (sex, J = 7.6 Hz, 2H), 1.65 (quin, J = 7.6 Hz, 2H), 2.53 (s, 6H), 3.06 (t, J = 7.6 Hz, 2H), 3.82 (s, 2H), 6.41 (s, 2H), 7.21–7.31 (m, 3H), 7.58 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 21.0, 22.9, 31.6, 34.2, 114.9, 115.3 (2C), 126.3 (2C), 129.4, 130.3, 136.2, 141.8, 142.4, 147.5, 151.4; EIMS(70 eV) *m/z* (rel intensity) 281 (M^+; 9), 135 (31), 120 (100); Anal. Found: C, 77.12; H, 8.34; N, 14.77%. Calcd for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24; N, 14.93%.

2.7. Synthesis of 4-[2-(butylphenylazo)]phenylene ethers **30**–**36**

To an acetone solution (10 mL) of 2-butyl-4'-hydroxyazobenzene (**29**, 250 mg, 1.0 mmol) were added an alkyl iodide (**F**, 2.0 mmol) and potassium carbonate (280 mg, 2.0 mmol). The mixture was refluxed for 24 h. After the reaction was completed, the solvent was removed *in vacuo*. The resultant precipitate was poured into water (20 mL). The product was extracted with ethyl acetate (20 mL × 2) and purified by silica gel column chromatography (AcOEt: C_6H_{14} = 1: 20).

2.7.1. 2-Butyl-4'-methoxyazobenzene (**30**)

Yield 82%; ^{1}H NMR ($CDCl_3$) δ = 0.94 (t, J = 7.5 Hz, 3H), 1.40 (sex, J = 7.5 Hz, 2H), 1.67 (quin, J = 7.5 Hz, 2H), 3.13 (t, J = 7.5 Hz, 2H), 3.89 (s, 3H), 7.03 (d, J = 9.2 Hz, 2H), 7.27 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 22.5, 31.1, 34.3, 55.5, 114.1 (2C), 115.2, 124.7 (2C), 126.4, 130.3, 130.4, 142.3, 147.4, 150.3, 161.8; EIMS (70 eV) *m/z* (rel intensity) 268 (M^+; 79), 122 (100); Anal. Found: C, 76.36; H, 7.49; N, 10.50%. Calcd for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44%.

2.7.2. 2-Butyl-4'-ethoxyazobenzene (**31**)

Yield 87%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.6 Hz, 3H), 1.38 (sex, J = 7.6 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.65 (quin, J = 7.6 Hz, 2H), 3.11 (t, J = 7.6 Hz, 2H), 4.09 (q, J = 7.1 Hz, 2H), 7.00 (d, J = 9.2 Hz, 2H), 7.23–7.34 (m, 3H), 7.61 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 14.8, 22.5, 31.1, 34.3, 63.8, 114.6 (2C), 115.3, 124.8 (2C), 126.4, 130.3, 130.4, 142.3, 147.3, 150.4, 161.3; EIMS (70 eV) *m/z* (rel intensity) 282 (M^+; 65), 239 (39), 136 (100), 108 (97); Anal. Found: C, 76.45; H, 8.05; N, 10.13%. Calcd for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92%.

2.7.3. 2-Butyl-4'-propyloxyazobenzene (**32**)

Yield 90%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.5 Hz, 3H), 1.06 (t, J = 7.4 Hz, 3H), 1.38 (sex, J = 7.5 Hz, 2H), 1.65 (quin, J = 7.5 Hz, 2H), 1.84 (sex, J = 7.4 Hz, 2H), 3.11 (t, J = 7.5 Hz, 2H), 4.00 (t, J = 7.4 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 7.21–7.37 (m, 3H), 7.61 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 10.5, 14.0, 22.5 (2C), 31.1, 34.3, 69.8, 114.7 (2C), 115.3, 124.7 (2C), 126.4, 130.3, 130.4, 142.3, 147.3, 150.4, 161.4; EIMS(70 eV) *m/z* (rel intensity) 296 (M^+; 11), 253 (12), 135 (24), 108 (100); Anal. Found: C, 77.27; H, 8.20; N, 9.29%. Calcd for $C_{19}H_{24}N_2O$: C, 76.99; H, 8.16; N, 9.45%.

2.7.4. 4-Butoxy-2'-butylazobenzene (**33**)

Yield 92%; ^{1}H NMR ($CDCl_3$) δ = 0.92 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H), 1.39 (sex, J = 7.5 Hz, 2H), 1.52 (sex, J = 7.5 Hz, 2H), 1.65 (quin, J = 7.5 Hz, 2H), 1.81 (quin, J = 7.5 Hz, 2H), 3.11 (t, J = 7.5 Hz, 2H), 4.05 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 13.8, 14.0, 19.2, 22.5, 31.1, 31.2, 34.3, 68.0, 114.6 (2C), 115.2, 124.7 (2C), 126.4, 130.2, 130.4, 142.2, 147.3, 150.4, 161.5; EIMS (70 eV) *m/z* (rel intensity) 310 (M^+; 100), 164 (24); Anal. Found: C, 77.60; H, 8.49; N, 8.89%. Calcd for $C_{20}H_{26}N_2O$: C, 77.38; H, 8.44; N, 9.02%.

2.7.5. 2-Butyl-4'-octyloxyazobenzene (**34**)

Yield 95%; ^{1}H NMR ($CDCl_3$) δ = 0.90 (t, J = 7.4 Hz, 3H), 0.92 (t, J = 7.7 Hz, 3H), 1.30–1.45 (m, 12H), 1.65 (quin, J = 7.4 Hz, 2H), 1.81 (quin, J = 7.7 Hz, 2H), 3.11 (t, J = 7.4 Hz, 2H), 4.02 (t, J = 7.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 7.23–7.34 (m, 3H), 7.61 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 14.1, 22.5, 22.7, 26.0, 29.18, 29.24, 29.4, 31.1, 31.8, 34.3, 68.3, 114.6 (2C), 115.3, 124.7 (2C), 126.4, 130.2, 130.4, 142.3, 147.3, 150.4, 161.5; EIMS (70 eV) *m/z* (rel intensity) 366 (M^+; 60), 323 (29), 108 (100); Anal. Found: C, 78.96; H, 9.48; N, 7.65%. Calcd for $C_{24}H_{34}N_2O$: C, 78.64; H, 9.35; N, 7.64%.

2.7.6. 2-Butyl-4'-dodecyloxyazobenzene (**35**)

Yield 88%; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, J = 7.5 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H), 1.27–1.48 (m, 20H), 1.65 (quin, J = 7.4 Hz, 2H), 1.81 (quin, J = 7.5 Hz, 2H), 3.11 (t, J = 7.4 Hz, 2H), 4.03 (t, J = 7.5 Hz, 2H), 6.99 (d, J = 9.2 Hz, 2H), 7.24–7.34 (m, 3H), 7.61 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 14.1, 22.5, 22.7, 26.0, 29.2, 29.35, 29.38, 29.58, 29.60, 29.64, 29.67, 31.1, 31.9, 34.3, 68.3, 114.7 (2C), 115.3, 124.7 (2C), 126.4, 130.2, 130.4, 142.2, 147.3,

150.5, 161.5; EIMS (70 eV) *m/z* (rel intensity) 422 (M^+; 83), 379 (30), 108 (100); Anal. Found: C, 79.46; H, 10.13; N, 6.55%. Calcd for $C_{28}H_{42}N_2O$: C, 79.57; H, 10.02; N, 6.63%.

*2.7.7. 2-Butyl-4'-octadecyloxyazobenzene (**36**)*

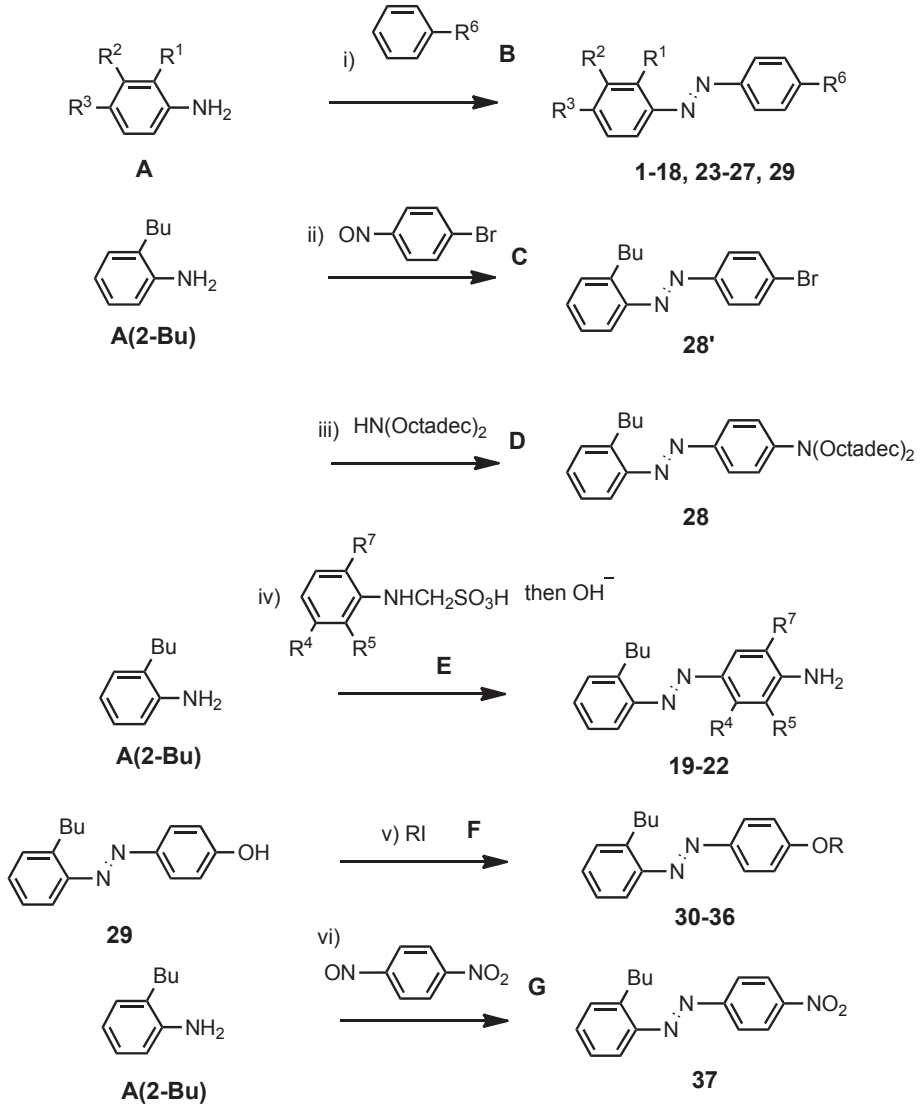
Yield 87%; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, J = 7.9 Hz, 3H), 0.93 (t, J = 7.6 Hz, 3H), 1.26–1.48 (m, 32H), 1.66 (quin, J = 7.6 Hz, 2H), 1.82 (quin, J = 7.9 Hz, 2H), 3.12 (t, J = 7.6 Hz, 2H), 4.04 (t, J = 7.9 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 7.25–7.34 (m, 3H), 7.61 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 14.1, 22.5, 22.7, 26.0, 29.2, 29.37 (2C), 29.59, 29.61, 29.70 (8C), 31.1, 31.9, 34.3, 68.4, 114.7 (2C), 115.3, 124.7 (2C), 126.4, 130.2, 130.4, 142.2, 147.3, 150.5, 161.5; EIMS (70 eV) *m/z* (rel intensity) 506 (M^+; 100), 463 (22), 361 (26), 108 (61); Anal. Found: C, 80.72; H, 10.95; N, 5.36%. Calcd for $C_{34}H_{54}N_2O$: C, 80.58; H, 10.74; N, 5.53%.

*2.8. Synthesis of 2-butyl-4'-nitroazobenzene (**37**)*

To acetic acid (0.3 mL) were added 2-butylaniline (**A(2-Bu)**, 92 mg, 0.6 mmol) and 4-nitrosonitrobenzene (**G**, 92 mg, 0.6 mmol). The mixture was stirred at room temperature for 5 min. To the mixture was added water (10 mL). The resulting precipitate was poured into water (20 mL), filtered, washed with water (20 mL × 3), dried and purified by silica gel column chromatography (CH_2Cl_2). Yield 15%; ^{1}H NMR ($CDCl_3$) δ = 0.93 (t, J = 7.4 Hz, 3H), 1.40 (sex, J = 7.4 Hz, 2H), 1.65 (quin, J = 7.4 Hz, 2H), 3.16 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 8.2 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.46 (t, J = 8.2 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 9.2 Hz, 2H), 8.37 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 22.5, 31.1, 34.5, 115.1, 123.4 (2C), 124.7 (2C), 126.5, 130.8, 132.5, 144.4, 148.5, 150.0, 155.9; EIMS (70 eV) *m/z* (rel intensity) 283 (M^+; 4), 282 (5), 254 (26), 240 (19), 194 (17), 146 (55), 130 (13) 118 (52), 106 (26), 91 (100); Anal. Found: C, 67.42; H, 5.98; N, 14.35%. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05; N, 14.83%.

*2.9. X-ray Crystal data for **1***

$C_{15}H_{17}N_3$, Mw = 239.32, orthorhombic, Pbca, Z = 8, a = 7.680(4), b = 15.393(8), c = 23.128(11) Å, D_{calcd} = 1.163 g cm^{-3}, T = 293 K, 20674 reflections were corrected, 4664 unique (R_{int} = 0.0420, 3122



Scheme 1. Reagents and conditions: i) **A** (1.0 equiv.), $NaNO_2$ (1.0 equiv.), HCl (6.0 equiv), H_2O-DMF, 0 °C, 1 h, then **B** (1.0 equiv.), 0 °C, overnight, ii) **A(2-Bu)** (1.0 equiv.), **C** (1.3 equiv.), AcOH-CH_2Cl_2, r.t., 12 h, iii) **28'** (1.0 equiv.), **D** (1.2 equiv.), $Pd_2(dba)_3$ (2 mol%), *t*-BuOH (1.2 equiv.), X-Phos (2 mol%), toluene, 80 °C, 12 h, iv) **A(2-Bu)** (1.0 equiv.), $NaNO_2$ (1.0 equiv.), HCl (3.0 equiv.), H_2O-DMF, 0 °C, 1 h then **E** (1.0 equiv.), 0 °C, overnight, then, 10% NaOH, 60 °C, 2 h, v) **29** (1.0 equiv.), **F** (2.0 equiv.), K_2CO_3 (2.0 equiv.), acetone, reflux, 24 h, vi) **A(2-Bu)** (1.0 equiv.), **G** (1.0 equiv.), AcOH, r.t., 5 min.

parameters, R_1 = 0.0956, wR_2 = 0.2407, G.O.F = 1.195, (CCDC 1412021).

2.10. X-ray Crystal data for **17**

$C_{32}H_{51}N_3$, Mw = 477.77, monochlinic, $P2_1/c$, Z = 4, a = 28.0213(2), b = 15.0726(4), c = 6.9055(1) Å, β = 92.504(6)°, D_{calcd} = 1.089 g cm^{-3}, T = 123 K, 9312 reflections were corrected, 4484 unique (R_{int} = 0.07509, 320 parameters, R_1 = 0.0727, wR_2 = 0.1852, (CCDC 1412022).

3. Results and discussion

3.1. Synthesis

Scheme 1 shows the synthesis of azo dyes. Azo dyes **1**–**18**, **23**–**27**, and **29** were obtained by the diazotization reaction of substituted anilines **A** followed by the reaction with coupling components **B**. As *N*,*N*-dioctadecylaniline was not soluble in DMF, compound **28** was obtained by the Buchwald–Hartwig reaction of bromo derivative **28′**, produced by the condensation reaction of 2-butylaniline (**A(2-Bu)**) with 4-bromonitrosobenzene (**C**), with dioctadecylamine (**D**). 4-Amino-2'-butyl derivatives **19**–**22** were prepared by the diazotization-coupling reaction of **A(2-Bu)** with protected anilines **E** followed by deprotection. 4-Alkoxy derivatives **30**–**36** were obtained by the Williamson ether reaction of **29** with alkyl iodides **F**. 2-Butyl-4'-nitroazobenzene (**37**) was produced by the condensation of **A(2-Bu)** with 4-nitrosonitrobenzene (**G**). Liquid products were purified by silica-gel column chromatography, alumina column chromatography, and finally silica-gel medium-pressure liquid chromatography. The purity of all the liquid products was checked by the ^{1}H NMR spectroscopy (Figure S1–S10). The elemental analysis data also support that these compounds are sufficiently pure.

3.2. Thermal analysis

Even the liquid derivatives were stored in a refrigerator for 1 month, they were not solidified. When they were chilled by liquid nitrogen, they solidified. They are viscous liquid at room temperature.

The synthesized azo dyes showed three kinds of differential scanning calorimetry (DSC) patterns. Typical examples are shown in Fig. 1. Fig. 1a shows the DSC of liquid **8**. This compound exhibited an endothermic peaks at −40 °C. No other peaks were observed till 20 °C. The heat of fusion was observed to be 0.66 kJ mol^{-1}. This value is significantly smaller than that of solid **13** (38.3 kJ mol^{-1}). Furthermore, the base line of **8** is not parallel for X-axis. It is concluded that compound **8** mainly showed its glass transition temperature (T_g) at −40 °C with the endothermic peak comes from partially crystallized molecule. Similar DSC chart was observed for liquid **30**, the T_g being −62 °C. The DSC chart of the other liquid derivatives **14**, **15**, **16**, **22**, **24**, **25**, **26**, **27**, and **30** are shown in the supporting information. Second one is observed for 4-alkoxy-2'-butylazobenzenes **31**, **32**, **33**, and **34**. Compound **33** showed a small peak assigned to T_g at −65 °C, an exothermic peak comes from the formation of metastable crystalline form at −35 °C, and an endothermic peak assigned to its melting point at 26 °C as depicted in Fig. 1c. Third one was observed for **35** and **36**. Compound **36** showed two endothermic peaks at 31 and 51 °C as indicated in Fig. 1d. In this case, the bigger peak observed at 51 °C was assigned to the melting point. The thermal analysis of the other compounds are shown in Figure S1–S35. The results are listed in Table 1.

The melting point of 2-methyl derivative **1** is lowest among the methyl-substituted 4-(dimethylamino)azobenzenes **1**–**3**. Therefore, the 2-substituted derivatives were intensively prepared. In a series of 2-alkyl-4'-(dimethylamino)azobenzenes **1**, **4**–**18**, the butyl **8**, hexyl **14**, octyl **15**, and dodecyl **16** derivatives were liquid, whereas the methyl **1**, trifluoromethyl **4**, ethyl **5**, propyl **6**,

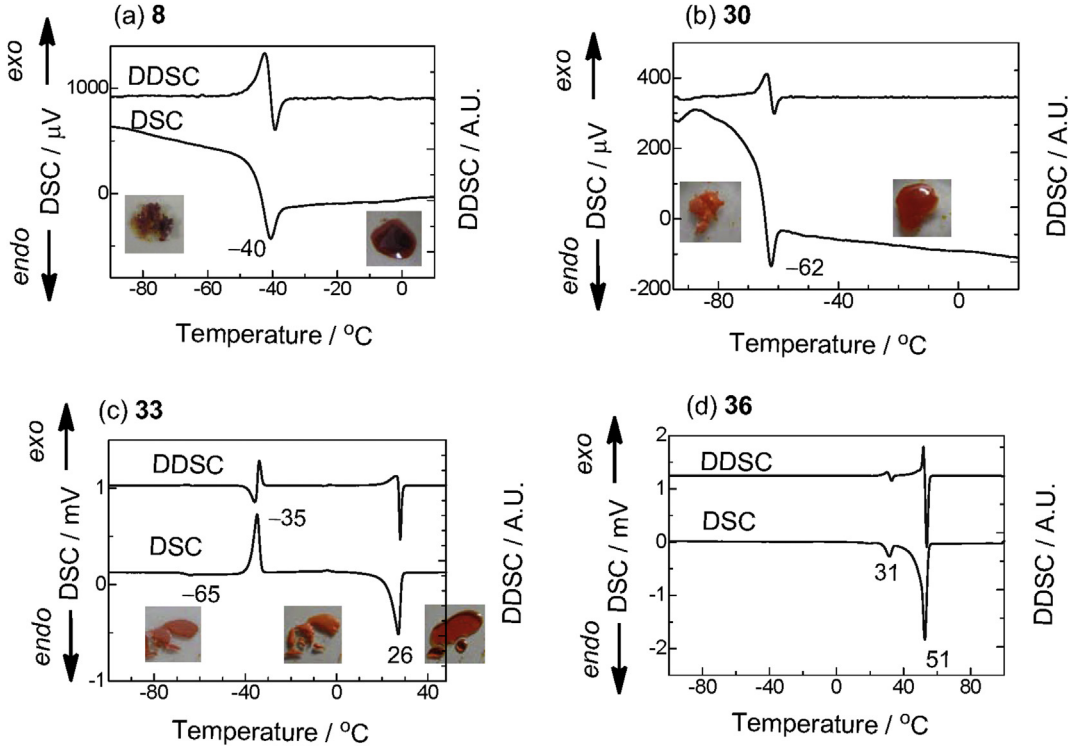
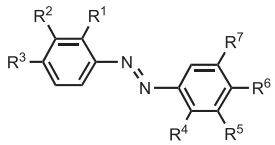


Fig. 1. DSC of (a) **8**, (b) **30**, (c) **33**, and (d) **36**. Heated from −100°C at 10 °C min^{-1}.

Table 1
Melting point or glass transition temperature (T_g) of azo dyes.



Compd	R^1	R^2	R^3	R^4	R^5	R^6	R^7	Mp/°C
1	Me	H	H	H	H	NMe_2	H	73-74[a]
2	H	Me	H	H	H	NMe_2	H	120-121[a]
3	H	H	Me	H	H	NMe_2	H	170-171[a]
4	CF_3	H	H	H	H	NMe_2	H	120[b]
5	Et	H	H	H	H	NMe_2	H	82-83[a]
6	Pr	H	H	H	H	NMe_2	H	65
7	*i*-Pr	H	H	H	H	NMe_2	H	69
8	Bu	H	H	H	H	NMe_2	H	−40[c]
9	*s*-Bu	H	H	H	H	NMe_2	H	65
10	*t*-Bu	H	H	H	H	NMe_2	H	71
11	C_4F_9	H	H	H	H	NMe_2	H	83
12	OBu	H	H	H	H	NMe_2	H	70
13	SBu	H	H	H	H	NMe_2	H	85
14	Hex	H	H	H	H	NMe_2	H	−80[c]
15	Oct	H	H	H	H	NMe_2	H	−54[c]
16	Dodec	H	H	H	H	NMe_2	H	−49[c]
17	Octadec	H	H	H	H	NMe_2	H	65
18	$CH_2C(CF_3)_2C_3F_7$	H	H	H	H	NMe_2	H	114
19	Bu	H	H	H	H	NH_2	H	37
20	Bu	H	H	Me	H	NH_2	H	71
21	Bu	H	H	Me	H	NH_2	Me	41
22	Bu	H	H	H	Me	NH_2	Me	−28[c]
23	Bu	H	H	H	H	NHMe	H	44
24	Bu	H	H	H	H	NEt_2	H	−46[c]
25	Bu	H	H	H	H	NBu_2	H	−51[c]
26	Bu	H	H	H	H	$NOct_2$	H	−66[c]
27	Bu	H	H	H	H	$NDodec_2$	H	−62[c]
28	Bu	H	H	H	H	$NOctadec_2$	H	33
29	Bu	H	H	H	H	OH	H	63
30	Bu	H	H	H	H	OMe	H	−62[c]
31	Bu	H	H	H	H	OEt	H	22
32	Bu	H	H	H	H	OPr	H	10
33	Bu	H	H	H	H	OBu	H	26
34	Bu	H	H	H	H	OOct	H	28
35	Bu	H	H	H	H	ODodec	H	24
36	Bu	H	H	H	H	OOctadec	H	51
37	Bu	H	H	H	H	NO_2	H	68

[a] Reference [17].
[b] Reference [18].
[c] T_g.

1-methylethyl **7**, perfluorobutyl **11**, butoxy **12**, butylthio **13**, and [3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl] derivatives **18** were solid. Furthermore, only butyl derivative **8** was liquid among the butyl **8**, 1-methylethyl **9**, and 1,1-dimethylethyl derivatives **10**. Thus, the introduction of *n*-alkyl group at the 2-position is very important to produce liquid azo dyes.

The relationship between the melting point or T_g of 2-*n*-alkyl-4'-(dimethylamino)azobenzenes **1**, **5**, **6**, **8**, and **14**–**17** and the number of carbon atoms at the alkyl group is shown in Fig. 2. It is clear that the methyl, ethyl, propyl, and octadecylalkyl derivatives are solid and that the medium alkyl derivatives are liquid at room temperature. It is of interest that the melting point of **17** is significantly high compared with the series of compounds.

In a series of 4-amino-2'-butylazobenzenes **19**–**22**, only compound **22**, in which two methyl groups are attached at the adjacent two *o*-positions for the amino group, was liquid, being the T_g −28 °C. Furthermore, the T_g of 2-butyl-4'-(dimethylamino)azobenzene (**8**) and the melting point of 2-butyl-4'-(methylamino)-azobenzene (**23**) were observed at −40 and 44 °C, respectively.

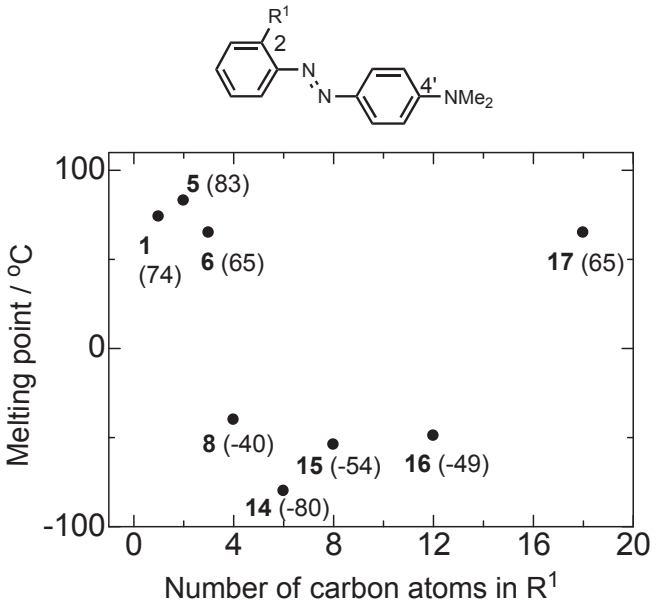


Fig. 2. Relationship between melting point or T_g and number of carbon atoms of R^1 in 2-*n*-alkyl-4'-(dimethylamino)azobenzenes.

Thus, the inhibition of hydrogen bonding at the amino group is effective to form liquid azo dyes.

The relationship between the melting point or T_g and the number of carbon atoms in the alkyl group of R′ in 2-butyl-4'-(dialkylamino)azobenzenes **8**, **19**, and **24**–**28** is shown in Fig. 3. In this series of azo dyes, compounds **8** and **24**–**27** were liquid, showing the T_g in the range of −40 to −66 °C. Interestingly, the 4'-dioctadecylamino derivative **28** was solid, the melting point being 33 °C.

2-Butyl-4'-hydroxyazobenzene (**29**) is solid, the melting point being 63 °C. As shown in Fig. 4, in a series of 4-alkoxy-2'-butylazobenzenes **30**–**36**, only the methoxy derivative **30** was liquid, the

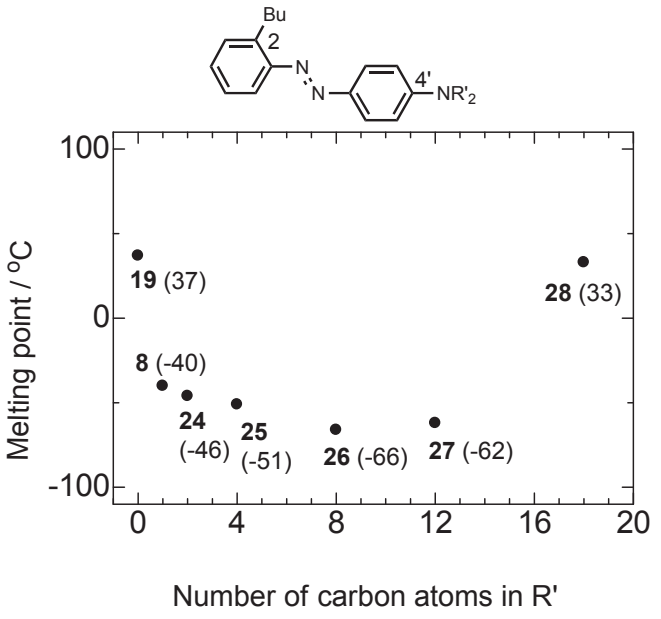


Fig. 3. Relationship between melting point or T_g and number of carbon atoms in R' in 2-butyl-4'-(dialkylamino)azobenznes.

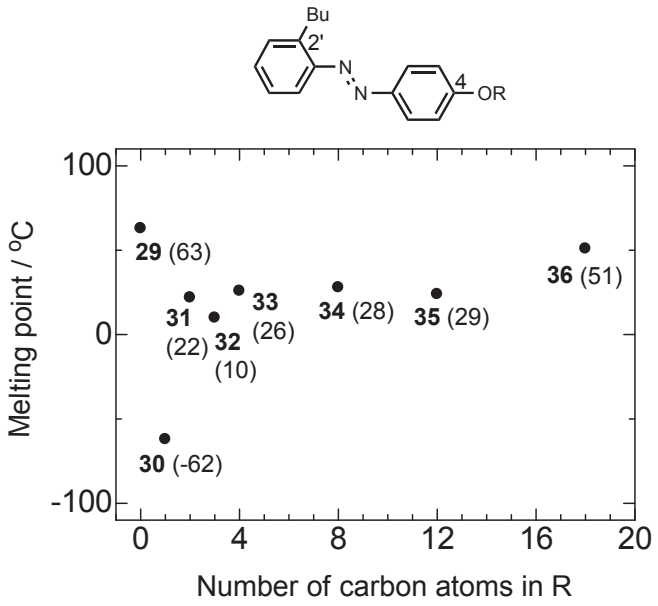


Fig. 4. Relationship between melting point or T_g and the number of carbon atoms of R in 4-alkoxy-2'-butylazobenznes.

T_g being −62 °C. The octadecyloxy derivative **36** showed slightly higher melting point than the other alkoxy derivatives.

2-Butyl-4'-nitroazobenzene (**37**) was solid, the melting point being 68 °C, owing to strongly polar nitro group.

3.3. Single X-ray crystallography

To understand why 2-(medium *n*-alkyl)-4'-(dimethylamino)-azobenzenes are liquid, the single X-ray crystallography of 2-methyl **1** and 2-octadecyl **17** derivatives recrystallized from hexane was performed.

Fig. 5 shows the single X-ray crystallography of **1**. Overview (1) depicts that molecules are packed in a zigzag form. Overview (2) indicates that molecule A is surrounded by molecules B, C, D, E, F, and G. Molecule A has CH/π and CH/n interactions with C, D, E, F, and G as shown in overview (3) and (4). Molecules A and B form a pair of head-to-tail dimer and are stacked at the 4-(dimethylamino)-phenylene moiety as shown in top view. Side view indicates that the interplanar distance is 3.50 Å. Thus, compound **1** has CH/π, CH/n, and π/π interactions.

Fig. 6 depicts the single X-ray crystallography of **17**. Overview (1) shows that molecules are arranged along the octadecyl group and that azobenzene moiety is also packed in parallel. Overview (2) indicates that molecule A has short contact with B, C, D, and E. Molecules A and B form a head-to-tail dimer due to alkyl–alkyl interactions with 4.34 Å, as shown in top view (1). Top view (2) depicts that molecules A, C, and D are aligned in the same direction. The distance between the octadecyl group is 4.38 Å. Side view (1) indicates that the interplanar distance among the aryl moieties of A, C, and D is 3.50 Å. CH/n interactions are also observed among A, C, and D. Molecules A and E also have alkyl–alkyl interactions with the distance of 4.05 Å as shown in top view (3) and side view (2). No π/π interactions are observed between A and E. Thus, the main driving forces for packing of **17** could come from the alkyl–alkyl interactions.

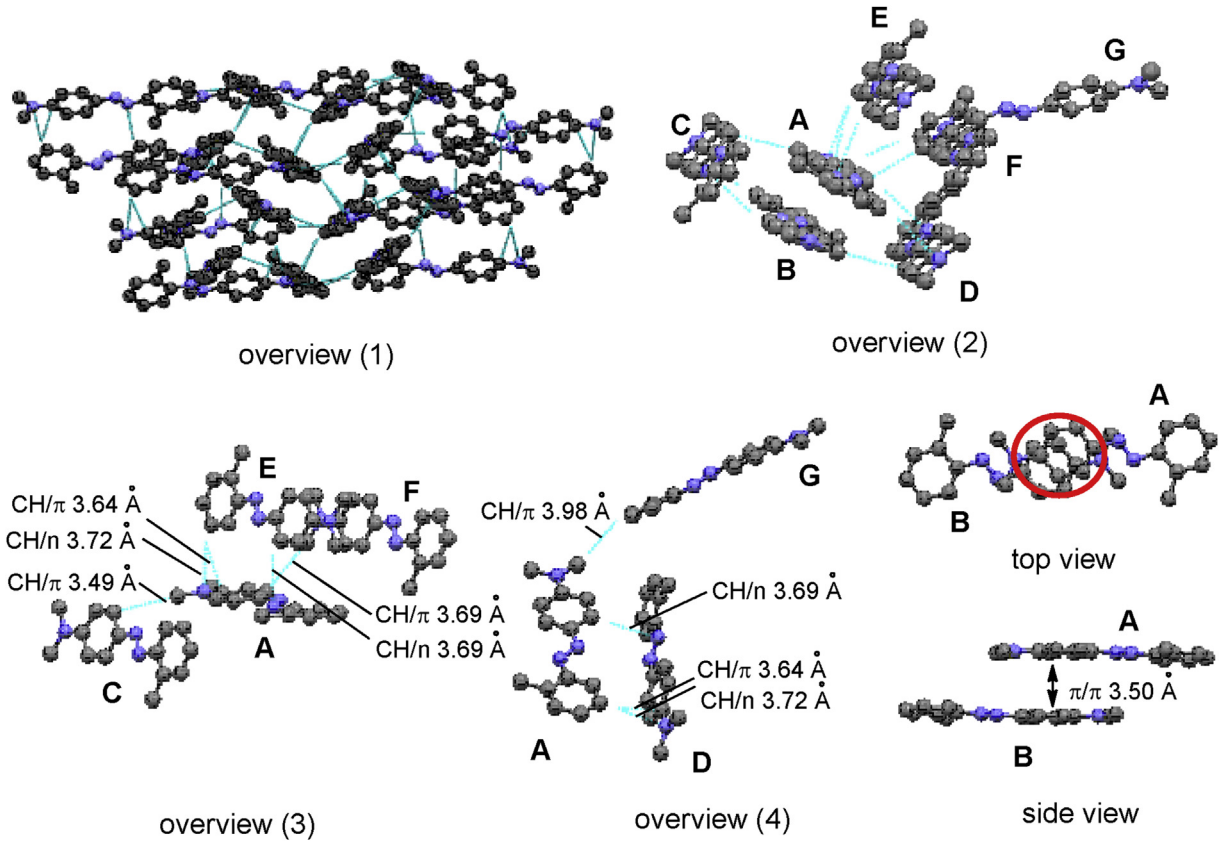


Fig. 5. Single X-ray crystallography of **1**.

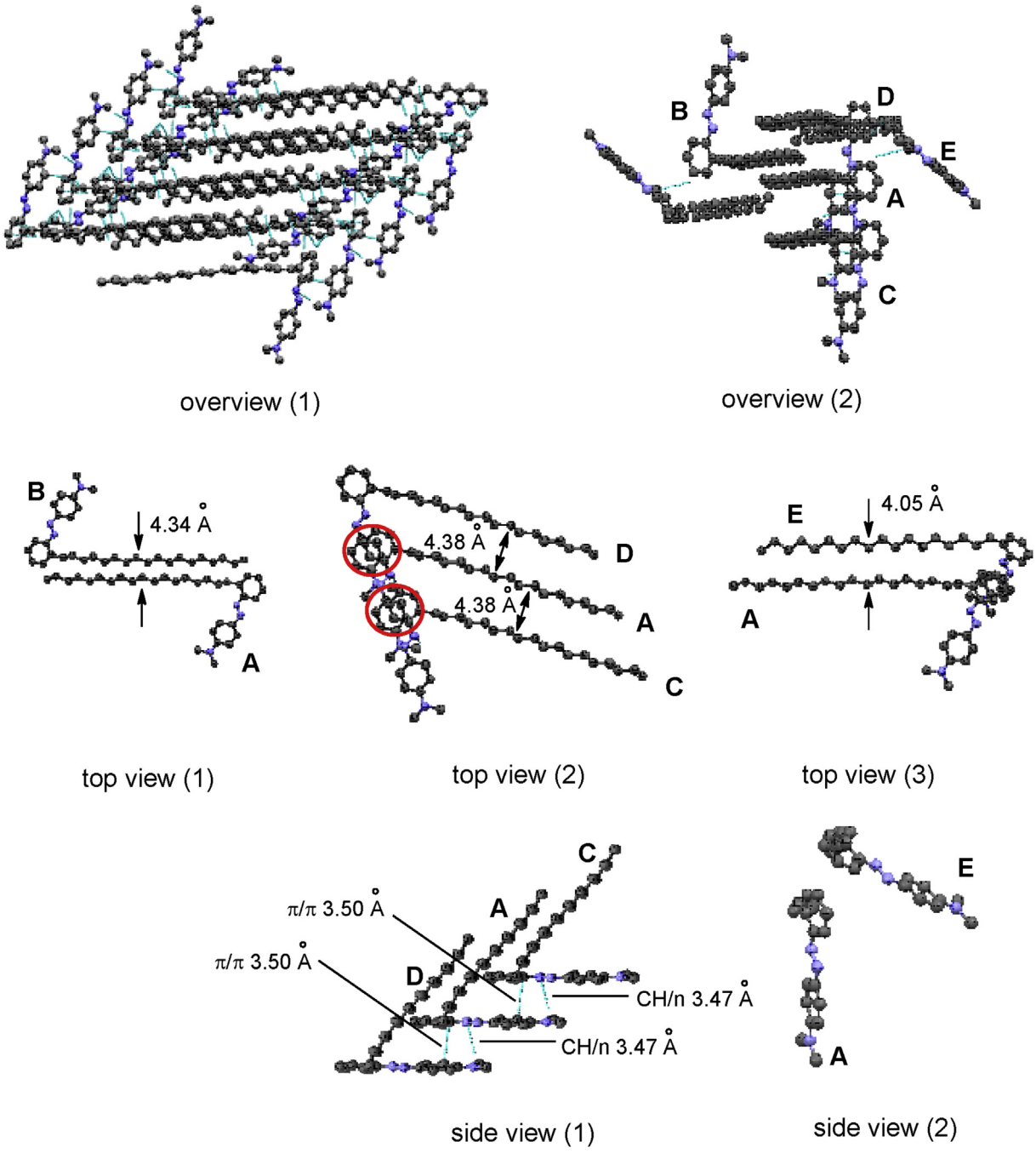


Fig. 6. Single X-ray crystallography of **17**.

In the case of 2-short alkyl 4'-(dimethylamino)azobenzene such as **1**, CH/π, CH/n, and π/π-interactions are predominant. When the alkyl moiety is medium such as butyl, hexyl, octyl, and dodecyl groups, these groups can act as steric hindrance to weaken the intermolecular interactions to make the compound viscous liquid. In the case of 2-octadecyl derivative **17**, the alkyl–alkyl interactions are strong to heighten the melting point. In the case of 2-butyl-4'-(dioctadecylamino)azobenzene (**28**) and 2-butyl-4'-octadecyloxyazobenzene (**36**), the octadecyl group(s) could also have strong alkyl–alkyl interactions to show significantly higher melting point in the respective series of derivatives. 2-Butyl-4'-(dimethylamino) azobenzene (**8**) and 4-amino-2'-butyl-3,5-dimethylazobenzene (**22**) were liquid, whereas 2-butyl-4'-(methylamino)- (**23**) and 4-amino-2'-butylazobenzene (**19**) were solid. Furthermore, 2-butyl-4'-methoxyazobenzene (**30**) was liquid, whereas 2-butyl-4'-hydroxyazobenzene (**29**) was solid. These results indicate that prevention of intermolecular hydrogen bond is also important to form liquid derivative.

4. Conclusions

We could produce liquid 2-butyl-, 2-hexyl-, 2-octyl-, and 2-dodecyl-4'-(dimethylamino)azobenzenes. 2-Butyl-4'-methoxy-, 4-amino-2'-butyl-3,5-dimethyl-, 2-butyl-4'-(diethylamino)-, 2-butyl-4'-(dihexylamino)-, 2-butyl-4'-(dioctylamino)-, and 2-butyl-4'-(didodecylamino)azobenzenes were also liquid. To produce

liquid azo dyes, it is essential to introduce medium *n*-alkyl group at *o*-position for the azo moiety and to inhibit hydrogen bonding at the hydroxy and amino moieties.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.10.024.

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