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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%.