Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Matsui, M. , Kamino, Y. , Hayashi, M. , Funabiki, K. , Shibata, K. , Muramatsu, H. , Abe, Y. and Kaneko, M.(1998) 'Fluorine-containing benzothiazolyl bisazo dyes-their application to guest-host liquid crystal displays', Liquid Crystals, 25: 2, 235 — 240
To link to this Article: DOI: 10.1080/026782998206380
URL: http://dx.doi.org/10.1080/026782998206380

LIQUID CRYSTALS, 1998, VOL. 25, NO. 2, 235–240

Fluorine-containing benzothiazolyl bisazo dyes—their application to guest-host liquid crystal displays

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(*Received 25 September 1997; accepted 7 January 1998*)

Perfluoroalkyl-substituted benzothiazolyl bisazo dyes showed higher solubility and greater bathochromicity than the corresponding alkyl derivatives. These dyes showed good dichroism (order parameter $S > 0{\cdot}75$).

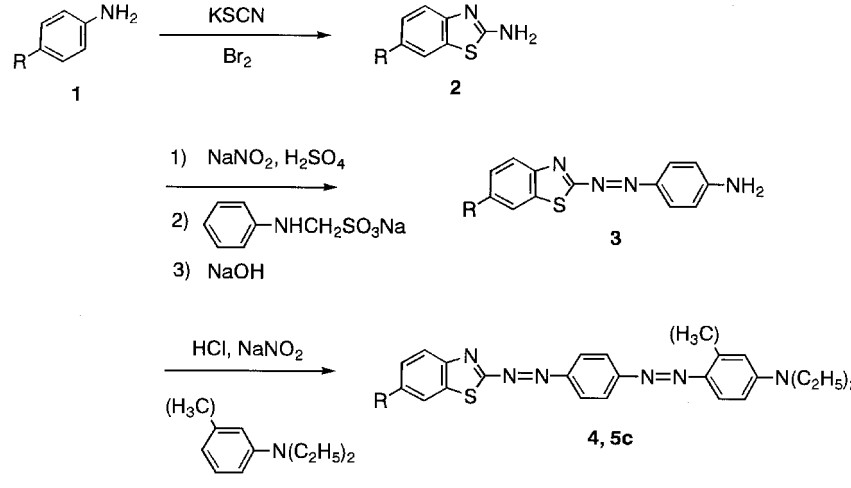
1. Introduction

Dichroic dyes used in guest-host liquid crystal displays are required to have good dichroism and solubility in liquid crystal materials. Although benzothiazolyl bisazo dyes are very important among the bathochromic positive dichroic azo dyes, their solubility is low. The series of phenyl bisazo dyes substituted with a perfluoroalkyl group have been reported to show higher solubility than the alkyl derivatives [1]; the dichroism of these derivatives is also high. Therefore, the synthesis of fluorine-containing benzothiazolyl bisazo dyes and their application to guest-host liquid crystal displays have been examined, with results described in this report.

2. Results and discussion

2.1. *Synthesis*

The synthesis of 6-substituted benzothiazolyl bisazo dyes **4a–f** and **5c** is shown in scheme 1. 6-Substituted 2-aminobenzothiazoles **2** were prepared in moderate yields by the reaction of anilines **1** with potassium thiocyanate in the presence of bromine. The diazotization-coupling reaction of **2** with sodium anilinomethanesulphonate followed by hydrolysis produced 4-(6-substituted 2-benzothiazolylazo)anilines **3** in low to moderate yields. A second diazotization-coupling reaction of **3** with *N*,*N*-diethylanilines afforded **4a–f** and **5c** in moderate yields.



Scheme 1.

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Scheme 2 indicates the synthesis of 4-[6-(perfluorobutyl)-2-benzothiazolylazo]pentafluoroazobenzene (**6c**). 4-[6-(Perfluorobutyl)-2-benzothiazolylazo]aniline (**3c**) reacted with pentafluoronitrosobenzene to give **6c** in 14% yield. The reaction of **6c** with diethylamine was complex, yielding several unidentified products in low yields. Compound **3c** did not react with 4-nitroso-2,3,5,6-tetrafluoro-*N*,*N*-diethylaniline due to the low electrophilicity of the nitroso derivative to **3c**.

2.2. *Absorption band*

The properties of the azo dyes are summarized in the table. The benzothiazolyl bisazo derivatives **4** were more bathochromic than the phenyl bisazo derivative **7a**. The bathochromicity of **4** was in the order of the substituent: C_4H_9, H < $C_4F_9CH_2CH_2S$ < C_4F_9S, C_4F_9, which was consistent with that of the electron-withdrawing nature (σ_p: $CH_3 = -0{\cdot}17$, $CH_3S = 0{\cdot}00$, $CF_3S = 0{\cdot}50$, $CF_3 = 0{\cdot}54$) of the substituents [2]. Azo dyes are intramolecular charge-transfer chromophores; the stronger the electron-withdrawing nature of the substituent at the benzothiazolyl moiety, the more bathochromic the derivative. A stronger push–pull derivative **5c** was more bathochromic than **4c**. The compound **6c** was extremely hypsochromic due to the electron-withdrawing nature of the pentafluorophenyl moiety (σ_m: F = 0·34, σ_p: F = 0·06).

2.3. *Solubility*

The benzothiazolyl bisazo dye **4a** was less soluble than the corresponding phenyl bisazo derivative **7a**. However, the introduction of a perfluoroalkyl group in the benzothiazolyl moiety improved the solubility. The solubility of the 6-substituted derivatives **4** was in the order of the substituent: H, C_4F_9S, $C_4F_9CH_2CH_2S$ < C_4H_9 < C_4F_9, C_6F_{13}. For the 6-C_4F_9 derivatives, the solubility was in the order of another terminal moiety: 4-(diethylamino)phenyl **4c** < 4-(diethylamino)-2-methylphenyl **5c** < pentafluorophenyl **6c**. Thus, the introduction of a perfluoroalkyl group at the benzothiazolyl ring and a pentafluorophenyl moiety to the other terminal end increased the solubility.

2.4. *Dichroism*

No remarkable difference in dichroism among the benzothiazolyl bisazo dyes **4**, **5**, and phenyl bisazo dye **7a** was observed. The dichroism of azo dyes could be examined by calculating both the deviation angle θ between the direction of the transition moment and that of the long axis, and the ratio *l*/*d*, where *l* and *d* represent the length of the long axis and diameter of the circumscribed cylinders of the molecule, respectively [3]. 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 as described previously [1]. The θ values of the benzothiazolyl bisazo dyes **4** and **5c** were small (< 10·4°). The *l*/*d* ratios of these dyes in the range of 3·07–3·44. These values are similar to those of the phenyl bisazo dye **7a**. These calculations could demonstrate a dichroism of the benzothiazolyl bisazo dyes **4** and **5c** similar to that of phenyl bisazo dyes.

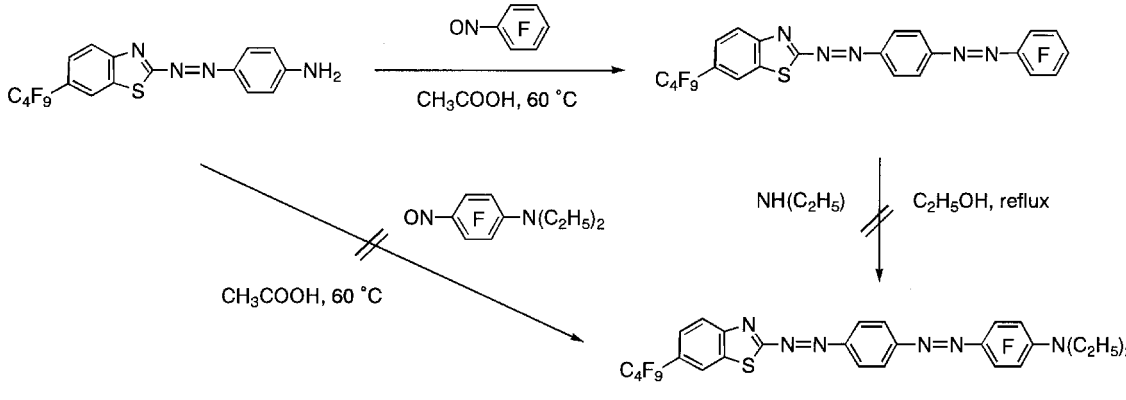
3. Conclusions

The solubility of bathochromic benzothiazolyl bisazo dyes was improved by the introduction of a perfluoroalkyl group at the 6-position in the benzothiazolyl moiety. The order parameter *S* of the benzothiazolyl bisazo dyes, except for **6c**, were higher than 0·75, being the practically required value.

4. Experimental

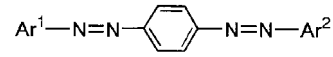
4.1. *Characterization*

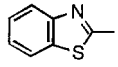
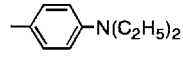
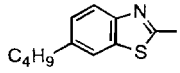
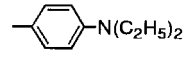
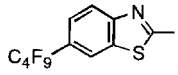
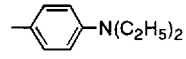
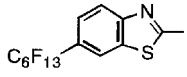
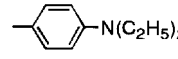
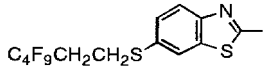
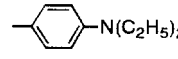
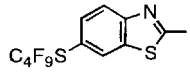
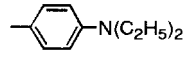
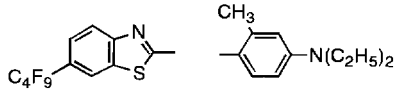
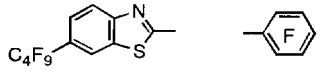
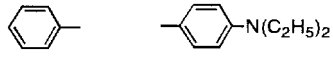
Melting points were measured with a Yanagimoto MP-S2 micro melting point apparatus. NMR spectra were recorded on a Jeol α-400 spectrometer. Mass spectra were required on a Shimadzu QP-1000 spectrometer. UV spectra were measured with a Shimadzu 160-A spectrometer.



Scheme 2.

Table 1. Properties of bisazo dyes.



Compound	Ar^1	Ar^2	λ_{max}[a] /nm	ε[a]	Solubility[b] /mg(100 ml)$^{-1}$ (mmol dm^{-3})	ZLI-1565 λ_{max} /nm	ZLI-1565 S	ZLI-4792 λ_{max} /nm	ZLI-4792 S	θ/°	l/d
4a			507	20500	2 (0·05)	560	0·76	553	0·77	0·9	3·07
4b			506	24000	9 (0·19)	557	0·78	552	0·77	3·4	3·44
4c			530	34000	20 (0·32)	583	0·77	578	0·77	2·8	3·37
4d			530	24100	28 (0·39)	583	0·77	578	0·77	10·4	3·29
4e			526	16500	5 (0·08)	582	0·77	566	0·79	6·7	3·31
4f			531	36200	5 (0·08)	583	0·77	579	0·79	6·2	3·36
5c			545	38700	127 (1·97)	602	0·76	597	0·75	2·2	3·37
6c			382	28500	170 (2·61)	394	0·66	394	0·69	1·9	3·16
7a[c]			454	55700	17 (0·48)	492	0·68	491	0·71	2·3	2·85

[a] In hexane.
[b] In hexane at 25°C.
[c] See reference [1].

4.2. *Materials*

4-Butylaniline (**1b**), benzothiazole (**2a**), *N*,*N*-diethylaniline and 3-methyl-*N*,*N*-diethylaniline were purchased from Tokyo Kasei Co., Ltd. 4-(Perfluorobutyl)aniline (**1c**) [1], 4-(perfluorohexyl)aniline (**1d**) [1], 4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)aniline (**1e**) [1], 4-(perfluorobutylthio)-aniline (**1f**) [1], and pentafluoronitrosobenzene [4] were prepared as described in the literature.

4.3. *Synthesis of 2-aminobenzothiazoles* **2**

To a 96% acetic acid solution (9 ml) of an aniline **1** (5 mmol) and potassium thiocyanate (1·95 g, 20 mmol) was added an acetic acid solution (4 ml) of bromine (0·8 g, 5 mmol) below 35°C and the mixture stirred for 15 h. When the reaction was complete, the resulting precipitate was filtered and washed with water. The filtrate was neutralized with ammonium hydroxide. The resulting compound **2** precipitate was filtered, dried, and purified by column chromatography. Physical and spectral data are given below.

4.3.1. *2-Amino-6-butylbenzothiazole* ***2b***

Yield 61%; m.p. 112–114°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}93$ (t, $J = 7{\cdot}5$ Hz, 3H), 1·36 (sextet, $J = 7{\cdot}5$ Hz, 2H), 1·61 (quintet, $J = 7{\cdot}5$ Hz, 2H), 2·65 (t, $J = 7{\cdot}5$ Hz, 2H), 5·09 (br s, 2H), 7·13 (dd, $J = 8{\cdot}2$ and 1·5 Hz, 1H), 7·40 (d, $J = 1{\cdot}5$ Hz, 1H), 7·46 (d, $J = 8{\cdot}2$ Hz,

1H). EI MS (70 eV) *m/z* (relative intensity, %) 206 $[M]^+$ (29), 163 (100), 162 (99).

4.3.2. *2-Amino-6-(perfluorobutyl)benzothiazole* **2c**
Yield 77%; m.p. 124–126°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6{\cdot}11$ (br s, 2H), 7·51 (dd, $J = 8{\cdot}4$ and 1·3 Hz, 1H), 7·57 (d, $J = 8{\cdot}4$ Hz, 1H), 7·80 (d, $J = 1{\cdot}3$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 368 $[M]^+$ (37), 199 (100).

4.3.3. *2-Amino-6-(perfluorohexyl)benzothiazole* **2d**
Yield 60%; m.p. 167–168°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 5{\cdot}52$ (br s, 2H), 7·51 (d, $J = 8{\cdot}5$ Hz, 1H), 7·62 (d, $J = 8{\cdot}5$ Hz, 1H), 7·82 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 468 $[M]^+$ (9), 199 (57), 172 (15), 142 (100), 69 (31).

4.3.4. *2-Amino-6-(1H,1H,2H,2H-perfluorohexylthio)-benzothiazole* **2e**
Yield 57%; m.p. 144–146°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2{\cdot}36$ (tt, $J = 16{\cdot}8$ and 8·3 Hz, 2H), 3·07 (tt, $J = 8{\cdot}3$ and 2·7 Hz, 2H), 5·33 (br s, 2H), 7·38 (dd, $J = 8{\cdot}4$ and 1·8 Hz, 1H), 7·50 (d, $J = 8{\cdot}4$ Hz, 1H), 7·68 (d, $J = 1{\cdot}8$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 428 $[M]^+$ (100), 181 (63).

4.3.5. *2-Amino-6-(perfluorobutylthio)benzothiazole* **2f**
Yield 72%; m.p. 170–172°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}77$ (br s, 2H), 7·53 (d, $J = 8{\cdot}3$ Hz, 1H), 7·57 (dd, $J = 8{\cdot}3$ and 1·7 Hz, 1H), 7·88 (d, $J = 1{\cdot}7$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 400 $[M]^+$ (33), 181 (100).

4.4. *Synthesis of 4-(2-benzothiazolylazo)anilines* **3**
Sodium nitrite (0·69 g, 10 mmol) was dissolved in conc. sulphuric acid (4·8 ml) at 70°C. To an acetic acid/propionic acid (25 ml/5 ml) solution of 2-aminobenzothiazole **2** (10 mmol) was added the nitrosyl sulphuric acid at 0°C and the mixture was stirred for 2 h. When the reaction was complete, the mixture was added to an acetic acid/propionic acid/ethanol (12·5 ml : 2·5 ml : 30 ml) solution of sodium anilinomethanesulphonate (2·1 g, 10 mmol) and sodium acetate (12 g) at 0°C. After 1 h stirring a saturated sodium chloride solution (250 ml) was then added to the mixture. The resulting precipitate was filtered off and dissolved in a 5% aqueous sodium hydroxide (30 ml) solution which was then heated at reflux for 5 h. The compound **3** product was extracted with dichloromethane and purified by column chromatography. Physical and spectral data are given below.

4.4.1. *4-(2-Benzothiazolylazo)aniline* **3a**
Yield 22%; m.p. 259–260°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}39$ (br s, 2H), 6·75 (d, $J = 8{\cdot}8$ Hz, 2H), 7·42 (t, $J = 7{\cdot}7$ Hz, 1H), 7·49 (t, $J = 7{\cdot}7$ Hz, 1H), 7·86 (d, $J = 7{\cdot}7$ Hz, 1H), 7·96 (d, $J = 8{\cdot}8$ Hz, 2H), 8·11 (d, $J = 7{\cdot}7$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 254 $[M]^+$ (8), 226 (48), 92 (100).

4.4.2. *4-(6-Butyl-2-benzothiazolylazo)aniline* **3b**
Yield 55%; m.p. 154–156°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}95$ (t, $J = 7{\cdot}5$ Hz, 3H), 1·40 (sextet, $J = 7{\cdot}5$ Hz, 2H), 1·68 (quintet, $J = 7{\cdot}5$ Hz, 2H), 2·75 (t, $J = 7{\cdot}5$ Hz, 2H), 4·36 (br s, 2H), 6·74 (d, $J = 9{\cdot}0$ Hz, 2H), 7·31 (dd, $J = 8{\cdot}4$ and 1·5 Hz, 1H), 7·65 (d, $J = 1{\cdot}5$ Hz, 1H), 7·94 (d, $J = 9{\cdot}0$ Hz, 2H), 8·00 (d, $J = 8{\cdot}4$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 310 $[M]^+$ (13), 239 (56), 92 (100).

4.4.3. *4-[6-(Perfluorobutyl)-2-benzothiazolylazo]aniline* **3c**
Yield 18%; m.p. 174–175°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}55$ (br s, 2H), 6·76 (d, $J = 9{\cdot}0$ Hz, 2H), 7·67 (dd, $J = 8{\cdot}5$ and 1·5 Hz, 1H), 7·98 (d, $J = 9{\cdot}0$ Hz, 2H), 8·10 (d, $J = 1{\cdot}5$ Hz, 1H), 8·19 (d, $J = 8{\cdot}5$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 472 $[M]^+$ (8), 120 (21), 92 (100).

4.4.4. *4-[6-(Perfluorohexyl)-2-benzothiazolylazo]aniline* **3d**
Yield 7%; m.p. 191–192°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}51$ (br s, 2H), 6·76 (d, $J = 8{\cdot}8$ Hz, 2H), 7·67 (d, $J = 8{\cdot}4$ Hz, 1H), 7·98 (d, $J = 8{\cdot}8$ Hz, 2H), 8·11 (s, 1H), 8·19 (d, $J = 8{\cdot}4$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 572 $[M]^+$ (7), 120 (21), 92 (100).

4.4.5. *4-[6-(1H,1H,2H,2H-Perfluorohexylthio)-2-benzothiazolylazo]aniline* **3e**
Yield 23%; m.p. 133–135°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2{\cdot}44$ (tt, $J = 16{\cdot}6$ and 8·3 Hz, 2H), 3·20 (tt, $J = 8{\cdot}3$ and 2·7 Hz, 2H), 4·54 (br s, 2H), 6·74 (d, $J = 8{\cdot}9$ Hz, 2H), 7·46 (dd, $J = 8{\cdot}5$ and 1·8 Hz, 1H), 7·83 (d, $J = 1{\cdot}8$ Hz, 1H), 7·93 (d, $J = 8{\cdot}9$ Hz, 2H), 8·02 (d, $J = 8{\cdot}5$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 532 $[M]^+$ (100), 120 (45), 92 (90).

4.4.6. *4-[6-(Perfluorobutylthio)-2-benzothiazolylazo]-aniline* **3f**
Yield 35%; m.p. 166–168°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}50$ (br s, 2H), 6·75 (d, $J = 8{\cdot}9$ Hz, 2H), 7·73 (dd, $J = 8{\cdot}5$ and 1·9 Hz, 1H), 7·97 (d, $J = 8{\cdot}9$ Hz, 2H), 8·11 (d, $J = 8{\cdot}5$ Hz, 1H), 8·17 (d, $J = 1{\cdot}9$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 504 $[M]^+$ (35), 120 (57), 92 (100).

4.5. *Synthesis of 4-[4-(2-benzothiazolylazo)-phenylazo]-N,N-diethylanilines* ***4*** *and* ***5c***

Sodium nitrite (0·14 g, 2 mmol) was dissolved in conc. sulphuric acid (1 ml) at 70°C. To an acetic acid/propionic acid (15 ml : 3 ml) solution of 4-(2-benzothiazolylazo)-aniline **3** (2 mmol) was added the nitrosyl sulphuric acid at 0°C and the mixture stirred for 2 h. When the reaction was complete, the mixture was added to an acetic acid/propionic acid/ethanol (5 ml : 1 ml : 30 ml) solution of an *N*,*N*-diethylaniline (2 mmol) and sodium acetate (2·4 g) at 0°C, with stirring for 1 h. The pH value of the solution was adjusted to 10·0 with dilute aqueous sodium hydroxide. The compound **4** product was extracted with dichloromethane and purified by column chromatography. Physical and spectral data are given below.

4.5.1. *4-[4-(2-Benzothiazolylazo)phenylazo]-N,N-diethylaniline* ***4a***

Yield 63%; m.p. 239–240°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}0$ Hz, 6H), 3·49 (q, $J = 7{\cdot}0$ Hz, 4H), 6·75 (d, $J = 8{\cdot}9$ Hz, 2H), 7·49 (t, $J = 7{\cdot}9$ Hz, 1H), 7·55 (t, $J = 7{\cdot}9$ Hz, 1H), 7·91 (d, $J = 8{\cdot}9$ Hz, 2H), 7·91 (d, $J = 7{\cdot}9$ Hz, 1H), 8·00 (d, $J = 8{\cdot}5$ Hz, 2H), 8·20 (d, $J = 8{\cdot}5$ Hz, 2H), 8·20 (d, $J = 7{\cdot}9$ Hz, 1H). EI MS (70 eV) *m/z* (relative intensity, %) 414 $[M]^+$ (80), 399 (38), 148 (100).

4.5.2. *4-[4-(6-Butyl-2-benzothiazolylazo)phenylazo]-N,N-diethylaniline* ***4b***

Yield 79%; m.p. 209–210°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}96$ (t, $J = 7{\cdot}5$ Hz, 3H), 1·26 (t, $J = 7{\cdot}1$ Hz, 6H), 1·41 (sextet, $J = 7{\cdot}5$ Hz, 2H), 1·69 (quintet, $J = 7{\cdot}5$ Hz, 2H), 2·78 (t, $J = 7{\cdot}5$ Hz, 2H), 3·49 (q, $J = 7{\cdot}1$ Hz, 4H), 6·75 (d, $J = 9{\cdot}4$ Hz, 2H), 7·36 (dd, $J = 8{\cdot}4$ and 1·4 Hz, 1H), 7·70 (d, $J = 1{\cdot}4$ Hz, 1H), 7·91 (d, $J = 9{\cdot}4$ Hz, 2H), 7·99 (d, $J = 8{\cdot}8$ Hz, 2H), 8·08 (d, $J = 8{\cdot}4$ Hz, 1H), 8·18 (d, $J = 8{\cdot}8$ Hz, 2H). EI MS (70 eV) *m/z* (relative intensity, %) 470 $[M]^+$ (8), 455 (14), 148 (100).

4.5.3. *4-{4-[6-(Perfluorobutyl)-2-benzothiazolylazo]-phenylazo}-N,N-diethylaniline* ***4c***

Yield 51%; m.p. 195–196°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}27$ (t, $J = 7{\cdot}1$ Hz, 6H), 3·50 (q, $J = 7{\cdot}1$ Hz, 4H), 6·75 (d, $J = 9{\cdot}3$ Hz, 2H), 7·73 (dd, $J = 8{\cdot}7$ and 1·5 Hz, 1H), 7·92 (d, $J = 9{\cdot}3$ Hz, 2H), 8·02 (d, $J = 9{\cdot}0$ Hz, 2H), 8·17 (d, $J = 1{\cdot}5$ Hz, 1H), 8·22 (d, $J = 9{\cdot}0$ Hz, 2H), 8·30 (d, $J = 8{\cdot}7$ Hz, 1H). ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) $\delta - 3{\cdot}18$ (3F), $-32{\cdot}19$ (2F), $-44{\cdot}53$ (2F), $-47{\cdot}75$ (2F). EI MS (70 eV) *m/z* (relative intensity, %) 632 $[M]^+$ (75), 617 (38), 148 (100). Elemental analysis calc. for $C_{27}H_{21}F_9N_6S$: C 51·27, H 3·35, N 13·29; found C 51·28, H 3·23, N 13·37%.

4.5.4. *4-{4-[6-(Perfluorohexyl)-2-benzothiazolylazo]-phenylazo}-N,N-diethylaniline* ***4d***

Yield 45%; m.p. 201–202°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}27$ (t, $J = 7{\cdot}1$ Hz, 6H), 3·50 (q, $J = 7{\cdot}1$ Hz, 4H), 6·75 (d, $J = 9{\cdot}3$ Hz, 2H), 7·74 (dd, $J = 8{\cdot}5$ and 0·7 Hz, 1H), 7·92 (d, $J = 9{\cdot}3$ Hz, 2H), 8·02 (d, $J = 8{\cdot}8$ Hz, 2H), 8·17 (d, $J = 0{\cdot}7$ Hz, 1H), 8·22 (d, $J = 8{\cdot}8$ Hz, 2H), 8·29 (d, $J = 8{\cdot}5$ Hz, 1H). ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) $\delta - 3{\cdot}67$ (3F), $-32{\cdot}67$ (2F), $-44{\cdot}31$ (4F), $-45{\cdot}69$ (2F), $-49{\cdot}02$ (2F). EI MS (70 eV) *m/z* (relative intensity, %) 732 $[M]^+$ (20), 717 (11), 210 (33), 148 (100), 133 (37). Elemental analysis calc. for $C_{29}H_{21}F_{13}N_6S$: C 47·55, H 2·89, N 11·47; found C 47·49, H 2·93, N 11·69%.

4.5.5. *4-{4-[6-(1H,1H,2H,2H-Perfluorohexylthio)-2-benzothiazolylazo]phenylazo}-N,N-diethylaniline* ***4e***

Yield 45%; m.p. 209–210°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}1$ Hz, 6H), 2·47 (tt, $J = 17{\cdot}1$ and 8·3 Hz, 2H), 3·24 (tt, $J = 8{\cdot}3$ and 2·8 Hz, 2H), 3·49 (q, $J = 7{\cdot}1$ Hz, 4H), 6·75 (d, $J = 9{\cdot}2$ Hz, 2H), 7·50 (dd, $J = 8{\cdot}5$ and 1·8 Hz, 1H), 7·87 (d, $J = 1{\cdot}8$ Hz, 1H), 7·91 (d, $J = 9{\cdot}2$ Hz, 2H), 8·00 (d, $J = 9{\cdot}0$ Hz, 2H), 8·12 (d, $J = 8{\cdot}5$ Hz, 1H), 8·19 (d, $J = 9{\cdot}0$ Hz, 2H). ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) $\delta - 3{\cdot}23$ (3F), $-36{\cdot}56$ (2F), $-46{\cdot}42$ (2F), $-48{\cdot}24$ (2F). EI MS (70 eV) *m/z* (relative intensity, %) 692 $[M]^+$ (100), 677 (33), 148 (92). Elemental analysis calc. for $C_{29}H_5F_9N_6S_2$: C 50·29, H 3·64, N 12·13; found C 50·47, H 3·58, N 12·14%.

4.5.6. *4-{4-[6-(Perfluorobutylthio)-2-benzothiazolylazo]-phenylazo}-N,N-diethylaniline* ***4f***

Yield 47%; m.p. 231–232°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}1$ Hz, 6H), 3·50 (q, $J = 7{\cdot}1$ Hz, 4H), 6·75 (d, $J = 9{\cdot}0$ Hz, 2H), 7·79 (dd, $J = 8{\cdot}6$ and 1·5 Hz, 1H), 7·92 (d, $J = 9{\cdot}0$ Hz, 2H), 8·01 (d, $J = 8{\cdot}5$ Hz, 2H), 8·21 (d, $J = 8{\cdot}5$ Hz, 2H), 8·21 (d, $J = 8{\cdot}6$ Hz, 1H), 8·24 (d, $J = 1{\cdot}5$ Hz, 1H). ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) $\delta - 3{\cdot}14$ (3F), $-8{\cdot}99$ (2F), $-42{\cdot}22$ (2F), $-47{\cdot}75$ (2F). EI MS (70 eV) *m/z* (relative intensity, %) 664 $[M]^+$ (100), 649 (22), 148 (77). Elemental analysis calc. for $C_{27}H_{21}F_9N_6S_2$: C 48·79, H 3·18, N 12·65; found C 48·66, H 3·21, N 12·68%.

4.5.7. *3-Methyl-4-{4-[6-(perfluorobutyl)-2-benzothiazolylazo]phenylazo}-N,N-diethylaniline* ***5c***

Yield 61%; m.p. 195–196°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}0$ Hz, 6H), 2·74 (s, 3H), 3·48 (q, $J = 7{\cdot}0$ Hz, 4H), 6·56 (s, 1H), 6·57 (d, $J = 8{\cdot}8$ Hz, 1H), 7·73 (dd, $J = 8{\cdot}5$ and 0·5 Hz, 1H), 7·85 (d, $J = 8{\cdot}8$ Hz, 1H), 8·01 (d, $J = 8{\cdot}8$ Hz, 2H), 8·17 (d, $J = 0{\cdot}5$ Hz, 1H), 8·21 (d, $J = 8{\cdot}8$ Hz, 2H), 8·29 (d, $J = 8{\cdot}5$ Hz, 1H).

^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ − 3·15 (3F), − 32·10 (2F), − 44·49 (2F), − 47·67 (2F). EI MS (70 eV) *m/z* (relative intensity, %) 646 $[M]^+$ (43), 631 (21), 162 (100). Elemental analysis calc. for $C_{28}H_{23}F_9N_6S$: C 52·01, H 3·59, N 13·00; found C 52·20, H 3·73, N 13·36%.

4.6. *Synthesis of 4-[6-(perfluorobutyl)-2-benzothiazolylazo]pentafluoroazobenzene (**6c**)*

To an acetic acid solution (10 ml) of 4-[4-(perfluorobutyl)phenylazo]aniline (0·47 g, 1 mmol) was added an acetic acid solution (5 ml) of polyfluoronitrosobenzene (0·2 g, 1 mmol) with stirring overnight at 70°C. When the reaction was complete, the mixture was poured into water; the resulting precipitate was filtered, dried, and purified by column chromatography (SiO_2, $CHCl_3$). Physical and spectral data are given below. Yield 14%; m.p. 217–218°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·77 (d, J = 8·5 Hz, 1H), 8·15 (d, J = 8·5 Hz, 1H), 8·21 (s, 1H), 8·29 (d, J = 8·5 Hz, 2H), 8·34 (d, J = 8·5 Hz, 2H). ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ = − 3·16 (3F), − 32·29 (2F), − 44·48 (2F), − 47·69 (2F), − 71·69 (2F), − 83·85 (2F). CI MS (200 eV, *iso*-C_4H_{10}) *m/z* (relative intensity, %) 652 $[MH]^+$ (30), 473 (100), 288 (80), 195 (16). Elemental analysis calc. for $C_{23}H_7F_{14}N_5S$: C 42·41, H 1·08, N 10·75; found C 42·58, H 1·00, N 11·06%.

4.7. *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 to transparent electrodes, on which polyimide was applied and rubbed. The absorption of the solution was measured. The order parameter (S) was calculated on the basis of the following equation: $S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$, where $A_{\parallel}$ and $A_{\perp}$ represent, respectively, the absorbance of light polarized parallel and perpendicular to the direction of alignment of the dye molecule in the liquid crystal medium.

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