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Synthesis of perfluoroalkylated azo dyes and their application to guest–host liquid crystal display

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A series of novel dis- and trisazo dyes containing a perfluoroalkyl, perfluoroalkylthio and perfluoroalkylsulphonyl groups have been synthesized. The absorption bands of these dyes were more bathochromic than the corresponding alkyl derivatives. The solubility of disazo dyes containing perfluoroalkyl and perfluoroalkylthio groups in hexane was larger than the alkyl derivatives. To obtain good dichroism, the azo dyes were required to have a large *l/d* ratio (>2·50). These novel azo compounds could be used practically as dichroic dyes in guest–host liquid crystal displays.

1. Introduction

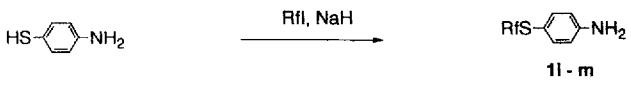
π-Conjugated organic compounds have been used as organic functional materials in information display systems, electro-photography, laser technology, energy-transfer systems and data storage [1]. Linear polyazo and anthraquinone dyes bearing long alkyl chain(s) have been used practically as dichroic dyes [2]. Organic compounds containing fluorine atoms and/or a perfluoroalkyl group can change the property of the molecule. For example, 3-(perfluoroalkyl)coumarins show excellent photostability [3], phthalocyanines substituted with perfluoroalkyl groups are very soluble in organic solvents [4], and photochromic diarylethenes containing a perfluorocyclopentenyl moiety are very thermally stable [5]. By introduction of the perfluoroalkyl moiety into dis- and trisazo dyes, variation in the shift of the absorption band due to its electron-withdrawing nature, higher solubility in organic solvents and host liquid crystals due to weak intermolecular interaction and the steric effect between the fluorine-containing moieties, and the higher contrast in their dichroism because of the rigidity of the perfluoroalkyl moiety are anticipated.

We describe here the synthesis of a series of dis- and trisazo dyes containing a perfluoroalkyl, perfluoroalkylthio, and perfluoroalkylsulphonyl group and their application to dichroic dyes in guest–host liquid crystal displays.

2. Results and discussion

2.1. *Synthesis*

4-(Perfluoroalkyl)anilines **1c–e** were prepared by the reaction of 4-iodoaniline with perfluoroalkyl iodide in the presence of copper in good yields [6]. 4-(Alkylthio) anilines [7] **1f–h** and 4-(alkylsulphonyl)anilines [8] **1m,o** were synthesized as described in the literature. 4-(Perfluoroalkylsulphonyl)anilines **1p–s** were obtained by *S*-perfluoroalkylation of 4-nitrothiophenol to afford 4-(perfluoroalkylthio)nitrobenzene, followed by oxidation of the sulphide moiety and reduction of the nitro group [9]. 4-(Perfluoroalkylthio)anilines **1i–m** were prepared by the reaction of 4-aminothiophenol with perfluoroalkyl iodide in the presence of sodium hydride in moderate to good yields (see Scheme 1).



Rf = C_4F_9, C_6F_{13}, C_8F_{17}, $C_4F_9CH_2CH_2$, $C_6F_{13}CH_2CH_2$
RfS = R^1

Scheme 1.

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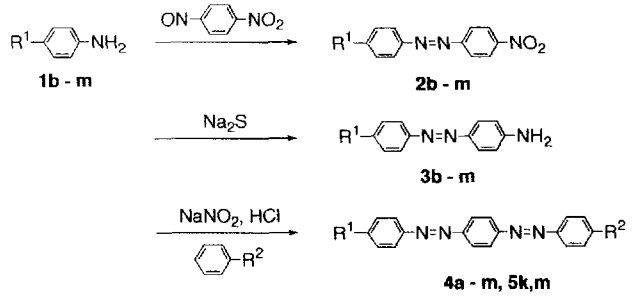


R^1 = H, C_4H_9, C_4F_9, C_6F_{13}, C_8F_{17}, C_4H_9S, $C_6H_{13}S$, $C_8H_{17}S$, $C_4F_9CH_2CH_2S$, $C_6F_{13}CH_2CH_2S$, C_4F_9S, $C_6F_{13}S$, $C_8F_{17}S$

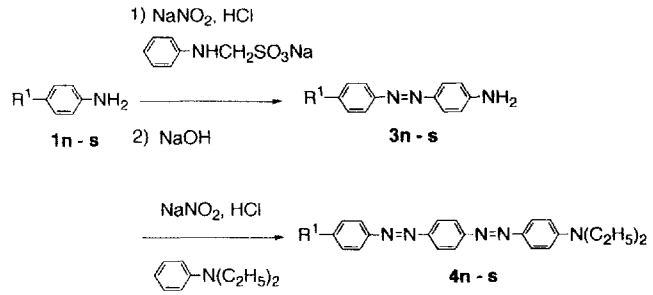
R^2 = $N(C_2H_5)_2$, $N(CH_3)_2$

Scheme 2.

Scheme 2 indicates the synthesis of the phenylene disazo dyes **4a–m** and **5k,m**. The anilines **1b–m** reacted with 4-nitrosonitrobenzene to give the corresponding 4-nitroazobenzenes **2b–m**, of which the nitro group was reduced by sodium sulphide to afford the 4-(arylazo)anilines **3b–m**, followed by diazotization-coupling reaction to form the phenylene disazo dyes **4a–m** and **5k,m**.

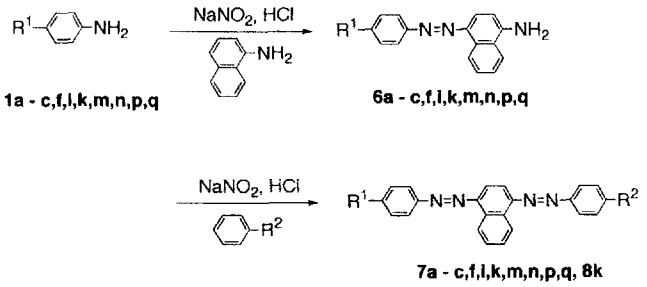
The synthesis of the phenylene disazo dyes **4n–s** bearing a RSO_2, $R_fCH_2CH_2SO_2$ and R_fSO_2 group, where R and R_f represent alkyl and perfluoroalkyl groups respectively, is shown in Scheme 3. Anilines **1n–s** did not react with 4-nitrosonitrobenzene, due to the strong electron-withdrawing nature of the substituents. The diazotization-coupling reaction of the anilines **1n–s** with sodium anilinomethanesulphonate followed by deprotection under alkaline conditions gave the 4-(arylazo)anilines **3n–s**, which further reacted with *N,N*-(diethyl)aniline to afford **4n–s**.

Scheme 4 shows the synthesis of the naphthylene disazo dyes **7** and **8**. Anilines **1** reacted with 1-naphthylamine to afford the 4-(arylazo)-1-naphthylamines **6**,



R^1 = $C_4H_9SO_2$, $C_6H_{13}SO_2$, $C_4F_9CH_2CH_2SO_2$, $C_4F_9SO_2$, $C_6F_{13}SO_2$, $C_8F_{17}SO_2$

Scheme 3.



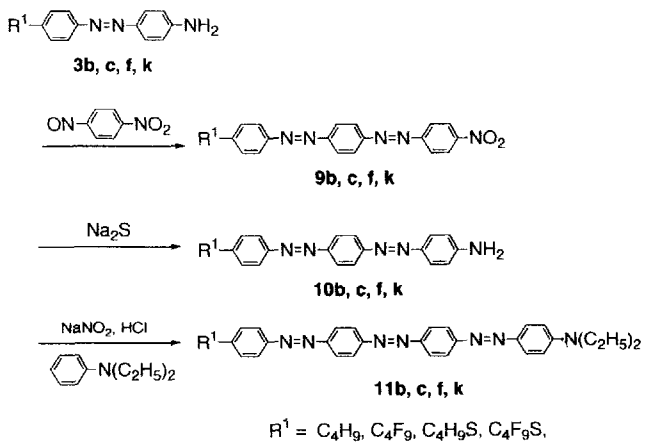
R^1 = H, C_4H_9, C_4F_9, C_4H_9S, $C_4H_9CH_2CH_2S$, C_4F_9S, $C_8F_{17}S$, $C_4H_9SO_2$, $C_4F_9CH_2CH_2SO_2$, $C_4F_9SO_2$

R^2 = $N(C_2H_5)_2$, $N(CH_3)_2$

Scheme 4.

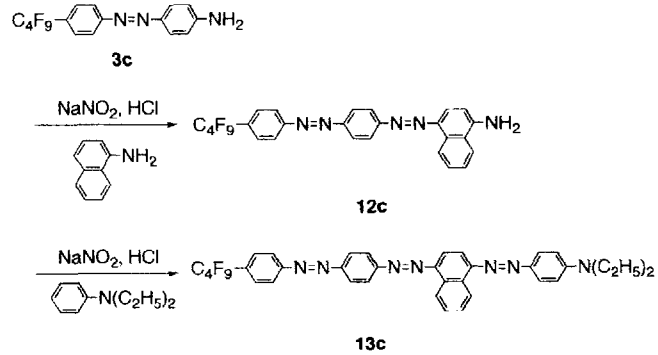
which further reacted with *N,N*-(dialkyl)anilines to give the naphthylene derivatives **7** and **8**.

Phenylene trisazo **11** and naphthylene trisazo dyes **13c** were similarly synthesized as shown in Schemes 5 and 6, respectively.



R^1 = C_4H_9, C_4F_9, C_4H_9S, C_4F_9S,

Scheme 5.



Scheme 6.

2.2. *Absorption band*

Table 1 summarizes the physical properties of azo dyes.

The absorption band of the phenylene disazo dyes **4** was more bathochromic in the order of substituent R^1: R, H < RS < $R_fCH_2CH_2S$ < R_fS, R_f < RSO_2, $R_fCH_2CH_2SO_2$ < R_fSO_2 (runs 1–19). The chromophore of the azo dyes has been reported to be an intramolecular charge-transfer system [10]. Therefore, the order of the bathochromicity is consistent with that of Hammett's σ_p constant of the substituent R^1 ($CH_3 = -0{\cdot}17$, H = 0·00, $CH_3S = 0{\cdot}00$, $CF_3S = 0{\cdot}50$, $CF_3 = 0{\cdot}54$, $CH_3SO_2 = 0{\cdot}68$, $CF_3SO_2 = 0{\cdot}93$) [11]. The chain length of the R and R_f moiety in each R^1 substituent did not affect the absorption bands, suggesting similar electron-withdrawing nature of the series of substituents (runs 3–19). The naphthylene disazo dyes **7** were more bathochromic than the corresponding phenylene derivatives **4**, due to an extended π-electron system (runs 1–3, 6, 9, 11, 13, 14, 16, 17, 22–31). *N*,*N*-Diethylamino derivatives were more bathochromic than the *N*,*N*-dimethylamino derivatives (runs 11, 13, 20, 21, 27, 32). Both the absorption bands of the naphthylene disazo **7** and phenylene trisazo dyes **11** were more bathochromic in the order of substituent R^1: C_4H_9 < C_4H_9S < C_4F_9S, C_4F_9 (runs 23–25, 27, 33–36). This is the same tendency as the phenylene

Physical properties of azo dyes.

Run	Compound	R^1	R^2	λ_{max}/nm[a]	Solubility[b]/mg/100 ml (mmol dm^{-3})	ZLI-1565		ZLI-4792			
						λ_{max}/nm	S	λ_{max}/nm	S	θ/°	I/d
1	**4a**	H	NEt_2	454	17 (0·48)	492	0·68	491	0·71	2·3	2·85
2	**4b**	C_4H_9	NEt_2	453	76 (1·84)	492	0·72	491	0·75	2·0	3·25
3	**4c**	C_4F_9	NEt_2	474	222 (3·86)	514	0·71	507	0·76	2·3	3·83
4	**4d**	C_6F_{13}	NEt_2	474	248 (3·67)	508	0·75	504	0·78	—[d]	—[d]
5	**4e**	C_8F_{17}	NEt_2	473	132 (1·70)	512	0·78	510	0·79	—[d]	—[d]
6	**4f**	C_4H_9S	NEt_2	462	24 (0·54)	499	0·73	499	0·76	1·5	3·16
7	**4g**	$C_6H_{13}S$	NEt_2	460	46 (0·97)	496	0·75	494	0·75	—[d]	—[d]
8	**4h**	$C_8H_{17}S$	NEt_2	460	23 (0·46)	499	0·75	498	0·77	—[d]	—[d]
9	**4i**	$C_4F_9CH_2CH_2S$	NEt_2	466	219 (3·45)	502	0·72	498	0·77	1·7	3·18
10	**4j**	$C_6F_{13}CH_2CH_2S$	NEt_2	468	293 (3·99)	501	0·76	501	0·77	—[d]	—[d]
11	**4k**	C_4F_9S	NEt_2	476	56 (0·92)	515	0·70	509	0·76	1·9	3·19
12	**4l**	$C_6F_{13}S$	NEt_2	475	62 (0·88)	514	0·77	511	0·78	—[d]	—[d]
13	**4m**	$C_8F_{17}S$	NEt_2	477	22 (0·27)	514	0·70	507	0·76	—[d]	—[d]
14	**4n**	$C_4H_9SO_2$	NEt_2	478	15 (0·31)	514	0·74	512	0·77	2·5	3·62
15	**4o**	$C_6H_{13}SO_2$	NEt_2	480	23 (0·46)	514	0·74	512	0·76	—[d]	—[d]
16	**4p**	$C_4F_9CH_2CH_2SO_2$	NEt_2	482	31 (0·46)	512	0·72	506	0·76	2·6	3·56
17	**4q**	$C_4F_9SO_2$	NEt_2	500	18 (0·28)	538	0·70	530	0·76	2·1	2·98
18	**4r**	$C_6F_{13}SO_2$	NEt_2	504	9 (0·12)	517	0·75	514	0·77	—[d]	—[d]
19	**4s**	$C_8F_{17}SO_2$	NEt_2	503	7 (0·08)	—[c]	—[c]	—[c]	—[c]	—[d]	—[d]
20	**5k**	C_4F_9S	NMe_2	456	26 (0·45)	499	0·76	498	0·77	—[d]	—[d]
21	**5m**	$C_8F_{17}S$	NMe_2	459	5 (0·06)	—[c]	—[c]	—[c]	—[c]	—[d]	—[d]
22	**7a**	H	NEt_2	495	29 (0·72)	531	0·67	525	0·68	1·7	2·28
23	**7b**	C_4H_9	NEt_2	494	110 (2·38)	532	0·71	525	0·73	1·4	2·52
24	**7c**	C_4F_9	NEt_2	513	356 (5·70)	555	0·70	549	0·75	1·1	2·50
25	**7f**	C_4H_9S	NEt_2	506	64 (1·29)	538	0·73	532	0·75	—[d]	—[d]
26	**7i**	$C_4F_9CH_2CH_2S$	NEt_2	508	241 (3·51)	541	0·72	536	0·74	—[d]	—[d]
27	**7k**	C_4F_9S	NEt_2	516	251 (3·82)	541	0·74	535	0·73	—[d]	—[d]
28	**7m**	$C_8F_{17}S$	NEt_2	515	13 (0·02)	560	0·66	545	0·72	—[d]	—[d]
29	**7n**	$C_4H_9SO_2$	NEt_2	518	19 (0·36)	560	0·74	554	0·74	—[d]	—[d]
30	**7p**	$C_4F_9CH_2CH_2SO_2$	NEt_2	527	21 (0·29)	566	0·73	531	0·75	—[d]	—[d]
31	**7q**	$C_4F_9SO_2$	NEt_2	543	40 (0·58)	585	0·73	578	0·75	—[d]	—[d]
32	**8k**	C_4F_9S	NMe_2	505	78 (1·24)	560	0·69	545	0·73	—[d]	—[d]
33	**11b**	C_4H_9	NEt_2	477	4 (0·07)	519	0·81	516	0·81	—[d]	—[d]
34	**11c**	C_4F_9	NEt_2	490	5 (0·08)	530	0·82	527	0·82	2·9	4·45
35	**11f**	C_4H_9S	NEt_2	483	2 (0·04)	—[c]	—[c]	—[c]	—[c]	—[d]	—[d]
36	**11k**	C_4F_9S	NEt_2	491	4 (0·06)	527	0·82	—[c]	—[c]	—[d]	—[d]
37	**13c**	C_4F_9	NEt_2	515	229 (3·14)	552	0·73	542	0·74	1·9	3·42

[a] In hexane.
[b] In hexane at 25°C.
[c] Insoluble in liquid crystals.
[d] No calculation.

disazo dyes **4**. Bathochromicity was almost in the order of dye skeleton: phenylene disazo < phenylene trisazo < naphthylene disazo, naphthylene trisazo (runs 3, 24, 34, 37).

2.3. *Solubility*

Solubility of the phenylene disazo dyes **4** in hexane was almost in the order of substituent R^1: R_fSO_2, $R_fCH_2CH_2SO_2$, $RSO_2 < RS$, $R_fS < H < R < R_fCH_2CH_2S$, R_f (runs 1–19). Especially, dyes **4c,d,i** and **j** containing a C_4F_9, C_6F_{13}, $C_4F_9CH_2CH_2S$ and $C_6F_{13}CH_2CH_2S$ group were very soluble (runs 3, 4, 9, 10). The maximum solubility of the perfluoroalkyl and perfluoroalkylthio derivatives **4c–e** and **4k–m** was observed around C4 to C6 chain length (runs 3–5, 11–13). This can be attributed to a weak intermolecular interaction and steric effects of perfluoroalkyl groups. A long perfluorooctyl group does not increase solubility, probably because of its oil-repelling nature. Alkylsulphonyl and perfluoroalkylsulphonyl derivatives were less soluble due to an increment of the inorganic nature of the substituents. The naphthylene disazo dyes **7** were more soluble than the phenylene derivatives **4** (runs 1–3, 6, 9, 11, 13, 14, 16, 17, 22–31). *N,N*-Diethylamino derivatives **4h,m** and **7k** were more soluble than the *N,N*-dimethylamino derivatives **5k,m** and **8k** (runs 11, 13, 20, 21, 27, 32). The phenylene trisazo dyes **11** were less soluble than the disazo dyes (runs 2, 3, 6, 11, 33–36). No improvement in solubility by the introduction of perfluoroalkyl moiety in dyes **11** was observed (runs 33–36). Thus, terminal perfluoroalkyl and dialkylamino moieties and central aromatic part(s) play very important role in affecting a change in the solubility. The solubility was almost in the order of dye skeleton: phenylene trisazo < naphthylene trisazo, phenylene disazo < naphthylene disazo (runs 3, 24, 34, 37). In order to dissolve these dyes in a liquid crystal, the value of the solubility in hexane at 25°C was required to be more than 0·01 mmol dm $^{-3}$.

2.4. *Dichroism*

A typical change in the absorption band of the dichroic dye **5k** in a liquid crystal (ZLI-1565) cell is depicted in figure 1.

The order parameter (S) is defined by the following equation: $S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$, where $A_{\parallel}$ and $A_{\perp}$ represent absorbances of light polarized parallel and perpendicular to the direction of the alignment of the dye molecule in the liquid crystal medium, respectively. The S value of **5k** was calculated to be 0·76.

Both the absorption band and S value were affected by the nature of the host liquid crystal. The absorption bands in ZLI-4792 (fluoro liquid crystal) were slightly hypsochromic compared to those in ZLI-1565 (cyano liquid crystal), because of the higher polarity of ZLI-1565. The S values in ZLI-4792 were larger than those in ZLI-1565. R^1-substituted dyes showed a higher dichroism than the unsubstituted dyes. For example, the S values of perfluoroalkyl derivatives **4c** and **7c** were larger than those of the unsubstituted **4a** and **7a**, respectively (runs 1, 3, 22, 24). Thus, introduction of a long and linear substituent in R^1 was very effective in

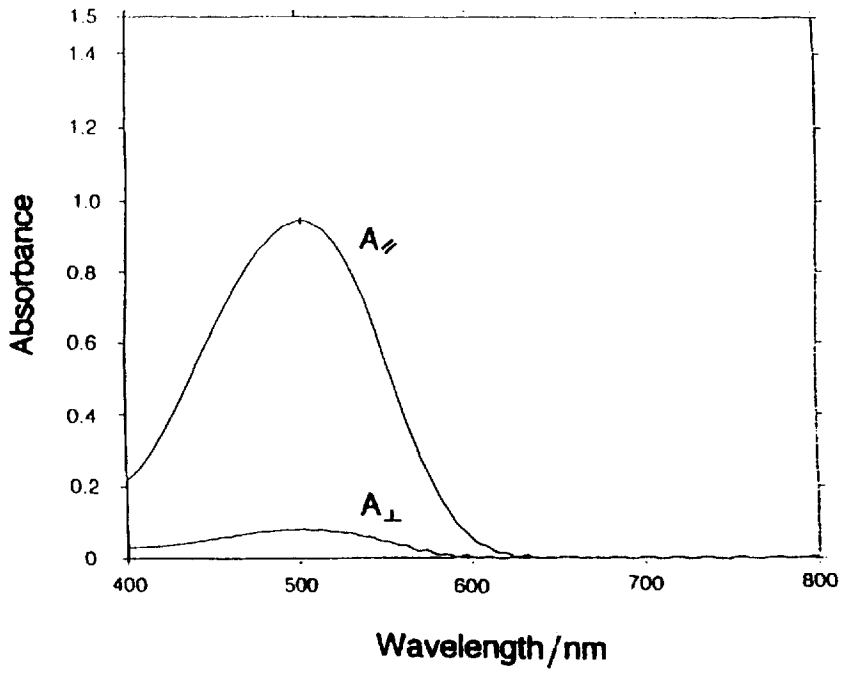


Figure 1. Dichroism of azo dye.

enhancing dichroism. No remarkable difference in dichroism among the substituents C_4H_9, C_4F_9, C_4H_9S, C_4F_9S, $C_4H_9SO_2$, and $C_4F_9SO_2$ was observed (runs 2, 3, 6, 11, 14, 17). The same tendency was observed for the naphthylene disazo and phenylene trisazo skeletons (runs 23–25, 27, 29, 31, 33, 34). *N,N*-Diethylamino derivatives **4k** and **7k** showed similar *S* values as *N,N*-dimethylamino derivatives **5k** and **8k** (runs 11, 20, 27, 32).

Dichroism of a molecule can be analysed by both the deviation of the angle (θ) between the direction of transition moment and the long axis, and *l*/*d* ratio, where *l* and *d* represent the length of long axis and diameter of circumscribed cylinders of the molecule, respectively. For the MO calculation, the π-conjugated skeleton of the azo dyes was assumed planar, azo linkage in the all-*trans* form, and the molecule with Cs symmetry. The van der Waals radius was also taken into account. The heat of formation of all conformations of the molecules was calculated. The value and *l*/*d* ratio in the most stable conformation were also calculated. A typical example is shown in figure 2. The calculated θ value of **4c** was 2·3°. The *l* and *d* values were calculated to be 28·34 and 7·39 Å respectively, the *l*/*d* ratio being 3·83.

The results of selected azo dyes are indicated in the table. All the θ values in the azo dyes were very small (<2·9°). No significant difference among unsubstituted, alkyl, alkylthio, alkylsulphonyl, perfluoroalkyl, perfluoroalkylthio and perfluoroalkylsulphonyl derivatives was observed (runs 1–3, 6, 9, 11, 14, 16, 17). No remarkable difference among the phenylene disazo, naphthylene disazo, phenylene trisazo, and naphthylene trisazo dyes was also observed (runs 3, 24, 34, 37). Thus, the structure of the azo dyes has a small θ value.

Introduction of a R^1 substituent increased the *l*/*d* ratio, resulting in enhanced dichroism (runs 1, 3, 22, 24). No remarkable difference in the ratio among butyl, butylthio, perfluorobutyl and perfluorobutylthio derivatives was observed (runs 2, 3, 6, 11). The *l*/*d* ratio was almost in the order of dye skeleton: naphthylene disazo < phenylene disazo, naphthylene trisazo < phenylene trisazo (runs 3, 24, 34, 37). This is consistent with the *S* value. Thus, dichroism of the azo dyes in liquid crystals was mainly affected by the *l*/*d* ratio of the molecule. To obtain good dichroism ($S > 0{\cdot}70$), the *l*/*d* ratio of the azo dyes was required to be more than 2·50.

3. Conclusions

Disazo dyes containing perfluoroalkyl and perfluoroalkylthio groups were more soluble than the corresponding alkyl derivatives. The *S* values of all the dis- and trisazo dyes were more than 0·70, the practically required value, indicating that these can be used as dichroic dyes in guest–host liquid crystal displays.

4. Experimental

Melting points were measured with a Yanagimoto MP-S2 micro melting point apparatus. NMR spectra were taken on Jeol α-400 spectrometer. Mass spectra were measured with Shimadzu 9020-DF and QP-1000

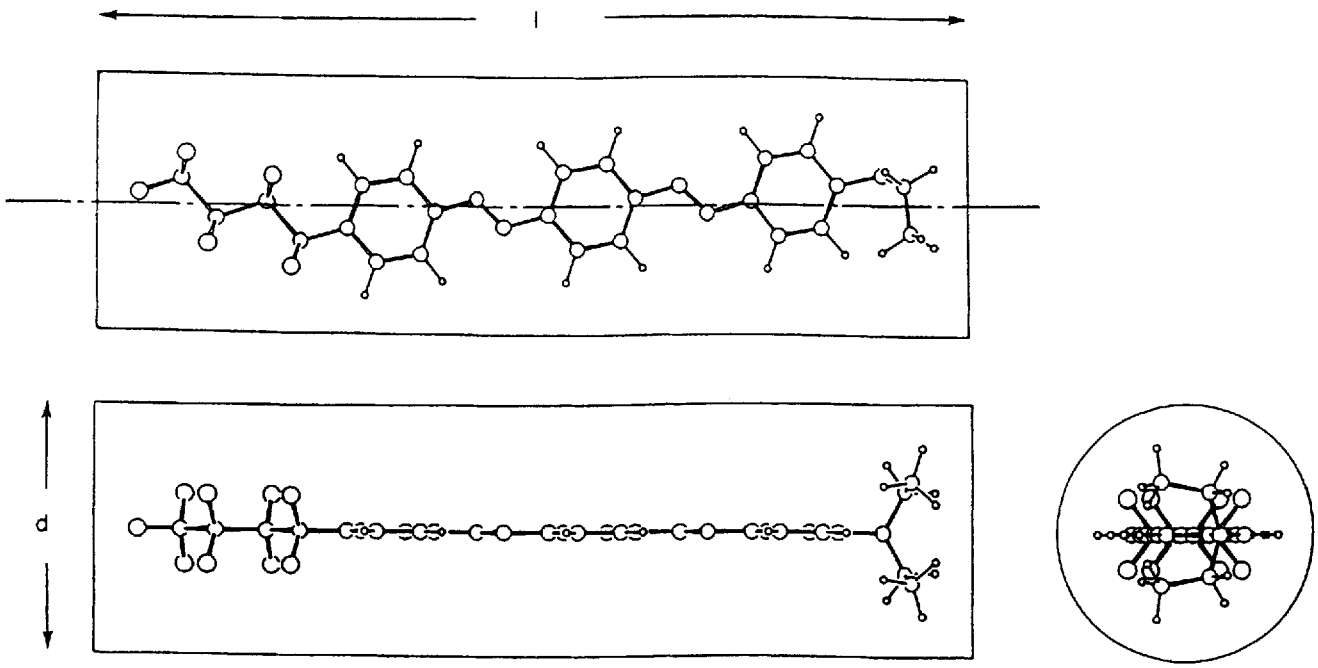


Figure 2. Calculation of *l*/*d* ratio of azo dye **4c**.

spectrometers. UV spectra were recorded on a Shimadzu 160-A spectrometer.

4.1. *Materials*

4-Butylaniline (**1b**) and 4-aminoazobenzene (**3a**) were purchased from Tokyo Kasei Co. Ltd.

4.2. *Synthesis of anilines **1i–m***

To a DMF solution (20 ml) of thiophenol (24 mmol) was added sodium hydride (720 mg, 30 mmol). The mixture was stirred for 3 h at room temperature. Perfluoroalkyl iodide (30 mmol) was added to the solution and stirred under a nitrogen atmosphere at room temperature overnight. The mixture was poured into water (150 ml), the product extracted with ether (100 ml × 2), washed with brine and dried over anhydrous sodium sulphate. After evaporation of the solvent, the product was distilled under reduced pressure. Physical and spectral data are given below.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylthio)aniline (**1i**). Yield 73 per cent; b.p. 114–116°C/200 Pa. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2·31 (tt, J = 16·8 and 8·2 Hz, 2 H), 2·93 (tt, J = 8·2 and 3·2 Hz, 2 H), 3·75 (br s, 2 H), 6·65 (d, J = 8·5 Hz, 2 H), 7·62 (d, J = 8·5 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 371 $[M]^+$ (100), 124 (88).

4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctylthio)aniline (**1j**). Yield 55 per cent; b.p. 119–120°C/170 Pa. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2·32 (tt, J = 17·7 and 8·2 Hz, 2 H), 2·93 (tt, J = 8·2 and 3·1 Hz, 2 H), 3·72 (br s, 2 H), 6·63 (d, J = 8·2 Hz, 2 H), 7·26 (d, J = 8·2 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 471 $[M]^+$ (25), 124 (100).

4-(Perfluorobutylthio)aniline (**1k**). Yield 87 per cent; b.p. 80°C/130 Pa. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3·96 (br s, 2 H), 6·59 (d, J = 8·6 Hz, 2 H), 7·38 (d, J = 8·6 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 343 $[M]^+$ (69), 124 (100).

4-(Perfluorohexylthio)aniline (**1l**). Yield 54 per cent; b.p. 100–102°C/260 Pa. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3·78 (br s, 2 H), 6·59 (d, J = 8·5 Hz, 2 H), 7·37 (d, J = 8·5 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 443 $[M]^+$ (12), 124 (100), 69 (30).

4-(Perfluorooctylthio)aniline (**1m**). Yield 51 per cent; b.p. 99–101°C/130 Pa. m.p. 37·0–38·0°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3·87 (br s, 2 H), 6·62 (d, J = 8·6 Hz, 2 H), 7·39 (d, J = 8·6 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 543 $[M]^+$ (45), 124 (100).

4.3. *Synthesis of 4-nitroazobenzenes **2b–m***

To an acetic acid solution (10 ml) of aniline **1** (0·80 mmol) was added 4-nitrosonitrobenzene (122 mg, 0·80 mmol) and stirred overnight at room temperature. The resulting precipitate was filtered, washed with water, dried and purified by column chromatography. Physical and spectral data are shown below.

4-Butyl-4′-nitroazobenzene (**2b**). Yield 98 per cent; m.p. 77–78°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·95 (t, J = 7·4 Hz, 3 H), 1·39 (sextet, J = 7·4 Hz, 2 H), 1·66 (quintet, J = 7·4 Hz, 2 H), 2·71 (t, J = 7·4 Hz, 2 H), 7·35 (d, J = 8·5 Hz, 2 H), 7·89 (d, J = 8·5 Hz, 2 H), 8·00 (d, J = 9·2 Hz, 2 H), 8·36 (d, J = 9·2 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 283 $[M]^+$ (53), 161 (26), 133 (100).

4-Nitro-4′-(perfluorobutyl)azobenzene (**2c**). Yield 60 per cent; m.p. 143–144°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·80 (d, J = 8·4 Hz, 2 H), 8·07 (d, J = 8·4 Hz 2 H), 8·09 (d, J = 9·2 Hz, 2 H), 8·42 (d, J = 9·2 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 445 $[M]^+$ (54), 150 (39), 122 (100).

4-Nitro-4′-(perfluorohexyl)azobenzene (**2d**). Yield 73 per cent; m.p. 152–153°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·80 (d, J = 8·6 Hz, 2 H), 8·07 (d, J = 8·6 Hz, 2 H), 8·10 (d, J = 9·0 Hz, 2 H), 8·42 (d, J = 9·0 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 545 $[M]^+$ (5), 395 (100).

4-Nitro-4′-(perfluorooctyl)azobenzene (**2e**). Yield 83 per cent; m.p. 157–158°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·80 (d, J = 9·2 Hz, 2 H), 8·09 (d, J = 9·2 Hz, 4 H), 8·42 (d, J = 9·2 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 645 $[M]^+$ (18), 122 (100), 76 (34).

4-Butylthio-4′-nitroazobenzene (**2f**). Yield 56 per cent; m.p. 87–89°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·97 (t, J = 7·3 Hz, 3 H), 1·47–1·55 (m, 2 H), 1·67–1·76 (m, 2 H), 3·04 (t, J = 7·3 Hz, 2 H), 7·39 (d, J = 8·8 Hz, 2 H), 7·90 (d, J = 8·8 Hz, 2 H), 8·01 (d, J = 9·2 Hz, 2 H), 8·37 (d, J = 9·2 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 315 $[M]^+$ (82), 193 (15), 165 (100).

4-(Hexylthio)-4′-nitroazobenzene (**2g**). Yield 87 per cent; m.p. 72–74°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·91 (t, J = 7·3 Hz, 3 H), 1·31–1·53 (m, 6 H), 1·74 (sextet, J = 7·3 Hz, 2 H), 3·03 (t, J = 7·3 Hz, 2 H), 7·39 (d, J = 8·5 Hz, 2 H), 7·89 (d, J = 8·5 Hz, 2 H), 8·00 (d, J = 9·2 Hz, 2 H), 8·37 (d, J = 9·2 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 343 $[M]^+$ (60), 193 (69), 122 (39), 55 (100).

4-Nitro-4′-(octylthio)azobenzene (**2h**). Yield 83 per cent; m.p. 63–64°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·87 (t, J = 7·5 Hz, 3 H), 1·26–1·52 (m, 10 H), 1·73 (sextet, J = 7·5 Hz, 2 H), 3·03 (t, J = 7·5 Hz, 2 H), 7·39 (d, J = 8·6 Hz, 2 H), 7·89 (d, J = 8·6 Hz, 2 H), 8·00 (d, J = 8·9 Hz, 2 H), 8·37 (d, J = 8·9 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 371 $[M]^+$ (56), 69 (100).

4-Nitro-4′-(1*H*,1*H*,2*H*,2*H*-perfluorohexylthio)azobenzene (**2i**). Yield 83 per cent; m.p. 119–121°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2·49 (tt, J = 16·5 and 8·2 Hz, 2 H), 3·26 (tt, J = 8·2 and 3·2 Hz, 2 H), 7·45 (d, J = 8·8 Hz, 2 H), 7·96 (d, J = 8·8 Hz, 2 H), 8·03 (d, J = 9·1 Hz, 2 H), 8·39 (d, J = 9·1 Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 505 $[M]^+$ (52), 355 (100), 122 (22).

4-Nitro-4′-(1*H*,1*H*,2*H*,2*H*-perfluorooctylthio)azobenzene (**2j**). Yield 74 per cent; m.p. 129–130°C. ^{1}H NMR

(400 MHz, $CDCl_3$) $\delta = 2{\cdot}49$ (tt, $J = 16{\cdot}8$ and $8{\cdot}1$ Hz, 2 H), 3·26 (tt, $J = 8{\cdot}1$ and $3{\cdot}1$ Hz, 2 H), 7·45 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·96 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·03 (d, $J = 9{\cdot}0$ Hz, 2 H), 8·39 (d, $J = 9{\cdot}0$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 605 $[M]^+$ (30), 455 (100), 122 (63).

4-Nitro-4′-(perfluorobutylthio)azobenzene (**2k**). Yield 63 per cent; m.p. 141–142°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}85$ (d, $J = 8{\cdot}4$ Hz, 2 H), 8·01 (d, $J = 8{\cdot}4$ Hz, 2 H), 8·07 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·41 (d, $J = 8{\cdot}8$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 477 $[M]^+$ (57), 327 (90), 122 (72), 108 (100).

4-Nitro-4′-(perfluorohexylthio)azobenzene (**2l**). Yield 90 per cent; m.p. 141–143°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}85$ (d, $J = 8{\cdot}4$ Hz, 2 H), 8·01 (d, $J = 8{\cdot}4$ Hz, 2 H), 8·07 (d, $J = 9{\cdot}0$ Hz, 2 H), 8·41 (d, $J = 9{\cdot}0$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 577 $[M]^+$ (36), 108 (100), 76 (47).

4-Nitro-4′-(perfluorooctylthio)azobenzene (**2m**). Yield 64 per cent; m.p. 161–163°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}85$ (d, $J = 8{\cdot}4$ Hz, 2 H), 8·01 (d, $J = 8{\cdot}4$ Hz, 2 H), 8·07 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·41 (d, $J = 8{\cdot}8$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 677 $[M]^+$ (48), 527 (100), 108 (96).

4.4. *Synthesis of 4-(Arylazo)anilines* ***3b–m***

To an 85 per cent ethanol solution (20 ml) of 4-nitroazobenzene **2** (0·5 mmol) was added an aqueous solution (5 ml) of sodium sulphide (1 mmol) and heated at reflux for 1 h. After the reaction, the mixture was poured into water (30 ml). The resulting precipitate was filtered, washed with water, dried and purified by column chromatography. Physical and spectral data are shown below.

4-(4-Butylphenylazo)aniline (**3b**). Yield 62 per cent; m.p. 119–120°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}93$ (t, $J = 7{\cdot}3$ Hz, 3 H), 1·37 (sextet, $J = 7{\cdot}3$ Hz, 2 H), 1·63 (quintet, $J = 7{\cdot}3$ Hz, 2 H), 2·67 (t, $J = 7{\cdot}3$ Hz, 2 H), 4·76 (s, 2 H), 6·73 (d, $J = 9{\cdot}2$ Hz, 2 H), 7·28 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·76 (d, $J = 8{\cdot}5$ Hz, 2 H) 7·84 (d, $J = 9{\cdot}2$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 253 $[M]^+$ (44), 92 (100).

4-[4-(Perfluorobutyl)phenylazo]aniline (**3c**). Yield 56 per cent; m.p. 111–113°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}16$ (br s, 2 H), 6·75 (d, $J = 8{\cdot}4$ Hz, 2 H), 7·69 (d, $J = 8{\cdot}4$ Hz, 2 H), 7·84 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·93 (d, $J = 8{\cdot}8$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 415 $[M]^+$ (22), 120 (32), 92 (100).

4-[4-(Perfluorohexyl)phenylazo]aniline (**3d**). Yield 41 per cent; m.p. 91–93°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}02$ (s, 2 H), 6·67 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·62 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·76 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·85 (d, $J = 8{\cdot}5$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 515 $[M]^+$ (37), 120 (51), 92 (100).

4-[4-(Perfluorooctyl)phenylazo]aniline (**3e**). Yield 42 per cent; m.p. 110–112°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}05$ (s, 2 H), 7·62 (d, $J = 8{\cdot}7$ Hz, 2 H), 7·75 (d, $J = 8{\cdot}9$ Hz, 2 H), 7·76 (d, $J = 8{\cdot}9$ Hz, 2 H), 7·85 (d, $J = 8{\cdot}7$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 615 $[M]^+$ (5), 120 (35), 92 (100).

4-[4-(Butylthio)phenylazo]aniline (**3f**). Yield 56 per cent; m.p. 87–90°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}94$ (t, $J = 7{\cdot}1$ Hz, 3 H), 1·41–1·54 (m, 2 H), 1·63–1·74 (m, 2 H), 2·99 (t, $J = 7{\cdot}1$ Hz, 2 H), 4·03 (br s, 2 H), 6·73 (d, $J = 8{\cdot}4$ Hz, 2 H), 7·37 (d, $J = 8{\cdot}6$ Hz, 2 H), 7·77 (d, $J = 8{\cdot}4$ Hz, 2 H), 7·79 (d, $J = 8{\cdot}6$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 285 $[M]^+$ (42), 92 (100).

4-[4-(Hexylthio)phenylazo]aniline (**3g**). Yield 74 per cent; m.p. 62–65°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}89$ (t, $J = 7{\cdot}1$ Hz, 3 H), 1·26–1·47 (m, 6 H), 1·68 (sextet, $J = 7{\cdot}1$ Hz, 2 H), 2·99 (t, $J = 7{\cdot}1$ Hz, 2 H), 4·05 (s, 2 H), 6·74 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·37 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·77 (d, $J = 8{\cdot}1$ Hz, 2 H), 7·80 (d, $J = 8{\cdot}1$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 313 $[M]^+$ (26), 120 (37), 92 (100).

4-[4-(Octylthio)phenylazo]aniline (**3h**). Yield 77 per cent; m.p. 66–68°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}88$ (t, $J = 7{\cdot}3$ Hz, 3 H), 1·26–1·65 (m, 10 H), 1·69 (sextet, $J = 7{\cdot}3$ Hz, 2 H), 2·97 (t, $J = 7{\cdot}3$ Hz, 2 H), 4·03 (s, 2 H), 6·73 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·37 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·77 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·79 (d, $J = 8{\cdot}5$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 341 $[M]^+$ (30), 92 (100).

4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylthio)phenylazo]-aniline (**3i**). Yield 66 per cent; m.p. 91–93°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 2{\cdot}44$ (tt, $J = 16{\cdot}6$ and $8{\cdot}1$ Hz, 2 H), 3·19 (tt, $J = 8{\cdot}1$ and $2{\cdot}9$ Hz, 2 H), 4·06 (br s, 2 H), 6·74 (d, $J = 8{\cdot}9$ Hz, 2 H), 7·43 (d, $J = 8{\cdot}7$ Hz, 2 H), 7·80 (d, $J = 8{\cdot}9$ Hz, 2 H), 7·82 (d, $J = 8{\cdot}7$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 475 $[M]^+$ (60), 120 (40), 92 (100).

4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctylthio)phenylazo]-aniline (**3j**). Yield 56 per cent; m.p. 114–115°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 2{\cdot}44$ (tt, $J = 17{\cdot}1$ and $8{\cdot}1$ Hz, 2 H), 3·19 (tt, $J = 8{\cdot}1$ and $3{\cdot}1$ Hz, 2 H), 4·06 (br s, 2 H), 6·74 (d, $J = 8{\cdot}9$ Hz, 2 H), 7·43 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·80 (d, $J = 8{\cdot}9$ Hz, 2 H), 7·82 (d, $J = 8{\cdot}5$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 575 $[M]^+$ (38), 120 (39), 92 (100).

4-[4-(Perfluorobutylthio)phenylazo]aniline (**3k**). Yield 94 per cent; m.p. 90–93°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}13$ (br s, 2 H), 6·74 (d, $J = 8{\cdot}9$ Hz, 2 H), 7·75 (d, $J = 8{\cdot}4$ Hz, 2 H), 7·83 (d, $J = 8{\cdot}9$ Hz, 2 H), 7·86 (d, $J = 8{\cdot}4$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 447 $[M]^+$ (19), 120 (35), 92 (100).

4-[4-(Perfluorohexylthio)phenylazo]aniline (**3l**). Yield 41 per cent; m.p. 110–111°C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}02$ (br s, 2 H), 6·67 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·62 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·76 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·85 (d, $J = 8{\cdot}5$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 547 $[M]^+$ (76), 120 (33), 92 (100).

4-[4-(Perfluorooctylthio)phenylazo]aniline (**3m**). Yield 57 per cent; m.p. 128–130°C. ^1H NMR (400 MHz,

$CDCl_3$) $\delta = 6{\cdot}33$ (br s, 2 H), 6·68 (d, $J = 8{\cdot}7$ Hz, 2 H), 7·70 (d, $J = 8{\cdot}7$ Hz, 2 H), 7·81–7·83 (m, 4 H). EI MS *m/z* (relative intensity, per cent): 647 $[M]^+$ (19), 120 (45), 92 (100).

4.5. *Synthesis of 4-[4-(alkylsulphonyl- and perfluoroalkylsulphonyl) phenylazo]anilines* **3n–s**

To an acetone–water mixed solution (10 ml) of aniline **1** (2 mmol) was added concentrated hydrochloric acid (6 mmol). After cooling the solution to 0°C, 20 per cent aqueous sodium nitrite solution was added (2 mmol). After 15 min, an aqueous solution of sodium anilinomethanesulphonate (2 mmol) was added and stirred for 1 h. This reaction mixture was then poured into water. After filtration, the product was heated at reflux in an aqueous solution (100 ml) of sodium hydroxide (4 g) for 5 h. After cooling the mixture, the product was extracted with dichloromethane and purified by column chromatography. Physical and spectral data are shown below.

4-[4-(Butylsulphonyl)phenylazo]aniline (**3n**). Yield 48 per cent; m.p. 154–155°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}90$ (t, $J = 7{\cdot}9$ Hz, 3 H), 1·40 (sextet, $J = 7{\cdot}9$ Hz, 2 H), 1·71 (quintet, $J = 7{\cdot}9$ Hz, 2 H), 3·12 (t, $J = 7{\cdot}9$ Hz, 2 H), 4·22 (br s, 2 H), 6·75 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·85 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·96 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·00 (d, $J = 8{\cdot}5$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 317 $[M]^+$ (88), 120 (100), 92 (98).

4-[4-(Hexylsulphonyl)phenylazo]aniline (**3o**). Yield 54 per cent; m.p. 173–174°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}85$ (t, $J = 7{\cdot}4$ Hz, 3 H), 1·24–1·27 (m, 4 H), 1·34 (q, $J = 7{\cdot}4$ Hz, 2 H), 1·72 (quintet, $J = 7{\cdot}4$ Hz, 2 H), 3·12 (t, $J = 7{\cdot}9$ Hz, 2 H), 4·21 (br s, 2 H), 6·75 (d, $J = 8{\cdot}7$ Hz, 2 H), 7·85 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·95 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·01 (d, $J = 8{\cdot}8$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 345 $[M]^+$ (23), 120 (63), 92 (100).

4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylsulphonyl)phenylaxo]aniline (**3p**). Yield 50 per cent; m.p. 197–198°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2{\cdot}62$ (tt, $J = 18{\cdot}0$ and $8{\cdot}2$ Hz, 2 H), 3·37 (tt, $J = 8{\cdot}2$ and $4{\cdot}8$ Hz, 2 H), 4·22 (br s, 2 H), 6·76 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·86 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·02 (d, $J = 3{\cdot}0$ Hz, 4 H). EI MS *m/z* (relative intensity, per cent): 507 $[M]^+$ (18), 120 (42), 92 (100).

4-[4-(Perfluorobutylsulphonyl)phenylazo]aniline (**3q**). Yield 50 per cent; m.p. 90–92°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}28$ (br s, 2 H), 6·75 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·87 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·02 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·12 (d, $J = 8{\cdot}7$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 479 $[M]^+$ (7), 120 (25), 92 (100).

4-[4-(Perfluorohexylsulphonyl)phenylazo]aniline (**3r**). Yield 27 per cent; m.p. 133–135°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}27$ (br s, 2 H), 6·75 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·87 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·03 (d, $J = 8{\cdot}4$ Hz, 2 H), 8·13 (d, $J = 8{\cdot}4$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 579 $[M]^+$ (30), 120 (55), 92 (100).

4-[4-(Perfluorooctylsulphonyl)phenylazo]aniline (**3s**). Yield 44 per cent; m.p. 160–161°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}27$ (br s, 2 H), 6·75 (d, $J = 8{\cdot}7$ Hz, 2 H), 7·87 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·03 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·13 (d, $J = 8{\cdot}7$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 678 $[M]^+$ (1), 120 (45), 92 (100), 65 (20).

4.6. *Synthesis of 4-arylazo-1-naphthylamines* **6**

To an aqueous solution (50 ml) of aniline **1** (10 mmol) and concentrated hydrochloric acid (2·5 ml, 30 mmol) was added a 20 per cent aqueous solution of sodium nitrite (0·7 g, 10 mmol) at 0°C. The mixture was stirred for 3 h at 0°C. To the suspension was added an acetic acid–water ($AcOH : H_2O = 2 : 1$) mixed solution (30 ml) of 1-naphthylamine (1·5 g, 10 mmol) and stirred overnight at 0–20°C. After the reaction, the suspension was neutralized with a dilute aqueous sodium hydroxide solution. The resulting precipitate was filtered, dried, purified by column chromatography (SiO_2, $CHCl_3$), and recrystallized from hexane. Physical and spectral data are shown below.

4-Phenylazo-1-naphthylamine (**6a**). Yield 73 per cent; m.p. 122–124°C (lit. [12] 123°C).

4-(4-Butylphenylazo)-1-naphthylamine (**6b**). Yield 80 per cent; m.p. 64–66°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}95$ (t, $J = 7{\cdot}0$ Hz, 3 H), 1·35–1·43 (m, 2 H), 1·63–1·68 (m, 2 H), 2·69 (t, $J = 7{\cdot}0$ Hz, 2 H), 4·55 (s, 2 H), 6·81 (d, $J = 8{\cdot}4$ Hz, 1 H), 7·32 (d, $J = 7{\cdot}3$ Hz, 2 H), 7·53–7·56 (m, 1 H), 7·60–7·63 (m, 1 H), 7·81 (d, $J = 8{\cdot}4$ Hz, 1 H), 7·89 (d, $J = 7{\cdot}3$ Hz, 2 H), 7·90 (d, $J = 8{\cdot}1$ Hz, 1 H), 9·04 (d, $J = 8{\cdot}1$ Hz, 1 H). EI MS *m/z* (relative intensity, per cent): 303 $[M]^+$ (63), 142 (100).

4-[4-(Perfluorobutyl)phenylazo]-1-naphthylamine (**6c**). Yield 23 per cent; m.p. 140–143°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}72$ (br s, 2 H), 6·83 (d, $J = 8{\cdot}4$ Hz, 1 H), 7·54–7·60 (m, 1 H), 7·64–7·71 (m, 1 H), 7·74 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·83 (d, $J = 8{\cdot}4$ Hz, 1 H), 7·99 (d, $J = 8{\cdot}4$ Hz, 1 H), 8·06 (d, $J = 8{\cdot}8$ Hz, 2 H), 9·05 (d, $J = 8{\cdot}4$ Hz, 1 H). EI MS *m/z* (relative intensity, per cent): 465 $[M]^+$ (55), 142 (100).

4-[4-(Butylthio)phenylazo]-1-naphthylamine (**6f**). Yield 83 per cent; m.p. 79–81°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}95$ (t, $J = 7{\cdot}4$ Hz, 3 H), 1·49 (sextet, $J = 7{\cdot}4$ Hz, 2 H), 1·71 (quintet, $J = 7{\cdot}4$ Hz, 2 H), 3·01 (t, $J = 7{\cdot}4$ Hz, 2 H), 4·60 (s, 2 H), 6·82 (d, $J = 7{\cdot}3$ Hz, 1 H), 7·42 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·56 (t, $J = 7{\cdot}3$ Hz, 1 H), 7·63 (t, $J = 7{\cdot}3$ Hz, 1 H), 7·83 (d, $J = 7{\cdot}3$ Hz, 1 H), 7·92 (d, $J = 7{\cdot}3$ Hz, 1 H), 7·92 (d, $J = 8{\cdot}5$ Hz, 2 H), 9·04 (d, $J = 7{\cdot}3$ Hz, 1 H). EI MS *m/z* (relative intensity, per cent): 335 $[M]^+$ (95), 142 (100).

4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylthio)phenylazo]-1-naphthylamine (**6i**). Yield 81 per cent; m.p. 89–91°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2{\cdot}46$ (tt, $J = 16{\cdot}5$ and $8{\cdot}2$ Hz, 2 H), 3·21 (tt, $J = 8{\cdot}2$ and $3{\cdot}1$ Hz, 2 H), 4·46 (s,

2 H), 6·82 (d, J = 7·9 Hz, 1 H), 7·47 (d, J = 8·9 Hz, 2 H), 7·55 (t, J = 7·9 Hz, 1 H), 7·65 (t, J = 7·9 Hz, 1 H), 7·83 (d, J = 7·9 Hz, 1 H), 7·94 (d, J = 7·9 Hz, 1 H), 7·95 (d, J = 8·9 Hz, 2 H), 9·04 (d, J = 7·9 Hz, 1 H). EI MS m/z (relative intensity, per cent): 525 $[M]^+$ (97), 142 (100), 69 (16).

4-[4-(Perfluorobutylthio)phenylazo]-1-naphthylamine (**6k**). Yield 55 per cent; m.p. 146–148°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4·72 (br s, 2 H), 6·82 (d, J = 8·2 Hz, 1 H), 7·53–7·59 (m, 1 H), 7·64–7·69 (m, 1 H), 7·80 (d, J = 8·5 Hz, 2 H), 7·82 (d, J = 8·2 Hz, 1 H), 7·98 (d, J = 8·5 Hz, 2 H), 7·99 (d, J = 8·2 Hz, 1 H), 9·04 (d, J = 8·2 Hz, 1 H). EI MS m/z (relative intensity, per cent): 497 $[M]^+$ (37), 142 (100).

4-[4-(Perfluorooctylthio)phenylazo]-1-naphthylamine (**6m**). Yield 30 per cent; m.p. 147–149°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4·73 (br s, 2 H), 6·82 (d, J = 8·4 Hz, 1 H), 7·53–7·59 (m, 1 H), 7·63–7·69 (m, 1 H), 7·79 (d, J = 8·8 Hz, 2 H), 7·84 (d, J = 8·4 Hz, 1 H), 7·98 (d, J = 8·4 Hz, 1 H), 7·99 (d, J = 8·8 Hz, 2 H), 9·04 (d, J = 8·4 Hz, 1 H). EI MS m/z (relative intensity, per cent): 697 $[M]^+$ (24), 142 (100).

4-[4-(Butylsulphonyl)phenylazo]-1-naphthylamine (**6n**). Yield 46 per cent; m.p. 125–126°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·90 (t, J = 7·7 Hz, 3 H), 1·41 (sextet, J = 7·7 Hz, 2 H), 1·73 (quintet, J = 7·7 Hz, 2 H), 3·14 (t, J = 7·7 Hz, 2 H), 4·83 (br s, 2 H), 6·80 (d, J = 8·3 Hz, 1 H), 7·55 (t, J = 7·0 Hz, 1 H), 7·67 (t, J = 7·0 Hz, 1 H), 7·82 (d, J = 8·3 Hz, 1 H), 7·98–8·05 (m, 5 H), 9·03 (d, J = 8·3 Hz, 1 H). EI MS m/z (relative intensity, per cent): 367 $[M]^+$ (33), 142 (100).

4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylsulphonyl)phenylazo]-1-naphthylamine (**6p**). Yield 54 per cent; m.p. 184–185°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2·64 (tt, J = 17·4 and 8·3 Hz, 2 H), 3·37 (tt, J = 8·3 and 3·5 Hz, 2 H), 4·83 (br s, 2 H), 6·83 (d, J = 8·3 Hz, 1 H), 7·41–7·47 (m, 1 H), 7·55–7·61 (m, 1 H), 7·70 (d, J = 8·7 Hz, 1 H), 7·79–7·85 (m, 1 H), 8·03–8·17 (m, 4 H), 9·04 (d, J = 8·3 Hz, 1 H). EI MS m/z (relative intensity, per cent): 557 $[M]^+$ (14), 142 (100).

4-[4-(Perfluorobutylsulphonyl)phenylazo]-1-naphthylamine (**6q**). Yield 50 per cent; m.p. 114–115°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4·92 (br s, 2 H), 6·86 (d, J = 8·2 Hz, 1 H), 7·55–7·65 (m, 1 H), 7·67–7·77 (m, 1 H), 7·84 (d, J = 9·4 Hz, 1 H), 8·06 (d, J = 9·4 Hz, 1 H), 8·16 (d, J = 6·7 Hz, 2 H), 8·21 (d, J = 6·7 Hz, 2 H), 9·04 (d, J = 8·2 Hz, 1 H). EI MS m/z (relative intensity, per cent): 529 $[M]^+$ (16), 142 (100).

4.7. *Synthesis of disazo dyes **4**, **5**, **7** and **8***

To a DMF solution (20 ml) of 4-substituted arylamine **3** or **6** (3 mmol) and concentrated hydrochloric acid (0·8 ml, 9 mmol) was added an aqueous solution of sodium nitrite (0·2 g, 3 mmol) and stirred for 2 h at 0°C. To the suspension was added an aqueous solution (100 ml) of coupling component (3 mmol) and stirred overnight at 0–20°C. After the reaction, the resulting precipitate was filtered, dried, purified by column chromatography (SiO_2, $CHCl_3$ then AcOEt:C_6H_{14} = 1:4), and crystallized from a chloroform–hexane mixed solution. Physical and spectral data are shown below.

4-[4-(Phenylazo)phenylazo]-*N*,*N*-diethylaniline (**4a**). Yield 75 per cent; m.p. 194–195°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·24 (t, J = 7·0 Hz, 6 H), 3·47 (q, J = 7·0 Hz, 4 H), 6·64 (d, J = 9·2 Hz, 2 H), 7·47–7·56 (m, 3 H), 7·90 (d, J = 9·2 Hz, 2 H), 7·93–8·06 (m, 6 H). EI MS m/z (relative intensity, per cent): 357 $[M]^+$ (100), 342 (59), 148 (90), 77 (54).

4-[4-(4-Butylphenylazo)phenylazo]-*N*,*N*-diethylaniline (**4b**). Yield 90 per cent; m.p. 165–166°C (lit. [13] 163°C).

4-[4-[4-(Perfluorobutyl)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4c**). Yield 78 per cent; m.p. 129–130°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·26 (t, J = 7·0 Hz, 6 H), 3·48 (q, J = 7·0 Hz, 4 H), 6·75 (d, J = 9·2 Hz, 2 H), 7·76 (d, J = 8·5 Hz, 2 H), 7·90 (d, J = 9·2 Hz, 2 H), 7·98 (d, J = 8·5 Hz, 2 H), 8·01 (d, J = 8·6 Hz, 2 H), 8·07 (d, J = 8·6 Hz, 2 H). EI MS m/z (relative intensity, per cent): 575 $[M]^+$ (49), 560 (32), 148 (100). Elemental analysis calculated for $C_{26}H_{22}F_9N_5$: C, 54·27; H, 3·85; N, 12·17. Found: C, 54·16: H, 3·88; N, 12·48.

4-[4-[4-(Perfluorohexyl)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4d**). Yield 85 per cent; m.p. 153–155°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·23 (t, J = 7·1 Hz, 6 H), 3·45 (q, J = 7·1 Hz, 4 H), 6·72 (d, J = 9·2 Hz, 2 H), 7·74 (d, J = 9·2 Hz, 2 H), 7·85 (d, J = 8·9 Hz, 2 H), 7·90 (d, J = 8·9 Hz, 2 H), 7·98 (d, J = 8·9 Hz, 2 H), 8·05 (d, J = 8·9 Hz, 2 H). EI MS m/z (relative intensity, per cent): 675 $[M]^+$ (32), 660 (20), 150 (100). Elemental analysis calculated for $C_{28}H_{22}F_{13}N_5$: C, 49·79; H, 3·28; N, 10·37. Found: C, 50·01; H, 3·04; N, 10·09.

4-[4-[4-(Perfluorooctyl)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4e**). Yield 82 per cent; m.p. 143–145°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·26 (t, J = 7·0 Hz, 6 H), 3·48 (q, J = 7·0 Hz, 4 H), 6·75 (d, J = 8·7 Hz, 2 H), 7·76 (d, J = 8·7 Hz, 2 H), 7·91 (d, J = 9·2 Hz, 2 H), 7·98 (d, J = 8·9 Hz, 2 H), 8·01 (d, J = 9·2 Hz, 2 H), 8·07 (d, J = 8·9 Hz, 2 H). EI MS m/z (relative intensity, per cent): 775 $[M]^+$ (48), 760 (23), 176 (16), 148 (100), 76 (16). Elemental analysis calculated for $C_{30}H_{22}F_{17}N_5$: C, 46·46; H, 2·86; N, 9·03. Found: C, 46·68; H, 2·80; N, 9·21.

4-[4-[4-(Butylthio)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4f**). Yield 76 per cent; m.p. 163–166°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·96 (t, J = 7·3 Hz, 3 H), 1·24 (t, J = 7·1 Hz, 6 H), 1·45–1·54 (m, 2 H), 1·65–1·74 (m, 2 H), 3·02 (t, J = 7·3 Hz, 2 H), 3·47 (q, J = 7·1 Hz, 4 H), 6·74 (d, J = 9·3 Hz, 2 H), 7·39 (d, J = 8·6 Hz, 2 H), 7·87 (d, J = 8·6 Hz, 2 H), 7·89 (d, J = 9·3 Hz, 2 H), 7·94–8·03 (m, 4 H). EI MS m/z (relative intensity, per

cent): 445 $[M]^+$ (100), 148 (82). Elemental analysis calculated for $C_{26}H_{31}N_5S$: C, 70·08; H, 7·01; N, 15·72. Found: C, 69·92; H, 7·02; N, 15·78.

4-[4-[4-(Hexylthio)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4g**). Yield 89 per cent; m.p. 136–138°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·90 (t, J = 7·3 Hz, 3 H), 1·22–1·56 (m, 12 H), 1·72 (sextet, J = 7·3 Hz, 2 H), 3·01 (t, J = 7·3 Hz, 2 H), 3·47 (q, J = 7·1 Hz, 4 H), 6·74 (d, J = 8·9 Hz, 2 H), 7·39 (d, J = 8·9 Hz, 2 H), 7·87 (d, J = 8·9 Hz, 2 H), 7·89 (d, J = 8·9 Hz, 2 H), 7·95 (d, J = 8·9 Hz, 2 H), 8·01 (d, J = 8·9 Hz, 2 H). EI MS m/z (relative intensity, per cent): 473 $[M]^+$ (71), 458 (26), 148 (59), 92 (100). Elemental analysis calculated for $C_{28}H_{35}N_5S$: C, 71·00; H, 7·45; N, 14·78. Found: C, 71·25; H, 7·30; N, 14·88.

4-[4-[4-(Octylthio)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4h**). Yield 70 per cent; m.p. 127–129°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·89 (t, J = 7·5 Hz, 3 H), 1·23–1·60 (m, 16 H), 1·69 (sextet, J = 7·5 Hz, 2 H), 3·01 (t, J = 7·5 Hz, 2 H), 3·48 (q, J = 7·0 Hz, 4 H), 6·79 (d, J = 7·8 Hz, 2 H), 7·39 (d, J = 7·8 Hz, 2 H), 7·87 (d, J = 9·0 Hz, 2 H), 7·92 (d, J = 8·9 Hz, 2 H), 7·97 (d, J = 9·0 Hz, 2 H), 8·02 (d, J = 8·9 Hz, 2 H). EI MS m/z (relative intensity, per cent): 501 $[M]^+$ (100), 486 (32), 148 (76). Elemental analysis calculated for $C_{30}H_{39}N_5S$: C, 71·82; H, 7·84; N, 13·96. Found: C, 72·08; H, 7·83; N, 13·92.

4-[4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylthio)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4i**). Yield 61 per cent; m.p. 138–140°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·25 (t, J = 7·0 Hz, 6 H), 2·47 (tt, J = 18·0 and 8·2 Hz, 2 H), 3·23 (tt, J = 8·2 and 2·9 Hz, 2 H), 3·48 (q, J = 7·0 Hz, 4 H), 6·75 (d, J = 9·2 Hz, 2 H), 7·45 (d, J = 8·4 Hz, 2 H), 7·90 (d, J = 9·2 Hz, 2 H), 7·92 (d, J = 8·4 Hz, 2 H), 7·97 (d, J = 8·8 Hz, 2 H), 8·03 (d, J = 8·8 Hz, 2 H). EI MS m/z (relative intensity, per cent): 635 $[M]^+$ (40), 620 (18), 148 (100). Elemental analysis calculated for $C_{28}H_{26}F_9N_5S$: C, 52·91; H, 4·12; N, 11·02. Found: C, 53·26; H, 4·15; N, 11·29.

4-[4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctylthio)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4j**). Yield 58 per cent; m.p. 118–120°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·25 (t, J = 7·3 Hz, 6 H), 2·47 (tt, J = 17·1 and 8·2 Hz, 2 H), 3·23 (tt, J = 8·2 and 3·1 Hz, 2 H), 3·48 (q, J = 7·3 Hz, 4 H), 6·74 (d, J = 9·2 Hz, 2 H), 7·45 (d, J = 9·2 Hz, 2 H), 7·90 (d, J = 9·2 Hz, 2 H), 7·92 (d, J = 8·5 Hz, 2 H), 7·96 (d, J = 9·2 Hz, 2 H), 8·03 (d, J = 8·5 Hz, 2 H). EI MS m/z (relative intensity, per cent): 735 $[M]^+$ (95), 720 (38), 148 (100). Elemental analysis calculated for $C_{30}H_{26}F_{13}N_5S$: C, 48·98; H, 3·56; N, 9·52. Found: C, 49·47; H, 3·54; N, 9·25.

4-[4-[4-(Perfluorobutylthio)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4k**). Yield 92 per cent; m.p. 188–189°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·25 (t, J = 7·0 Hz, 6 H), 3·48 (q, J = 7·0 Hz, 4 H), 6·74 (d, J = 9·3 Hz, 2 H), 7·81 (d, J = 8·5 Hz, 2 H), 7·90 (d, J = 9·3 Hz, 2 H), 7·96 (d, J = 8·5 Hz, 2 H), 7·97 (d, J = 9·0 Hz, 2 H), 8·05 (d, J = 9·0 Hz, 2 H). EI MS m/z (relative intensity, per cent): 607 $[M]^+$ (48), 592 (27), 148 (100). Elemental analysis calculated for $C_{26}H_{22}F_9N_5S$: C, 51·40; H, 3·65; N, 11·53. Found: 51·55; H, 3·60; N, 11·56.

4-[4-[4-(Perfluorohexylthio)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4l**). Yield 84 per cent; m.p. 180–182°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·25 (t, J = 7·0 Hz, 6 H), 3·47 (q, J = 7·0 Hz, 4 H), 6·75 (d, J = 8·9 Hz, 2 H), 7·82 (d, J = 8·9 Hz, 2 H), 7·90 (d, J = 8·9 Hz, 2 H), 7·97 (d, J = 8·9 Hz, 2 H), 7·98 (d, J = 8·9 Hz, 2 H), 8·06 (d, J = 8·9 Hz, 2 H). EI MS m/z (relative intensity, per cent): 707 $[M]^+$ (8), 148 (100), 133 (34), 108 (41). Elemental analysis calculated for $C_{28}H_{22}F_{13}N_5S$: C, 47·53; H, 3·13; N, 9·90. Found: C, 47·23; H, 3·01; N, 9·96.

4-[4-[4-(Perfluorooctylthio)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4m**). Yield 39 per cent; m.p. 192–194°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·28 (t, J = 7·1 Hz, 6 H), 3·51 (q, J = 7·1 Hz, 4 H), 7·82 (d, J = 8·6 Hz, 2 H), 7·97 (d, J = 8·6 Hz, 2 H), 8·03–8·06 (m, 8 H). EI MS m/z (relative intensity, per cent): 807 $[M]^+$ (6), 148 (100). Elemental analysis calculated for $C_{30}H_{22}F_{17}N_5S$: C, 44·62; H, 2·75; N, 8·67. Found: C, 44·58; H, 2·61; N, 8·47.

4-[4-[4-(Butylsulphonyl)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4n**). Yield 42 per cent; m.p. 175–176°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·90 (t, J = 7·2 Hz, 3 H), 1·25 (t, J = 7·1 Hz, 6 H), 1·43 (sextet, J = 7·2 Hz, 2 H), 1·73 (quintet, J = 7·2 Hz, 2 H), 3·14 (t, J = 7·2 Hz, 2 H), 3·48 (q, J = 7·1 Hz, 4 H), 6·74 (d, J = 9·2 Hz, 2 H), 7·90 (d, J = 9·2 Hz, 2 H), 7·98 (d, J = 8·9 Hz, 2 H), 8·06–8·10 (m, 6 H). EI MS m/z (relative intensity, per cent): 477 $[M]^+$ (100), 462 (59), 148 (96), 133 (33).

4-[4-[4-(Hexylsulphonyl)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4o**). Yield 50 per cent; m.p. 179–180°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·86 (t, J = 7·4 Hz, 3 H), 1·23–1·28 (m, 10 H), 1·36 (sextet, J = 7·4 Hz, 2 H), 1·73 (quintet, J = 7·4 Hz, 2 H), 3·14 (t, J = 7·4 Hz, 2 H), 3·47 (q, J = 6·7 Hz, 4 H), 6·74 (d, J = 9·2 Hz, 2 H), 7·90 (d, J = 9·2 Hz, 2 H), 7·98 (d, J = 8·8 Hz, 2 H), 8·06–8·10 (m, 6 H). EI MS m/z (relative intensity, per cent): 505 $[M]^+$ (90), 490 (28), 148 (100), 133 (28).

4-[4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylsulphonyl)phenylazo]phenylazo]-*N*,*N*-diethylaniline (**4p**). Yield 15 per cent; m.p. 194–195°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·26 (t, J = 7·0 Hz, 6 H), 2·64 (tt, J = 18·0 and 8·4 Hz, 2 H), 3·39 (tt, J = 8·4 and 4·0 Hz, 2 H), 3·49 (q, J = 7·0 Hz, 4 H), 6·75 (d, J = 9·2 Hz, 2 H), 7·91 (d, J = 9·2 Hz, 2 H), 7·99 (d, J = 8·7 Hz, 2 H), 8·10 (d, J = 8·7 Hz, 2 H), 8·11 (s, 4 H). EI MS m/z (relative intensity, per cent): 667 $[M]^+$ (23), 148 (100). Elemental analysis calculated for $C_{28}H_{26}F_9N_5O_2S$: C, 50·38; H, 3·93; N, 10·49. Found: C, 50·58, H, 3·76; N, 10·23.

4- [4- [4- (Perfluorobutylsulphonyl)phenylazo] -phenylazo]-*N*,*N*-diethylaniline (**4q**). Yield 9 per cent; m.p. 222–223°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}0$ Hz, 6 H), 3·48 (q, $J = 7{\cdot}0$ Hz, 4 H), 6·75 (d, $J = 9{\cdot}1$ Hz, 2 H), 7·91 (d, $J = 9{\cdot}1$ Hz, 2 H), 7·99 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·10 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·15 (d, $J = 9{\cdot}0$ Hz, 2 H), 8·20 (d, $J = 9{\cdot}0$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 639 $[M]^+$ (100), 624 (45), 356 (26), 341 (45), 148 (82), 133 (25). Elemental analysis calculated for $C_{26}H_{22}F_9N_5O_2S$: C, 48·83; H, 3·47; N, 10·95. Found: C, 48·50; H, 3·36; N, 10·99.

4-[4-[4-(Perfluorohexylsulphonyl)phenylazo]-phenylazo]-*N*,*N*-diethylaniline (**4r**). Yield 33 per cent; m.p. 199–200°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}1$ Hz, 6 H), 3·49 (q, $J = 7{\cdot}1$ Hz, 4 H), 6·75 (d, $J = 9{\cdot}3$ Hz, 2 H), 7·91 (d, $J = 9{\cdot}3$ Hz, 2 H), 7·99 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·10 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·14 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·20 (d, $J = 8{\cdot}5$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 739 $[M]^+$ (54), 341 (40), 148 (100). Elemental analysis calculated for $C_{28}H_{22}F_{13}N_5O_2S$: C, 45·47; H, 3·00; N, 9·47. Found: C, 45·28; H, 2·97; N, 9·24.

4-[4-[4-(Perfluorooctylsulphonyl)phenylazo]-phenylazo]-*N*,*N*-diethylaniline (**4s**). Yield 6 per cent; m.p. 170–171°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}0$ Hz, 6 H), 3·49 (q, $J = 7{\cdot}0$ Hz, 4 H), 6·75 (d, $J = 9{\cdot}2$ Hz, 2 H), 7·91 (d, $J = 9{\cdot}2$ Hz, 2 H), 7·99 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·10 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·15 (d, $J = 8{\cdot}2$ Hz, 2 H), 8·20 (d, $J = 8{\cdot}2$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 839 $[M]^+$ (70), 356 (39), 341 (51), 148 (100), 76 (55). Elemental analysis calculated for $C_{30}H_{22}F_{17}N_5O_2S$: C, 42·92; H, 2·64; N, 8·34. Found: C, 43·15; H, 2·57; N, 8·53.

4-[4-[4-(Perfluorobutylthio)phenylazo]phenylazo]-*N*,*N*-dimethylaniline (**5k**). Yield 58 per cent; m.p. 169–170°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 3{\cdot}11$ (s, 6 H), 6·77 (d, $J = 9{\cdot}2$ Hz, 2 H), 7·81 (d, $J = 8{\cdot}3$ Hz, 2 H), 7·93 (d, $J = 9{\cdot}2$ Hz, 2 H), 7·97 (d, $J = 8{\cdot}3$ Hz, 2 H), 8·03 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·06 (d, $J = 8{\cdot}5$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 579 $[M]^+$ (81), 120 (100). Elemental analysis calculated for $C_{24}H_{18}F_9N_5S$: C, 49·74; H, 3·13; N, 12·09. Found: C, 49·89; H, 2·95; N, 11·98.

4-[4-[4-(Perfluorooctylthio)phenylazo]phenylazo]-*N*,*N*-dimethylaniline (**5m**). Yield 24 per cent; m.p. 149–150°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 3{\cdot}12$ (s, 6 H), 6·78 (d, $J = 9{\cdot}2$ Hz, 2 H), 7·82 (d, $J = 8{\cdot}6$ Hz, 2 H), 7·93 (d, $J = 9{\cdot}2$ Hz, 2 H), 7·97 (d, $J = 8{\cdot}6$ Hz, 2 H), 8·03 (d, $J = 10{\cdot}0$ Hz, 2 H), 8·06 (d, $J = 10{\cdot}0$ Hz, 2 H). EI MS *m/z* (relative intensity, per cent): 779 $[M]^+$ (18), 120 (100). Elemental analysis calculated for $C_{28}H_{18}F_{17}N_5S$: C, 43·14; H, 2·33; N, 8·98. Found: C, 43·17; H, 2·14; N, 8·96.

4-[4-(Phenylazo)naphthylazo]-*N*,*N*-diethylaniline (**7a**). Yield 52 per cent; m.p. 173–178°C (lit. [14] 170–171°C).

4-[4-(4-Butylphenylazo)naphthylazo]-*N*,*N*-diethylaniline (**7b**). Yield 40 per cent; m.p. 130–134°C (lit. [14] 131·5–133°C).

4-[4-[4-(Perfluorobutyl)phenylazo]naphthylazo]-*N*,*N*-diethylaniline (**7c**). Yield 15 per cent; m.p. 113–114°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}25$ (t, $J = 7{\cdot}0$ Hz, 6 H), 3·47 (q, $J = 7{\cdot}0$ Hz, 4 H), 6·76 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·68–7·72 (m, 2 H), 7·74 (d, $J = 8{\cdot}4$ Hz, 1 H), 7·78 (d, $J = 8{\cdot}4$ Hz, 1 H), 7·98 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·02 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·13 (d, $J = 8{\cdot}8$ Hz, 2 H), 9·00–9·03 (m, 2 H). EI MS *m/z* (relative intensity, per cent): 625 $[M]^+$ (100), 610 (20), 302 (18), 176 (29), 133 (55). Elemental analysis calculated for $C_{30}H_{24}F_9N_5$: C, 57·60; H, 3·87; N, 11·20. Found: C, 57·44; H, 3·91; N, 11·04.

4-[4-(4-Butylthiophenylazo)naphthylazo]-*N*,*N*-diethylaniline (**7f**). Yield 50 per cent; m.p. 141–143°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}97$ (t, $J = 7{\cdot}4$ Hz, 3 H), 1·27 (t, $J = 7{\cdot}1$ Hz, 3 H), 1·51 (sextet, $J = 7{\cdot}4$ Hz, 2 H), 1·73 (quintet, $J = 7{\cdot}4$ Hz, 2 H), 3·05 (t, $J = 7{\cdot}4$ Hz, 2 H), 3·50 (q, $J = 7{\cdot}1$ Hz, 2 H), 6·79 (d, $J = 9{\cdot}2$ Hz, 2 H), 7·44 (d, $J = 8{\cdot}6$ Hz, 2 H), 7·70 (m, 2 H), 7·87 (d, $J = 8{\cdot}6$ Hz, 1 H), 7·95 (d, $J = 8{\cdot}6$ Hz, 1 H), 8·00 (d, $J = 8{\cdot}6$ Hz, 2 H), 8·03 (d, $J = 9{\cdot}2$ Hz, 2 H), 9·01–9·03 (m, 2 H). EI MS *m/z* (relative intensity, per cent): 495 $[M]^+$ (100), 480 (11), 302 (13), 148 (87).

4-[4-[4-(1*H*, 1*H*, 2*H*, 2*H*-Perfluorohexylthio) phenylazo]naphthylazo]-*N*,*N*-diethylaniline (**7i**). Yield 56 per cent; m.p. 74–76°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}27$ (t, $J = 7{\cdot}1$ Hz, 6 H), 2·49 (tt, $J = 16{\cdot}1$ and 8·2 Hz, 2 H), 3·25 (tt, $J = 8{\cdot}2$ and 2·9 Hz, 2 H), 3·50 (q, $J = 7{\cdot}1$ Hz, 4 H), 6·78 (d, $J = 9{\cdot}3$ Hz, 2 H), 7·49 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·70–7·73 (m, 2 H), 7·87 (d, $J = 8{\cdot}3$ Hz, 1 H), 7·97 (d, $J = 8{\cdot}3$ Hz, 1 H), 8·03 (d, $J = 9{\cdot}3$ Hz, 2 H), 8·05 (d, $J = 8{\cdot}5$ Hz, 2 H), 9·00–9·03 (m, 2 H). EI MS *m/z* (relative intensity, per cent): 685 $[M]^+$ (51), 670 (6), 148 (100). Elemental analysis calculated for $C_{32}H_{28}F_9N_5S$: C, 56·06; H, 4·12; N, 10·21. Found: C, 56·35; H, 3·90; N, 9·90.

4-[4-[4-(Perfluorobutylthio)phenylazo]naphthylazo]-*N*,*N*-diethylaniline (**7k**). Yield 43 per cent; m.p. 123–126°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}1$ Hz, 6 H), 3·49 (q, $J = 7{\cdot}1$ Hz, 4 H), 6·77 (d, $J = 9{\cdot}3$ Hz, 2 H), 7·70–7·73 (m, 2 H), 7·84 (d, $J = 8{\cdot}4$ Hz, 1 H), 7·86 (d, $J = 8{\cdot}4$ Hz, 2 H), 7·98 (d, $J = 8{\cdot}4$ Hz, 1 H), 8·02 (d, $J = 9{\cdot}3$ Hz, 2 H), 8·07 (d, $J = 8{\cdot}4$ Hz, 2 H), 9·00–9·04 (m, 2 H). EI MS *m/z* (relative intensity, per cent): 657 $[M]^+$ (100), 642 (16), 148 (64). Elemental analysis calculated for $C_{30}H_{24}F_9N_5S$: C, 54·79; H, 3·68; N, 10·65. Found: C, 54·56; H, 3·56; N, 10·54.

4-[4-[4-(Perfluorooctylthio)phenylazo]naphthylazo]-*N*,*N*-diethylaniline (**7m**). Yield 15 per cent; m.p. 138–140°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}23$ (t, $J = 7{\cdot}1$ Hz, 6 H), 3·47 (q, $J = 7{\cdot}1$ Hz, 4 H), 6·74 (d, $J = 9{\cdot}4$ Hz, 2 H), 7·67–7·71 (m, 2 H), 7·81 (d, $J = 8{\cdot}4$ Hz, 1 H), 7·84 (d, $J = 8{\cdot}6$ Hz, 2 H), 7·95 (d, $J = 8{\cdot}4$ Hz, 1 H), 8·00 (d, $J = 9{\cdot}4$ Hz, 2 H), 8·04 (d, $J = 8{\cdot}6$ Hz, 2 H), 8·96–9·92 (m,

2 H). EI MS *m/z* (relative intensity, per cent): 857 $[M]^+$ (16), 842 (3), 148 (100). Elemental analysis calculated for $C_{34}H_{24}F_{17}N_5S$: C, 47·62; H, 2·82; N, 8·17. Found: C, 47·88; H, 2·55; N, 7·69.

4-[4-[4-(Butylsulphonyl)phenylazo]naphthylazo]-*N*,*N*-diethylaniline (**7n**). Yield 19 per cent; m.p. 179–180°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·89 (t, J = 7·7 Hz, 3 H), 1·27 (t, J = 7·0 Hz, 6 H), 1·43 (sextet, J = 7·7 Hz, 2 H), 1·76 (quintet, J = 7·7 Hz, 2 H), 3·16 (t, J = 7·7 Hz, 2 H), 3·49 (q, J = 7·0 Hz, 4 H), 6·78 (d, J = 9·3 Hz, 2 H), 7·70–7·77 (m, 2 H), 7·82 (d, J = 8·2 Hz, 1 H), 8·01 (d, J = 8·2 Hz, 1 H), 8·03 (d, J = 9·3 Hz, 2 H), 8·09 (d, J = 8·5 Hz, 2 H), 8·19 (d, J = 8·5 Hz, 2 H), 9·00–9·05 (m, 2 H). EI MS *m/z* (relative intensity, per cent): 527 $[M]^+$ (100), 512 (20), 148 (46).

4-[4-[4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexylsulphonyl)-phenylazo]naphthylazo]-*N*,*N*-diethylaniline (**7p**). Yield 28 per cent; m.p. 179–180°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·25 (t, J = 6·9 Hz, 6 H), 2·66 (tt, J = 17·1 and 8·5 Hz, 2 H), 3·41 (tt, J = 8·5 and 4·1 Hz, 2 H), 3·50 (q, J = 6·9 Hz, 4 H), 6·78 (d, J = 8·2 Hz, 2 H), 7·68–7·74 (m, 2 H), 7·88 (d, J = 8·1 Hz, 1 H), 8·02 (d, J = 8·8 Hz, 3 H), 8·12 (d, J = 8·6 Hz, 2 H), 8·23 (d, J = 8·6 Hz, 2 H), 9·00–9·05 (m, 2 H). EI MS *m/z* (relative intensity, per cent): 717 $[M]^+$ (100), 148 (83), 133 (29). Elemental analysis calculated for $C_{32}H_{28}F_9N_5O_2S$: C, 53·56; H, 3·93; N, 9·76. Found: C, 53·40; H, 3·87; N, 9·82.

4-[4-[4-(Perfluorobutylsulphonyl) naphthylazo] *N*,*N*-diethylaniline (**7q**). Yield 9 per cent; m.p. 100–101°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·27 (t, J = 6·9 Hz, 6 H), 3·49 (q, J = 6·9 Hz, 4 H), 6·77 (d, J = 7·5 Hz, 2 H), 7·70–7·75 (m, 2 H), 7·84 (d, J = 8·2 Hz, 1 H), 7·97 (d, J = 8·2 Hz, 1 H), 8·01 (d, J = 7·5 Hz, 2 H), 8·02 (d, J = 6·2 Hz, 2 H), 8·22 (d, J = 6·2 Hz, 2 H), 9·00–9·03 (m, 2 H). EI MS *m/z* (relative intensity, per cent): 689 $[M]^+$ (32), 406 (23), 148 (100), 133 (23). Elemental analysis calculated for $C_{30}H_{24}F_9N_5O_2S$: C, 52·25; H, 3·51; N, 10·16. Found: C, 52·16; H, 3·45; N, 9·90.

4-[4-[4-(Perfluorobutylthio)phenylazo]naphthylazo]-*N*,*N*-dimethylaniline (**8k**). Yield 41 per cent; m.p. 171–173°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3·15 (s, 6 H), 6·82 (d, J = 9·5 Hz, 2 H), 7·72–7·75 (m, 2 H), 7·85 (d, J = 8·2 Hz, 1 H), 7·88 (d, J = 9·2 Hz, 2 H), 7·99 (d, J = 8·2 Hz, 1 H), 8·06 (d, J = 9·5 Hz, 2 H), 8·09 (d, J = 9·2 Hz, 2 H), 9·00–9·05 (m, 2 H). EI MS *m/z* (relative intensity, per cent): 629 $[M]^+$ (40), 120 (100). Elemental analysis calculated for $C_{28}H_{20}F_9N_5S$: C, 53·42; H, 3·20; N, 11·12. Found: C, 53·12; H, 2·96; N, 11·24.

4.8. *Synthesis of 4-nitro-4′-(4-arylazo)azobenzenes* ***9***

To an acetic acid solution (10 ml) of 4-(arylazo)aniline **3** (0·8 mmol) was added 4-nitrosonitrobenzene (1·12 g, 0·8 mmol) and this was stirred overnight at room temperature. The resulting precipitate was filtered, washed with water, dried and purified by column chromatography. Physical and spectral data are shown below.

4-(4-Butylphenylazo)-4′-nitroazobenzene (**9b**). Yield 67 per cent; m.p. 165–167°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·96 (t, J = 7·5 Hz, 3 H), 1·40 (sextet, J = 7·5 Hz, 2 H), 1·67 (quintet, J = 7·5 Hz, 2 H), 2·71 (t, J = 7·5 Hz, 2 H), 7·35 (d, J = 8·3 Hz, 2 H), 7·90 (d, J = 8·3 Hz, 2 H), 8·04 (d, J = 8·8 Hz, 2 H), 8·11 (d, J = 8·8 Hz, 2 H), 8·40 (d, J = 8·8 Hz, 2 H), 8·50 (d, J = 8·8 Hz, 2 H). EI MS (70 eV) *m/z* (relative intensity, per cent): 387 $[M]^+$ (29), 226 (19), 133 (100), 76 (42).

4-Nitro-4′-[4-(perfluorobutyl)phenylazo]azobenzene (**9c**). Yield 80 per cent; m.p. 182–183°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·80 (d, J = 8·8 Hz, 2 H), 8·09 (d, J = 8·8 Hz, 2 H), 8·13 (d, J = 9·3 Hz, 2 H), 8·16 (d, J = 9·1 Hz, 2 H), 8·40 (d, J = 9·1 Hz, 2 H), 8·42 (d, J = 9·3 Hz, 2 H). EI MS (70 eV) *m/z* (relative intensity, per cent): 549 $[M]^+$ (21), 226 (54), 150 (49), 76 (100).

4-[4-(Butylthio)phenylazo]-4′-nitroazobenzene (**9f**). Yield 61 per cent; m.p. 177–178°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·96 (t, J = 7·3 Hz, 3 H), 1·50 (sextet, J = 7·3 Hz, 2 H), 1·72 (quintet, J = 7·3 Hz, 2 H), 3·30 (t, J = 7·3 Hz, 2 H), 7·40 (d, J = 8·5 Hz, 2 H), 7·90 (d, J = 8·5 Hz, 2 H), 8·06 (d, J = 9·5 Hz, 2 H), 8·08 (d, J = 9·5 Hz, 2 H), 8·12 (d, J = 9·0 Hz, 2 H), 8·40 (d, J = 9·0 Hz, 2 H). EI MS (70 eV) *m/z* (relative intensity, per cent): 419 $[M]^+$ (45), 165 (100), 109 (42), 76 (60).

4-Nitro-4′-[4-(perfluorobutylthio)phenylazo]azobenzene (**9k**). Yield 68 per cent; m.p. 190–191°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·85 (d, J = 8·5 Hz, 2 H), 8·01 (d, J = 8·5 Hz, 2 H), 8·10 (d, J = 9·0 Hz, 2 H), 8·14 (d, J = 9·0 Hz, 2 H), 8·15 (d, J = 9·0 Hz, 2 H), 8·42 (d, J = 9·0 Hz, 2 H). EI MS (70 eV) *m/z* (relative intensity, per cent): 581 $[M]^+$ (17), 431 (19), 327 (74), 76 (100).

4.9. *Synthesis of 4-[4-(4-arylazo)phenylazo]anilines* ***10***

To an 85 per cent ethanol solution (20 ml) of 4-[4-(arylazo)phenylazo]-4′-nitroazobenzene **9** (0·5 mmol) was added an aqueous solution (5 ml) of sodium sulphide (1 mmol) and heated at reflux for 1 h. The mixture was then filtered, washed with water, dried and purified by column chromatography. Physical and spectral data are shown below.

4-[4-[4-(4-Butylphenylazo)phenylazo]phenylazo]-aniline (**10b**). Yield 86 per cent; m.p. 149–150°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·95 (t, J = 7·5 Hz, 3 H), 1·39 (sextet, J = 7·5 Hz, 2 H), 1·66 (quintet, J = 7·5 Hz, 2 H), 2·70 (t, J = 7·5 Hz, 2 H), 4·11 (s, 2 H), 6·76 (d, J = 8·5 Hz, 2 H), 7·33 (d, J = 8·1 Hz, 2 H), 7·85 (d, J = 8·5 Hz, 2 H), 7·87 (d, J = 8·1 Hz, 2 H), 7·98 (d, J = 8·8 Hz, 2 H), 8·02 (d, J = 8·8 Hz, 2 H). EI MS (70 eV) *m/z* (relative intensity, per cent): 357 $[M]^+$ (90), 120 (85), 92 (100), 65 (33).

4-[4-[4-[4-(Perfluorobutyl)phenylazo]phenylazo]-

phenylazo]aniline (**10c**). Yield 47 per cent; m.p. 168–169°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4·14 (s, 2 H), 6·77 (d, J = 8·8 Hz, 2 H), 7·70 (d, J = 8·8 Hz, 2 H), 7·76 (d, J = 8·8 Hz, 2 H), 7·86 (d, J = 8·8 Hz, 2 H), 7·93 (d, J = 8·8 Hz, 2 H), 8·00 (d, J = 8·8 Hz, 2 H). EI MS (70 eV) m/z (relative intensity, per cent): 519 $[M]^+$ (27), 120 (50), 92 (100), 65 (36).

4-[4-[4-[4-(Butylthio)phenylazo]phenylazo]phenylazo]aniline (**10f**). Yield 84 per cent; m.p. 149–150°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·96 (t, J = 7·1 Hz, 3 H), 1·49–1·57 (m, 2 H), 1·58–1·71 (m, 2 H), 3·03 (t, J = 7·1 Hz, 2 H), 4·11 (s, 2 H), 6·76 (d, J = 8·8 Hz, 2 H), 7·40 (d, J = 8·8 Hz, 2 H), 7·85 (d, J = 9·0 Hz, 2 H), 7·88 (d, J = 9·0 Hz, 2 H), 7·99 (d, J = 9·3 Hz, 2 H), 8·02 (d, J = 9·3 Hz, 2 H). EI MS (70 eV) m/z (relative intensity, per cent): 389 $[M]^+$ (70), 196 (17), 165 (23), 92 (100).

4-[4-[4-[4-(Perfluorobutylthio)phenylazo]phenylazo]phenylazo]aniline (**10k**). Yield 81 per cent; m.p. 179–181°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4·14 (s, 2 H), 6·76 (d, J = 8·8 Hz, 2 H), 7·82 (d, J = 8·3 Hz, 2 H), 7·84 (d, J = 8·3 Hz, 2 H), 7·86 (d, J = 8·8 Hz, 2 H), 7·97 (d, J = 8·5 Hz, 2 H), 8·07 (d, J = 8·5 Hz, 2 H). EI MS (70 eV) m/z (relative intensity, per cent): 551 $[M]^+$ (27), 120 (52), 92 (100), 65 (36).

4.10. *Synthesis of 4-[4-[4-(arylazo)phenylazo]-phenylazo]-N,N-diethylanilines* **11**

To a DMF solution (20 ml) of 4-[4-(arylazo)-phenylazo]aniline **10** (3·0 mmol) and concentrated hydrochloric acid (0·8 ml, 9·0 mmol) was added an aqueous solution of sodium nitrite (0·2 g, 3·0 mmol) and stirred for 2 h at 0°C. To the suspension was added an aqueous solution of *N,N*-diethylaniline (0·45 g, 3·0 mmol) and stirred overnight between 0–20°C. The resulting precipitate was filtered, dried, purified by column chromatography and recrystallized from ethanol. Physical and spectral data are shown below.

4-[4-[4-(4-Butylphenylazo)phenylazo]phenylazo]-*N,N*-diethylaniline (**11b**). Yield 33 per cent; m.p. 191–193°C (lit. [13] 192·5°C).

4-[4-[4-[4-(Perfluorobutyl)phenylazo]phenylazo]phenylazo]-*N,N*-diethylaniline (**11c**). Yield 35 per cent; m.p. 247–249°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·25 (t, J = 7·3 Hz, 6 H), 3·48 (q, J = 7·3 Hz, 4 H), 6·75 (d, J = 7·8 Hz, 2 H), 7·78 (d, J = 7·3 Hz, 2 H), 7·90 (d, J = 7·3 Hz, 2 H), 7·92 (d, J = 7·8 Hz, 2 H), 7·99 (d, J = 8·5 Hz, 2 H), 8·01 (d, J = 7·0 Hz, 2 H), 8·09 (d, J = 7·0 Hz, 2 H), 8·11 (d, J = 8·5 Hz, 2 H). EI MS (70 eV) m/z (relative intensity, per cent): 679 $[M]^+$ (16), 148 (100), 91 (17), 76 (39). Elemental analysis calculated for $C_{32}H_{26}F_9N_7$: C, 56·56; H, 3·86; N, 14·43. Found: C, 56·36; H, 3·74; N, 14·27.

4-[4-[4-[4-(Butylthio)phenylazo]phenylazo]phenylazo]-*N,N*-diethylaniline (**11f**). Yield 83 per cent; m.p. 191–192°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0·97 (t, J = 7·3 Hz, 3 H), 1·25 (t, J = 6·9 Hz, 6 H), 1·51 (sextet, J = 7·3 Hz, 2 H), 1·71 (quintet, J = 7·3 Hz, 2 H), 3·03 (t, J = 7·3 Hz, 2 H), 3·48 (q, J = 6·9 Hz, 4 H), 6·74 (d, J = 8·2 Hz, 2 H), 7·40 (d, J = 8·2 Hz, 2 H), 7·89 (d, J = 8·7 Hz, 2 H), 7·91 (d, J = 9·0 Hz, 2 H), 7·98 (d, J = 8·7 Hz, 2 H), 8·05 (d, J = 9·0 Hz, 2 H), 8·07 (d, J = 9·0 Hz, 2 H), 8·09 (d, J = 9·0 Hz, 2 H). EI MS (70 eV) m/z (relative intensity, per cent): 549 $[M]^+$ (48), 534 (16), 148 (100), 120 (51). Elemental analysis calculated for $C_{32}H_{35}N_7S$: C, 69·91; H, 6·42; N, 17·84. Found: C, 69·75; H, 6·61; N, 17·58.

4-[4-[4-[4-(Perfluorobutylthio)phenylazo]phenylazo]phenylazo]-*N,N*-diethylaniline (**11k**). Yield 21 per cent; m.p. 242–244°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·26 (t, J = 7·0 Hz, 6 H), 3·49 (q, J = 7·0 Hz, 4 H), 6·75 (d, J = 9·1 Hz, 2 H), 7·84 (d, J = 8·5 Hz, 2 H), 7·91 (d, J = 9·1 Hz, 2 H), 7·99 (d, J = 8·5 Hz, 2 H), 8·00 (d, J = 8·5 Hz, 2 H), 8·09 (d, J = 8·5 Hz, 2 H), 8·11 (s, 4 H). EI MS (70 eV) m/z (relative intensity, per cent): 711 $[M]^+$ (20), 148 (100), 133 (29). Elemental analysis calculated for $C_{32}H_{26}F_9N_7S$: C, 54·01; H, 3·68; N, 13·78. Found: C, 53·84; H, 3·54; N, 13·72.

4.11. *Synthesis of 4-[4-[4-(perfluorobutyl)-phenylazo]phenylazo]-1-naphthylamine* (**12c**)

To a DMF solution (20 ml) of 4-[4-(perfluorobutyl)-phenylazo]aniline **3c** (1·25 g, 3·0 mmol) and concentrated hydrochloric acid (0·8 ml, 9·0 mmol) was added an aqueous solution of sodium nitrite (0·2 g, 3·0 mmol) and stirred for 2 h at 0°C. To the suspension was added an aqueous solution (100 ml) of 1-naphthylamine (0·45 g, 3·0 mmol) and stirred overnight between 0–20°C. The resulting precipitate was filtered, dried, purified by column chromatography (SiO_2, $CHCl_3$) and crystallized from a chloroform–hexane solution. Yield 58 per cent; m.p. 171–172°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4·11 (s, 2 H), 6·84 (d, J = 8·3 Hz, 2 H), 7·59 (t, J = 8·1 Hz, 1 H), 7·69 (t, J = 8·1 Hz, 1 H), 7·77 (d, J = 8·1 Hz, 1 H), 7·84 (d, J = 8·1 Hz, 1 H), 8·01 (d, J = 8·5 Hz, 2 H), 8·06 (d, J = 8·3 Hz, 2 H), 8·07–8·13 (m, 2 H), 9·10 (d, J = 8·5 Hz, 2 H). EI MS (70 eV) m/z (relative intensity, per cent): 569 $[M]^+$ (35), 142 (100).

4.12. *Synthesis of 4-[4-[4-(perfluorobutyl)phenylazo]phenylazo]naphthylazo]-N,N-diethylaniline* (**13c**)

To a DMF solution (20 ml) of 4-[4-[4-(perfluorobutyl)phenylazo]phenylazo]-1-naphthylamine **12c** (1·71 g, 3·0 mmol) and concentrated hydrochloric acid (0·8 ml, 9·0 mmol) was added an aqueous solution of sodium nitrite (0·2 g, 3·0 mmol) and stirred for 2 h at 0°C. To the suspension was added an aqueous solution (100 ml) of *N,N*-diethylaniline (0·45 g, 3·0 mmol) and stirred overnight between 0–20°C. The resulting precipitate was filtered, dried, purified by column chromato-

graphy (SiO_2, $CHCl_3$:C_6H_{14}=1:1) and recrystallized from ethanol. Yield 12 per cent; m.p. 123–124°C. ^1H NMR (400 MHz, $CDCl_3$) δ=1·27 (t, J=7·2 Hz, 6 H), 3·50 (q, J=7·2 Hz, 4 H), 6·80 (d, J=7·6 Hz, 2 H), 7·74 (t, J=7·8 Hz, 1 H), 7·77 (t, J=7·8 Hz, 1 H), 7·80 (d, J=7·8 Hz, 1 H), 7·90 (d, J=7·8 Hz, 1 H), 7·98 (d, J=7·8 Hz, 1 H), 8·00 (d, J=8·3 Hz, 2 H), 8·04 (d, J=7·6 Hz, 2 H), 8·08 (d, J=7·8 Hz, 1 H), 8·18 (d, J=8·3 Hz, 2 H), 8·24 (d, J=8·3 Hz, 2 H), 9·04 (d, J=8·3 Hz, 2 H). EI MS (70 eV) m/z (relative intensity, per cent): 729 $[M]^+$ (100), 176 (16), 148 (94). Elemental analysis calculated for $C_{36}H_{28}F_9N_7$: C, 59·26; H, 3·87; N, 13·44. Found: C, 59·10; H, 3·97; N, 13·65.

4.13. *Calculation of θ values and l/d ratios*

Both the values were calculated from the geometry of the most stable conformer optimized by the MOPAC93 program [15] by the MNDO-PM3 method [16]. On optimization of conformations, dye molecules were assumed to have Cs symmetry. Transition moments of the dyes were calculated by the CNDO/S method [17] (singlet excitation, Nishimoto–Mataga equation, and 60 CI) using the geometry obtained by the MNDO-PM3 calculation. The long axes were based on the π-conjugation system of dyes.

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