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Synthesis of fluorine-containing disazo dyes extended with ester linkages and their application to guest–host liquid crystal displays

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The solubility of known azo dyes was in the order of dye skeleton: trisazo and aryloxycarbonyl disazo dyes < aryloxy disazo dyes < disazo dyes. The perfluoroalkyl derivatives were synthesized and found to be more soluble than the corresponding alkyl analogues except for a series of aryloxycarbonyl disazo dyes. Dichroism (order parameter, S) was in the order of dye skeleton: disazo dyes < aryloxycarbonyl and aroyloxy disazo dyes < trisazo dyes. No marked difference in the dichroism among perfluorobutyl, hexyl and octyl derivatives was observed. All the ester-type disazo dyes showed good S values (>0.76).

1. Introduction

There is much interest in π-conjugated organic compounds, because of their functionality [1]. For positive-type dichroic dyes used in guest–host liquid crystal displays, polyazo [2], anthraquinone [3], and other dye skeletons [4] have been proposed. They are required to have both good solubility and dichroism in the liquid crytalline phase. In our previous paper [5], perfluoroalkyl-substituted azo dyes were reported to show a larger solubility than the corresponding alkyl derivatives. Phenylene disazo dyes substituted with a perfluoroalkyl group showed a large solubility ($>1.70\,\mathrm{mmol\,dm^{-3}}$) and good dichroism ($S>0.76$), while the corresponding phenylene trisazo dyes showed a lower solubility ($<0.08\,\mathrm{mmol\,dm^{-3}}$) and excellent dichroism ($S=0.82$). Large l/d ratios, where l and d represent the length of the long axis and diameter of the circumscribed cylinders of the molecule, respectively, are required to promote good dichroism. Therefore, to improve the low solubility of phenylene trisazo dyes, ester-type disazo dyes containing a perfluoroalkyl group, with a similar l/d ratio of the trisazo dyes, have been synthesized and their application to positive dichroic dyes in guest–host liquid crystal displays have been examined in this report.

2. Results and discussion

2.1. *Synthesis*

The aryloxycarbonyl disazo dyes **8** were synthesized as shown in scheme 1. The 4-(perfluoroalkyl)phenols **2** were prepared by the reaction of 4-iodophenol with perfluoroalkyl iodide in the presence of copper. The aryloxycarbonyl disazo dyes **8** were obtained by the condensation reaction of 4-aminobenzoic acid (**3**) with 4-nitrosonitrobenzene to give 4-(4-nitrophenylazo)-benzoic acid (**4**), followed by dehydration to give the acid anhydride **5**, esterification with the phenols to afford **6**, reduction of the nitro group to give aryl 4-(4-aminophenylazo)benzoates **7**, and the diazotization-coupling reaction with *N*,*N*-diethylaniline.

The synthesis of the aroyloxy disazo dyes **17** and **18e** is shown in scheme 2. The 4-(perfluoroalkyl)benzoyl chlorides **12** were prepared by the perfluoroalkylation of 4-iodotoluene **9**, followed by the oxidation of the methyl group with sodium dichromate, and chlorination of the carboxylic group with thionyl chloride.

To obtain a longer ester-type disazo dye, the pentafluorophenyl derivative **18e** was reacted with butylamine to give **19** (see scheme 3). The reactions of **18e** with other nucleophiles such as butyllithium, sodium butoxide, and sodium *1H*,*1H*,*2H*,*2H*-perfluorohexyloxide were unsuccessful giving the hydrolysed products, **16** and pentafluorobenzoic acid.

2.2. *Absorption bands*

The physical properties of the azo dyes synthesized are summarized in the table. Bathochromicity of the dyes was in the order of dye skeleton: aroyloxy disazo dyes **17** < disazo dyes **20** < aryloxycarbonyl disazo dyes

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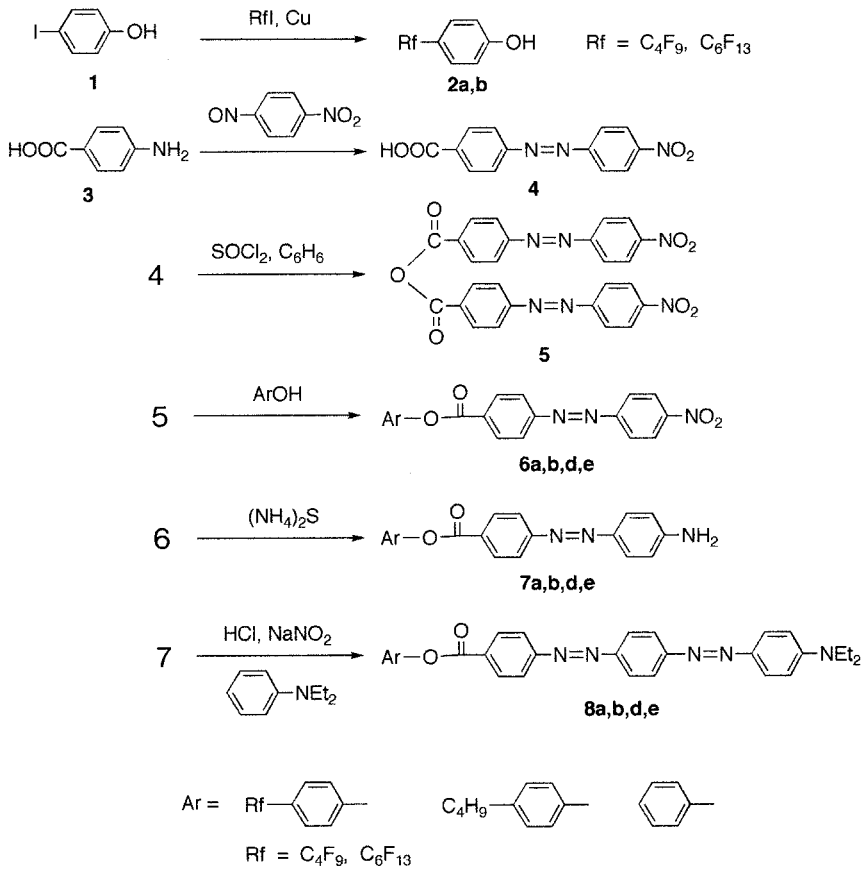


Scheme 1.

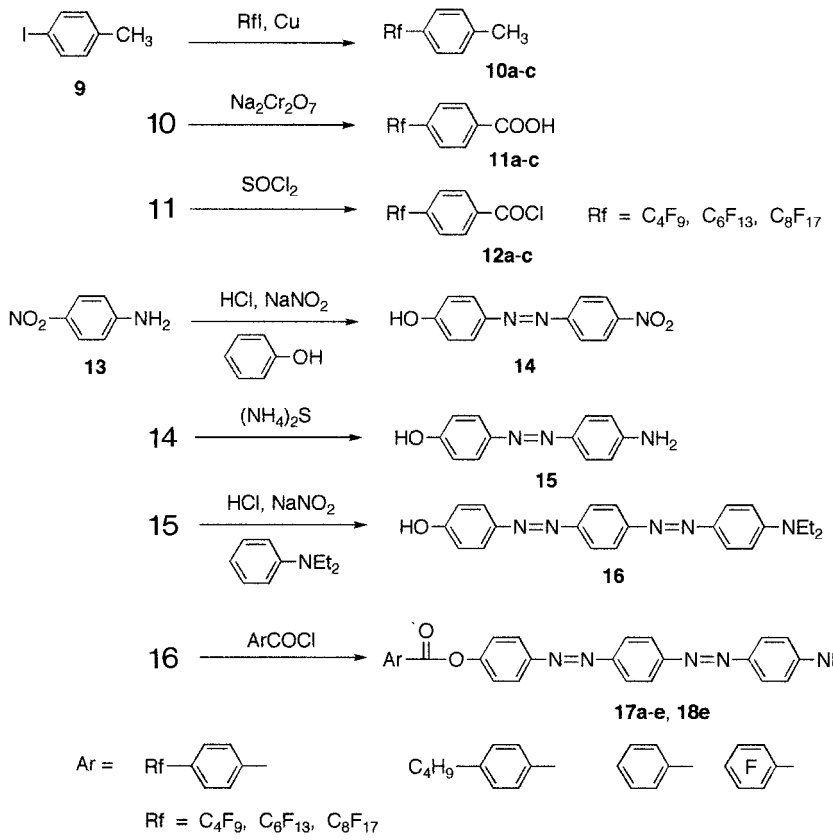
8 < trisazo dyes **21**. The trisazo dyes **21** were more bathochromic than diazo dyes **20** due to the extended π-electron system. The perfluoroalkyl derivatives were slightly more bathochromic than the alkyl analogues. For example, the absorption maxima of **17a** and **17d** were observed at 461 and 457 nm, respectively.

2.3. *Solubility*

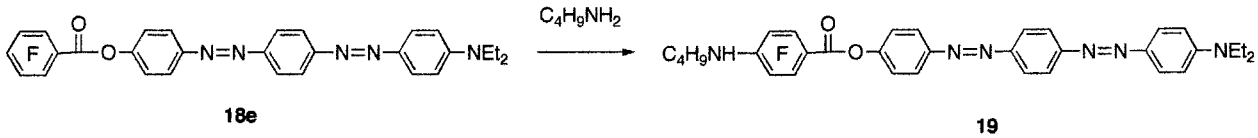
The solubility of the azo dyes was in the order of dye skeleton: trisazo dyes **21**, aryloxycarbonyl disazo dyes **8** < aroyloxy disazo dyes **17** < disazo dyes **20**. As expected, the perfluoroalkyl derivative **17a** (0·71 mmol dm^{-3}) was much more soluble that the corresponding alkyl derivative **17d** (0·16 mmol dm^{-3}). Both the affinity of the substrate to the solvent and intermolecular interaction between the substrates can affect the solubility. To examine the contribution of the affinity of the substrates to the solvents on the solubility, the org/inorg ratios of the dyes were calculated as described in the literature [6]. The relationship between the solubility and this parameter is indicated in figure 1. By the introduction of a perfluoroalkyl or pentafluorophenyl group, the org/inorg ratio decreases. In the cases of disazo **21**, aroyloxy disazo **17**, and trisazo dyes **20**, the smaller the org/inorg ratio, the larger the solubility. This indicates that the affinity of the substrate to solvents is not a major factor in the solubility of these dyes.

The melting point is a parameter of intermolecular interaction between substrates. The relationship between solubility and the melting points of the azo dyes is shown in figure 2. To obtain soluble ester-type disazo dyes, the melting point was required to be lower than 180°C. Below 180°C, the lower the melting points, the larger the solubility. Especially, in the series of aroyloxy disazo **17** and disazo dyes **20**, the melting points of the perfluoroalkyl derivatives were lower than those of unsubstituted and alkyl derivatives. The aroyloxy disazo dye **17c** was less solubles than expected, probably due to the lower lipophilicity of the perfluorooctyl substituent. The melting point of the pentafluorobenzoyloxy derivative **18e**, being more soluble than **17e**, was lower than that of the benzoyloxy derivative **17e**. While in the case of the aryloxycarbonyl dyes **8**, the melting points of the perfluoroalkyl derivatives were higher than those of unsubstituted and alkyl derivatives, resulting in lower solubilities of the perfluoroalkyl derivatives **8a** and **8b** than **8d** and **8e**.

It is concluded that the introduction of the



Scheme 2.



Scheme 3.

perfluoroalkyl group into the azo dyes can decrease intermolecular interactions between the aromatic azo moieties sufficiently to increase the solubility.

2.4. *Dichroism*

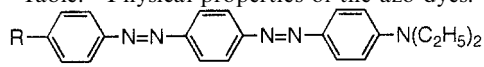
All the compounds exhibited good dichroism ($S > 0{\cdot}76$) in ZLI-4792. The S values were in the order of the dye skeleton: disazo dyes **20** < aryloxycarbonyl disazo dyes **8**, aroyloxy disazo dyes **17** < trisazo dyes **21**.

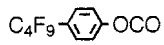
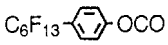
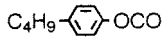
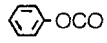
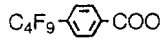
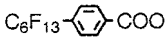
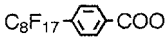
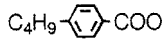
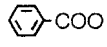
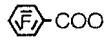
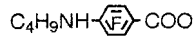
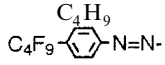
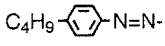
Dichroism of dyes can be theoretically analysed by calculating both the deviation of the angle (θ) between the direction of the transition moment and the long axis and *l*/*d* ratio, where *l* and *d* represent the length of the molecular long axis and the diameter of the circumscribed cylinders of the molecule, respectively. The θ values and *l*/*d* ratios of the most stable conformations were calculated as described in our previous paper [5]. These results are shown in the table. As expected, all the θ values of the azo dyes were very small ($< 3{\cdot}1°$), indicating these compounds possess good dichroism. The *l*/*d* ratios of the ester-type disazo dyes **8** and **17** and trisazo dyes **21** were larger than those of the disazo dyes **20**. No marked differences in the *l*/*d* ratios among **8**, **17** and **21** were observed. Nevertheless, the S values of the trisazo dyes **21** were larger than those of the ester-type disazo dyes **8** and **17**. This coulds be attributed to a free rotation between the C–O bonds in the ester moieties in **8** and **17** in the liquid crystal phase.

3. Conclusions

To improve the low solubility of trisazo dyes, a series of perfluoroalkyl-containing ester-type disazo dyes, with a similar *l*/*d* ratios to the trisazo dyes, have been synthesized. Aroyloxy-substituted disazo dyes were much more soluble than the trisazo dyes and showed good dichroism.

Table. Physical properties of the azo dyes.



Compound	*R*	λ_{max}/nm[a]	Solubility[b] mg/100 ml (mmol dm^{-3})	λ_{max}/nm[c]	*S*[c]	θ/°	*l*/*d*
8a		481	3 (0·05)	516	0·78	1·6	4·33
8b		481	2 (0·03)	515	0·79	1·5	4·33
8d		473	11 (0·20)	511	0·78	1·5	4·28
8e		474	3 (0·06)	508	0·77	1·5	3·68
17a		461	50 (0·71)	494	0·78	2·0	4·19
17b		462	34 (0·42)	494	0·80	2·0	4·34
17c		462	27 (0·31)	494	0·78	2·2	4·51
17d		457	8 (0·16)	492	0·76	2·3	4·23
17e		458	3 (0·06)	492	0·78	2·1	3·63
18e		462	14 (0·25)	496	0·78	3·1	3·60
19		458	1 (0·02)	494	0·77	2·1	4·30
20a[d]	C_4F_9	474	222 (3·86)	507	0·76	2·3	3·83
20d[d]	C_4H_9	453	76 (1·84)	491	0·75	2·0	3·25
21a[d]		490	5 (0·08)	527	0·82	3·1	4·45
21d[d]		477	4 (0·07)	516	0·81	2·7	4·02

[a] Measured in hexane.
[b] Measured in hexane at 25°C.
[c] Measured in ZLI-4792.
[d] Reference [5].

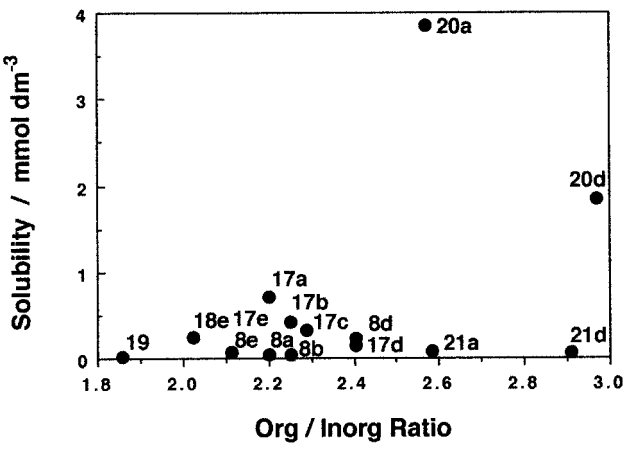


Figure 1. Relationship between solubility and *l*/*d* ratio.

4. Experimental

4.1. *Analysis*

Melting points were measured with a Yanagimoto MP-S2 micro melting point apparatus. NMR spectra were taken on a Jeol α-400 spectrometer. Mass spectra were recorded on Shimadzu QP-1000 and 9020-DF spectrometers. UV spectra were measured with a Shimadzu UV-160A spectrometer.

4.2. *Materials*

4-Iodophenol (**1**), 4-aminobenzoic acid (**3**), 4-iodotoluene (**9**) and 4-nitroaniline (**13**) were purchased from Tokyo Kasei Co., Ltd. 4-(Perfluorobutyl)toluene (**10a**) [7] and 4-nitrosonitrobenzene [8] were prepared as described in the literature.

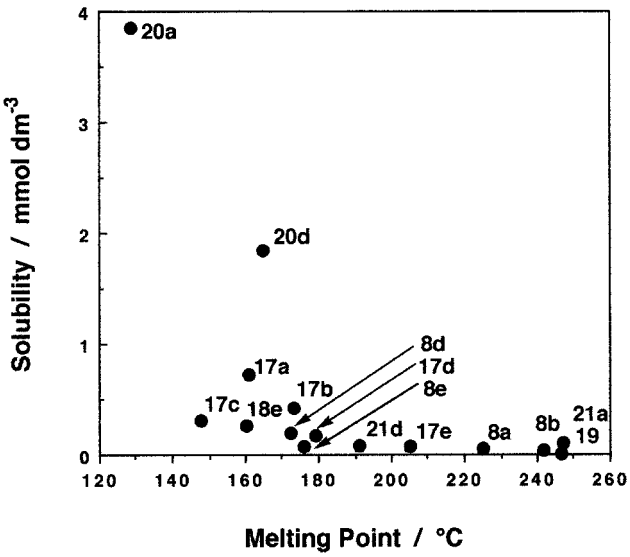


Figure 2. Relationship between solubility and melting point.

4.3. *Synthesis of the 4-(perfluoroalkyl)phenols* **2**

To a DMSO solution (40 ml) of 4-iodophenol **1** (4·4 g, 20 mmol) were added perfluoroalkyl iodide (25 mmol) and copper powder (4·3 g), and heated at 110°C overnight. After the reaction was complete, the mixture was poured into water (50 ml) and extracted with ether (50 ml × 3). The extract was dried over anhydrous sodium sulphate, filtered and the filtrate distilled under reduced pressure.

4-(Perfluorobutyl)phenol (**2a**). Yield 63 per cent; b.p. 121–124°C/40 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 5{\cdot}18$ (s, 1 H), 6·93 (d, $J = 8{\cdot}4$ Hz, 2 H), 7·47 (d, $J = 8{\cdot}4$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 312 $[M]^+$ (9), 143 (100), 95 (16), 69 (19).

4-(Perfluorohexyl)phenol (**2b**). Yield 35 per cent; b.p. 120–123°C/20 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 5{\cdot}13$ (s, 1 H), 6·93 (d, $J = 8{\cdot}8$ Hz, 2 H), 7·47 (d, $J = 8{\cdot}8$ Hz, 2 H), EI MS (70 eV) *m/z* (rel. intensity, per cent): 412 $[M]^+$ (70), 393 (26), 174 (17), 143 (100), 114 (21), 95 (25), 69 (48).

4.4. *Synthesis of 4-(4-nitrophenylazo)benzoic acid* **4**

To an acetic acid solution (70 ml) of 4-aminobenzoic acid **3** (6·9 g, 0·05 mol) was added an acetic acid solution (130 ml) of 4-nitrosonitrobenzene (7·6 g, 0·05 mol), and heated at 60°C for 6 h. After cooling, the resulting precipitate was filtered, washed with acetic acid, then recrystallized from acetic acid. Yield 94 per cent; m.p. >300°C. ^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 8{\cdot}06$ (d, $J = 8{\cdot}5$ Hz, 2 H), 8·14 (d, $J = 8{\cdot}9$ Hz, 2 H), 8·19 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·47 (d, $J = 8{\cdot}9$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 271 $[M]^+$ (35), 149 (43), 121 (97), 76 (55), 65 (100).

4.5. *Synthesis of 4-(nitrophenylazo)benzoic anhydride* **5**

To thionyl chloride (20 ml) were added 4-(4-nitrophenylazo)benzoic acid **4** (1·4 g, 5 mmol) and DMF (a few drops), and heated at reflux for 1·5 h. An excess amount of thionyl choride was removed by distillation under reduced pressure. The residue was dissolved in benzene (40 ml). The solution was added to a benzene solution (40 ml) of 4-(4-nitrophenylazo)benzoic acid **4** (1·4 g, 5 mmol) and pyridine (0·4 g, 5 mmol), and stirred at room temperature overnight. After the reaction was complete, the mixture was washed with water and a 10 per cent aqueous sodium hydrogen carbonate solution. The product was purified by column chromatography. Yield 92 per cent; m.p. 164–167°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8{\cdot}07$ (d, $J = 8{\cdot}4$ Hz, 4 H), 8·11 (d, $J = 9{\cdot}2$ Hz, 4 H), 8·32 (d, $J = 8{\cdot}4$ Hz, 4 H), 8·43 (d, $J = 9{\cdot}2$ Hz, 4 H), EI MS (70 eV) *m/z* (rel. intensity, per cent): 534 $[M]^+$ (56), 254 (100).

4.6. *Synthesis of the aryl 4-(4-nitrophenylazo)benzoates* **6**

To a benzene solution (100 ml) of 4-(nitrophenylazo)-benzoic anhydride **5** (2·48 g, 4·7 mmol) and phenol (4·7 mmol) was added conc. sulphuric acid (a few drops), and heated at reflux overnight. After the reaction was complete, the mixture was washed with water and a 10 per cent aqueous sodium hydrogen carbonate solution, and purified by column chromatography.

4-(Perfluorobutyl)phenyl 4-(4-nitrophenylazo)benzoate (**6a**). Yield 96 per cent; m.p. 134–135°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}44$ (d, $J = 8{\cdot}7$ Hz, 2 H), 7·71 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·11 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·12 (d, $J = 9{\cdot}0$ Hz, 2 H), 8·40 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·43 (d, $J = 9{\cdot}0$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 565 $[M]^+$ (6), 254 (100), 104 (30), 76 (34).

4-(Perfluorohexyl)phenyl 4-(4-nitrophenylazo)benzoate (**6b**). Yield 71 per cent; m.p. 152–154°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}44$ (d, $J = 8{\cdot}8$ Hz, 2 H), 7·71 (d, $J = 8{\cdot}8$ Hz, 2 H), 8·11 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·12 (d, $J = 9{\cdot}0$ Hz, 2 H), 8·40 (d, $J = 8{\cdot}7$ Hz, 2 H), 8·43 (d, $J = 9{\cdot}0$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 665 $[M]^+$ (2), 254 (100), 104 (34), 76 (25).

4-Butylphenyl 4-(4-nitrophenylazo)benzoate (**6d**). Yield 68 per cent; m.p. 97–98°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}95$ (t, $J = 7{\cdot}5$ Hz, 3 H), 1·39 (sextet, 7·5 Hz, 2 H), 1·63 (quintet, $J = 7{\cdot}5$ Hz, 2 H), 2·65 (t, $J = 7{\cdot}5$ Hz, 2 H), 7·15 (d, $J = 8{\cdot}5$ Hz, 2 H), 7·25 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·08 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·10 (d, $J = 9{\cdot}0$ Hz, 2 H), 8·39 (d, $J = 8{\cdot}5$ Hz, 2 H), 8·42 (d, $J = 9{\cdot}0$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 403 $[M]^+$ (6), 254 (100), 104 (24), 76 (17).

Phenyl 4-(4-nitrophenylazo)benzoate (**6e**). Yield 28 per cent; m.p. 212–214°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}25$–$7{\cdot}33$ (m, 3 H), 7·45–7·49 (m, 2 H), 8·09 (d,

$J = 8{\cdot}5$ Hz, 2H), 8·11 (d, $J = 8{\cdot}9$ Hz, 2H), 8·40 (d, $J = 8{\cdot}5$ Hz, 2H), 8·43 (d, $J = 8{\cdot}9$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 347 $[M]^+$ (11), 254 (100), 122 (14), 76 (37).

4.7. *Synthesis of the aryl 4-(4-aminophenylazo)-benzoates* **7**

An ethanol solution (150 ml) of aryl 4-(4-nitrophenylazo)benzoate **6** (1·2 mmol) and ammonium sulphide (10 mmol) was heated at reflux for 15 min. After the reaction was complete, the product was extracted with dichloromethane and purified by column chromatography.

4-(Perfluorobutyl)phenyl 4-(4-aminophenylazo)benzoate (**7a**). Yield 19 per cent; m.p. 168–170°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}18$ (br s, 2H), 6·77 (d, $J = 8{\cdot}7$ Hz, 2H), 7·42 (d, $J = 8{\cdot}2$ Hz, 2H), 7·69 (d, $J = 8{\cdot}2$ Hz, 2H), 7·87 (d, $J = 8{\cdot}7$ Hz, 2H), 7·95 (d, $J = 8{\cdot}5$ Hz, 2H), 8·31 (d, $J = 8{\cdot}5$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 535 $[M]^+$ (18), 224 (100), 92 (68), 76 (25).

4-(Perfluorohexyl)phenyl 4-(4-aminophenylazo)benzoate (**7b**). Yield 24 per cent; m.p. 169–171°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}18$ (br s, 2H), 6·77 (d, $J = 8{\cdot}5$ Hz, 2H), 7·42 (d, $J = 8{\cdot}7$ Hz, 2H), 7·69 (d, $J = 8{\cdot}7$ Hz, 2H), 7·87 (d, $J = 8{\cdot}5$ Hz, 2H), 7·95 (d, $J = 8{\cdot}5$ Hz, 2H), 8·32 (d, $J = 8{\cdot}5$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 635 $[M]^+$ (14), 224 (100), 92 (52), 76 (16).

4-Butylphenyl 4-(4-aminophenylazo)benzoate (**7d**). Yield 75 per cent; m.p. 154–156°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}95$ (t, $J = 7{\cdot}3$ Hz, 3H), 1·38 (sextet, $J = 7{\cdot}4$ Hz, 2H), 1·62 (quintet, $J = 7{\cdot}6$ Hz, 2H), 2·64 (t, $J = 7{\cdot}7$ Hz, 2H), 4·16 (br s, 2H), 6·76 (d, $J = 9{\cdot}0$ Hz, 2H), 7·14 (d, $J = 8{\cdot}7$ Hz, 2H), 7·24 (d, $J = 8{\cdot}7$ Hz, 2H), 7·86 (d, $J = 9{\cdot}0$ Hz, 2H), 7·93 (d, $J = 8{\cdot}8$ Hz, 2H), 8·31 (d, $J = 8{\cdot}8$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 373 $[M]^+$ (55), 224 (100).

Phenyl 4-(4-aminophenylazo)benzoate (**7e**). Yield 39 per cent; m.p. 180–181°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4{\cdot}15$ (br s, 2H), 6·76 (d, $J = 8{\cdot}8$ Hz, 2H), 7·24–7·31 (m, 3H), 7·43–7·47 (m, 2H), 7·87 (d, $J = 8{\cdot}8$ Hz, 2H), 7·94 (d, $J = 8{\cdot}8$ Hz, 2H), 8·32 (d, $J = 8{\cdot}8$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 317 $[M]^+$ (26), 224 (100), 92 (57), 76 (42).

4.8. *Synthesis of the 4-[4-[4-(aryloxycarbonyl)-phenylazo]phenylazo]-N,N-diethylanilines* ***8***

To an acetone–water mixed suspension (acetone: 20 ml, water: 35 ml) of aryl 4-(4-aminophenylazo)-benzoate **7** (1 mmol) was added conc. sulphuric acid (3 mmol), and heated to about 70°C. After cooling the mixture at 0°C, an aqueous solution (5 ml) of sodium nitrite (1 mmol) was added to the mixture and stirred at 0°C for 1 h. To the mixture was added an acetone solution (20 ml) of *N,N*-diethylaniline (1 mmol). The pH value of the mixture was adjusted to 5·0 by sodium acetate and stirred overnight. After the reaction was complete, the mixture was poured into water (800 ml). The resulting precipitate was filtered, dried, purified by column chromatography and crystallized from a chloroform–hexane solution.

4-[4-[4-[4-(Perfluorobutyl)phenyloxycarbonyl]phenylazo]phenylazo]-N,N-diethylaniline (**8a**). Yield 42 per cent; m.p. 225–227°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 7{\cdot}2$ Hz, 6H), 3·49 (q, $J = 7{\cdot}2$ Hz, 4H), 6·75 (d, $J = 9{\cdot}2$ Hz, 2H), 7·44 (d, $J = 8{\cdot}7$ Hz, 2H), 7·70 (d, $J = 8{\cdot}7$ Hz, 2H), 7·91 (d, $J = 8{\cdot}7$ Hz, 2H), 8·00 (d, $J = 8{\cdot}8$ Hz, 2H), 8·06 (d, $J = 8{\cdot}7$ Hz, 2H), 8·10 (d, $J = 8{\cdot}8$ Hz, 2H), 8·37 (d, $J = 8{\cdot}7$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 695 $[M]^+$ (91), 680 (15), 384 (25), 148 (100), 120 (21), 104 (28), 76 (19). Elemental analysis calculated for $C_{33}H_{26}F_9N_5O_2$: C, 56·98; H, 3·77; N, 10·07. Found: C, 56·69; H, 3·57; N, 9·77 per cent.

4-[4-[4-[4-(Perfluorohexyl)phenyloxycarbonyl]phenylazo]phenylazo]-N,N-diethylaniline (**8b**). Yield 20 per cent; m.p. 242–244°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}26$ (t, $J = 6{\cdot}7$ Hz, 6H), 3·49 (q, $J = 6{\cdot}7$ Hz, 4H), 6·75 (d, $J = 9{\cdot}3$ Hz, 2H), 7·44 (d, $J = 8{\cdot}8$ Hz, 2H), 7·70 (d, $J = 8{\cdot}8$ Hz, 2H), 7·91 (d, $J = 9{\cdot}3$ Hz, 2H), 7·99 (d, $J = 8{\cdot}8$ Hz, 2H), 8·06 (d, $J = 8{\cdot}8$ Hz, 2H), 8·10 (d, $J = 8{\cdot}8$ Hz, 2H), 8·37 (d, $J = 8{\cdot}8$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 795 $[M]^+$ (64), 780 (27), 384 (39), 185 (100), 148 (99), 104 (34), 76 (28). Elemental analysis calculated for $C_{35}H_{26}F_{13}N_5O_2$: C, 52·84; H, 3·29; N, 8·80. Found: C, 52·50; H, 3·36; N, 8·91 per cent.

4-[4-[4-[4-(Butylphenyl)oxycarbonyl]phenylazo]phenylazo]-N,N-diethylaniline (**8d**). Yield 47 per cent; m.p. 172–173°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}95$ (t, $J = 7{\cdot}5$ Hz, 3H), 1·25 (t, $J = 7{\cdot}1$ Hz, 6H), 1·39 (sextet, $J = 7{\cdot}5$ Hz, 2H), 1·63 (quintet, $J = 7{\cdot}5$ Hz, 2H), 2·65 (t, $J = 7{\cdot}5$ Hz, 2H), 3·48 (q, $J = 7{\cdot}1$ Hz, 4H), 6·75 (d, $J = 9{\cdot}0$ Hz, 2H), 7·15 (d, $J = 8{\cdot}5$ Hz, 2H), 7·25 (d, $J = 8{\cdot}5$ Hz, 2H), 7·91 (d, $J = 9{\cdot}0$ Hz, 2H), 7·99 (d, $J = 8{\cdot}5$ Hz, 2H), 8·04 (d, $J = 8{\cdot}5$ Hz, 2H), 8·09 (d, $J = 8{\cdot}5$ Hz, 2H), 8·36 (d, $J = 8{\cdot}5$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 533 $[M]^+$ (100), 518 (19), 384 (94), 148 (93), 76 (51).

4-[4-[4-(Phenyloxycarbonyl)phenylazo]phenylazo]-N,N-diethylaniline (**8e**). Yield 44 per cent; m.p. 176–178°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}25$ (t, $J = 7{\cdot}1$ Hz, 6H), 3·58 (q, $J = 7{\cdot}1$ Hz, 4H), 6·89 (d, $J = 9{\cdot}3$ Hz, 2H), 7·32–7·37 (m, 3H), 7·49–7·53 (m, 2H), 7·90 (d, $J = 9{\cdot}3$ Hz, 2H), 8·03 (d, $J = 8{\cdot}9$ Hz, 2H), 8·14 (d, $J = 8{\cdot}8$ Hz, 2H), 8·16 (d, $J = 8{\cdot}9$ Hz, 2H), 8·41 (d, $J = 8{\cdot}8$ Hz, 2H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 477 $[M]^+$ (100), 462 (41), 384 (31), 148 (81), 76 (34).

4.9. *Synthesis of the 4-(perfluoroalkyl)toluenes* ***10***

To a DMSO solution (30 ml) of 4-iodotoluene **9** (8·7 g, 40 mmol) were added copper powder (8·5 g) and

perfluoroalkyl iodide (44 mmol), and heated at 110°C for 12 h. After the reaction was complete, the mixture was poured into water and extracted with ether (50 ml × 3). The extract was dried over sodium sulphate and distilled under reduced pressure.

4-(Perfluorohexyl)toluene (**10b**). Yield 31 per cent; b.p. 93°C/19 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2·41 (s, 3 H), 7·29 (d, J = 7·9 Hz, 2 H), 7·47 (d, J = 7·9 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 410 $[M]^+$ (8), 141 (100).

4-(Perfluorooctyl)toluene (**10c**). Yield 50 per cent; b.p. 122–123°C/18 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2·35 (s, 3 H), 7·24 (d, J = 7·9 Hz, 2 H), 7·45 (d, J = 7·9 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 510 $[M]^+$ (5), 141 (100).

4.10. *Synthesis of the 4-(perfluoroalkyl)benzoic acids* ***11***

To a water–acetic acid solution (water: 30 ml, acetic acid: 170 ml) of 4-(perfluoroalkyl)toluene **10** (40 mmol) and sodium dichromate dihydrate (16·3 g, 55 mmol) was added conc. sulphuric acid (2·4 ml), and heated at reflux for 3 h. After cooling the mixture, the resulting precipitate was filtered, washed with water, then dried. The product was pure enough without further purification.

4-(Perfluorobutyl)benzoic acid (**11a**). Yield 82 per cent; m.p. 143–144°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·73 (d, J = 8·8 Hz, 2 H), 8·25 (d, J = 8·8 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 340 $[M]^+$ (10), 171 (100), 143 (25).

4-(Perfluorohexyl)benzoic acid (**11b**). Yield 41 per cent; m.p. 168–170°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·31 (d, J = 8·3 Hz, 2 H), 7·47 (d, J = 8·3 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 440 $[M]^+$ (5), 171 (100).

4-(Perfluorooctyl)benzoic acid (**11c**). Yield 82 per cent; m.p. 206–208°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·31 (d, J = 7·9 Hz, 2 H), 7·47 (d, J = 7·9 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 540 $[M]^+$ (3), 248 (61), 171 (86), 149 (100), 57 (21).

4.11. *Synthesis of the 4-(perfluoroalkyl)benzoyl chlorides* ***12***

To 4-(perfluoroalkyl)benzoic acid **11** (10 mmol) was added thionyl chloride (5 ml, 69 mmol) and heated at reflux for 4 h. After the reaction was complete, the product was distilled under reduced pressure.

4-(Perfluorobutyl)benzoyl chloride (**12a**). Yield 47 per cent; b.p. 109°C/18 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·77 (d, J = 8·2 Hz, 2 H), 8·27 (d, J = 8·2 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 323 $[M^+\text{-Cl}]$ (100), 126 (25).

4-(Perfluorohexyl)benzoyl chloride (**12b**). Yield 46 per cent; b.p. 141°C/25 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·77 (d, J = 8·6 Hz, 2 H), 8·27 (d, J = 8·6 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 423 $[M^+\text{-Cl}]$ (100), 126 (22).

4-(Perfluorooctyl)benzoyl chloride (**12c**). Yield 94 per cent; b.p. 150–152°C/25 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7·77 (d, J = 8·6 Hz, 2 H), 8·27 (d, J = 8·6 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 523 $[M^+\text{-Cl}]$ (100), 126 (50).

4.12. *Synthesis of 4-[4-(4-hydroxyphenylazo)-phenylazo]-N,N-diethylaniline* ***16***

To an aqueous solution (5 ml) of 4-(4-hydroxyphenylazo)aniline **15** (0·43 g, 2 mmol) were added conc. hydrochloric acid (0·5 ml, 6 mmol) and an aqueous solution (5 ml) of sodium nitrite (0·14 g, 2 mmol), then stirred for 2 h at 0°C. The mixture was added an acetone solution (20 ml) of *N,N*-diethylaniline (0·3 g, 2 mmol) and stirred overnight at 0°C. After the reaction was complete, the resulting precipitate was filtered and dried. The product was purified by column chromatography (SiO_2, CH_2Cl_2). Yield 31 per cent; m.p. 183–185°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), 5·56 (s, 1 H), 6·74 (d, J = 9·3 Hz, 2 H), 6·96 (d, J = 9·3 Hz, 2 H), 7·89 (d, J = 9·3 Hz, 2 H), 7·91 (d, J = 9·3 Hz, 2 H), 7·95 (d, J = 9·3 Hz, 2 H), 7·99 (d, J = 9·3 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 373 $[M]^+$ (100), 358 (22), 345 (22), 148 (30), 120 (22), 93 (20), 65 (31).

4.13. *Synthesis of the 4-[4-[4-(aroyloxy)phenylazo]-phenylazo]-N,N-diethylanilines* ***17*** *and* ***18e***

To a pyridine solution (10 ml) of 4-[4-(hydroxyphenylazo)phenylazo]-*N,N*-diethylaniline **16** (0·2 mmol) was added an acid chloride (0·5 mmol), then stirred for 3 h at room temperature. After the reaction was complete, the mixture was poured into water and extracted with dichloromethane. After drying the extract over anhydrous sodium sulphate, the product was isolated by column chromatography (SiO_2, $CH_3C_6H_5$) and crystallized from a chloroform–hexane solution.

4-[4-[4-[4-(Perfluorobutyl)benzoyloxy]phenylazo]phenylazo]-N,N-diethylaniline (**17a**). Yield 64 per cent; m.p. 161–163°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·25 (t, J = 7·2 Hz, 6 H), 3·48 (q, J = 7·2 Hz, 4 H), 6·75 (d, J = 8·9 Hz, 2 H), 7·41 (d, J = 8·9 Hz, 2 H), 7·79 (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), 8·06 (d, J = 8·9 Hz, 2 H), 8·38 (d, J = 8·9 Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 695 $[M]^+$ (5), 323 (69), 148 (100). Elemental analysis calculated for $C_{33}H_{26}F_9N_5O_2$: C, 56·98; H, 3·77; N, 10·07. Found: C, 5·15; H, 3·77; N, 10·31 per cent.

4-[4-[4-[4-(Perfluorohexyl)benzoyloxy]phenylazo]phenylazo]-N,N-diethylaniline (**17b**). Yield 46 per cent; m.p. 173–175°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1·26 (t, J = 7·3 Hz, 6 H), 3·48 (q, J = 7·3 Hz, 4 H), 6·76 (d, J = 9·2 Hz, 2 H), 7·41 (d, J = 9·2 Hz, 2 H), 7·79 (d, J = 9·2 Hz,

2 H), 7·91 (d, $J = 9·2$ Hz, 2 H), 7·98 (d, $J = 9·2$ Hz, 2 H), 8·02 (d, $J = 9·2$ Hz, 2 H), 8·05 (d, $J = 9·2$ Hz, 2 H), 8·38 (d, $J = 9·2$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 795 $[M]^+$ (8), 423 (63), 148 (100). Elemental analysis calculated for $C_{35}H_{26}F_{13}N_5O_2$: C, 52·84; H, 3·29; N, 8·80. Found: C, 52·72; H, 3·26; N, 8·64 per cent.

4-[4-[4-[4-(Perfluorooctyl)benzoyloxy]phenylazo] phenylazo]-N,N-diethylaniline (**17c**). Yield 42 per cent; m.p. 148–150°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1·25$ (t, $J = 7·1$ Hz, 6 H), 3·48 (q, $J = 7·1$Hz, 4 H), 6·75 (d, $J = 8·9$ Hz, 2 H), 7·41 (d, $J = 8·9$ Hz, 2 H), 7·79 (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), 8·05 (d, $J = 8·9$ Hz, 2 H), 8·38 (d, $J = 8·9$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 895 $[M]^+$ (2), 523 (77), 372 (26), 148 (100), 133 (31). Elemental analysis calculated for $C_{37}H_{26}F_{17}N_5O_2$: C, 49·62; H, 2·93; N, 7·82. Found: C, 49·72; H, 2·97; N, 7·61 per cent.

4-[4-[4-(4-Butylbenzoyloxy)phenylazo]phenylazo]-N,N-diethylaniline (**17d**). Yield 68 per cent; m.p. 179–181°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0·95$ (t, $J = 7·0$ Hz, 3 H), 1·25 (t, $J = 7·0$ Hz, 6 H), 1·39 (sextet, $J = 7·3$ Hz, 2 H), 1·63 (quintet, $J = 7·3$ Hz, 2 H), 2·72 (t, $J = 7·3$ Hz, 2 H), 3·48 (q, $J = 7·0$ Hz, 4 H), 6·75 (d, $J = 8·8$ Hz, 2 H), 7·34 (d, $J = 8·8$ Hz, 2 H), 7·39 (d, $J = 8·8$ Hz, 2 H), 7·90 (d, $J = 8·8$ Hz, 2 H), 7·97 (d, $J = 8·8$ Hz, 2 H), 8·03 (d, $J = 8·8$ Hz, 2 H), 8·04 (d, $J = 8·8$ Hz, 2 H), 8·14 (d, $J = 8·8$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 533 $[M]^+$ (47), 161 (100), 91 (37).

4-[4-[4-(Benzoyloxy)phenylazo]phenylazo]-N,N-diethylaniline (**17e**). Yield 67 per cent; m.p. 205–209°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1·25$ (t, $J = 7·0$ Hz, 6 H), 3·48 (q, $J = 7·0$ Hz, 4 H), 6·75 (d, $J = 8·9$ Hz, 2 H), 7·40 (d, $J = 8·9$ Hz, 2 H), 7·52—7·56 (m, 3 H), 7·90 (d, $J = 8·9$ Hz, 2 H), 7·97 (d, $J = 8·9$ Hz, 2 H), 8·03–8·06 (m, 4 H), 8·24 (d, $J = 8·9$ Hz, 2 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 477 $[M]^+$ (100), 462 (28), 148 (28), 105 (46), 77 (24).

4-[4-[4-[(Pentafluoro)benzoyloxy]phenylazo] phenylazo]-N,N-diethylaniline (**18e**). Yield 36 per cent; m.p. 160–162°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1·25$ (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), 7·42 (d, $J = 9·0$ Hz, 2 H), 7·90 (d, $J = 9·2$ Hz, 2 H), 7·97 (d, $J = 9·0$ Hz, 2 H), 8·05 (d, $J = 9·0$ Hz, 4 H). EI MS (70 eV) *m/z* (rel. intensity, per cent): 567 $[M]^+$ (45), 552 (32), 195 (56), 167 (56), 148 (100), 133 (38). Elemental analysis calculated for $C_{29}H_{22}F_5N_5O_2$: C, 61·38; H, 3·91; N, 12·34. Found: C, 61·11; H, 4.11; N, 12·40 per cent.

4.14. *Synthesis of 4-[4-[4-[4-(butylamino)-tetrafluorobenzoyloxy]phenylazo]phenylazo]-N,N-diethylaniline* ***19***

To an ethanol–dichloromethane (1 : 1) solution (60 ml) of 4-[4-[4-[(pentafluoro)benzoyloxy]phenylazo]phenylazo]-*N,N*-diethylaniline **18e** (0·34 g, 0·6 mmol) was added butylamine (0·073 g, 1 mmol), and heated at reflux for 4 h. After the reaction was complete, the product was extracted with dichloromethane, purified by column chromatography (SiO_2, $CH_3C_6H_5$), and crystallized from hexane–chloroform. Yield 23 per cent; m.p. 197–198°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0·98$ (t, $J = 7·4$ Hz, 3 H), 1·25 (t, $J = 7·1$ Hz, 6 H), 1·44 (sextet, $J = 7·4$ Hz, 2 H), 1·65 (quintet, $J = 7·4$ Hz, 2 H), 3·47 (q, $J = 7·1$ Hz, 4 H), 3·53 (q, $J = 7·1$ Hz, 2 H), 4·31 (br s, 1 H), 6·74 (d, $J = 9·3$ Hz, 2 H), 7·40 (d, $J = 8·7$ Hz, 2 H), 7·90 (d, $J = 9·3$ Hz, 2 H), 7·97 (d, $J = 8·7$ Hz, 2 H), 8·02 (d, $J = 7·1$ Hz, 2 H), 8·04 (d, $J = 7·1$ Hz, 2 H). ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) $\delta = -61·4$ (d, $J = 15·3$ Hz, 2 F), $-83·8$ (d, $J = 15·3$ Hz, 2 F). EI MS (70 eV) *m/z* (rel. intensity, per cent): 620 $[M]^+$ (6), 373 (27), 248 (100), 148 (62). Elemental analysis calculated for $C_{33}H_{32}F_4N_6O_2$: C, 63·86; H, 5·20; N, 13·54. Found: C, 63·93; H, 5·31; N, 13·58 per cent.

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