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LIQUID CRYSTALS, 1997, VOL. 23, NO. 6, 821–832

Fluorine-containing negative dichroic 1,4-bis(acylamino)anthraquinone dyes

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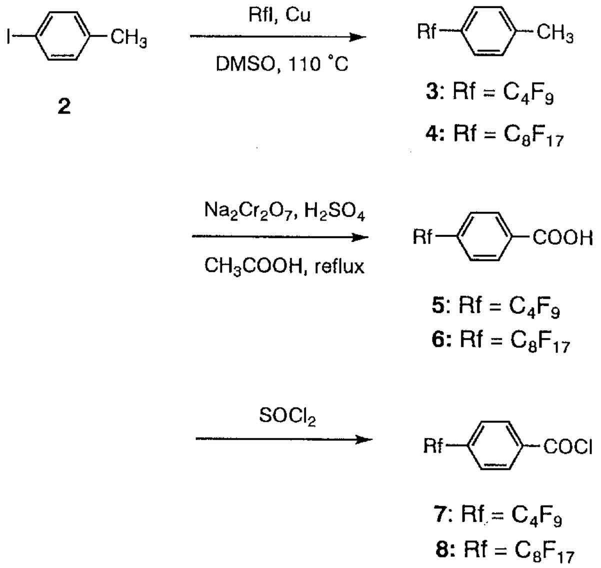
Fluorine-containing negative dichroic 1,4-bis(acylamino)anthraquinone dyes have been synthesized. The solubility of the dyes based on the acyl moieties in chloroform was in the order of hexanoyl > 4-butylbenzoyl > 3,5,6-trichloro-octafluorohexanoyl > perfluoroalkanoyl, 4-(perfluorobutyl)benzoyl, pentafluorobenzoyl, and benzoyl. The negative dichroism of the dyes was greater as the *l*/*d* ratio increased and the θ value was closer to 90°. Only some 3,5,6-trichloro-octafluorohexanoyl derivatives were sufficiently soluble. Their *S* values were $-0{\cdot}26$ to $-0{\cdot}29$ in ZLI-4792.

1. Introduction

Many dyes such as azo compounds [1], anthraquinones [2] and perylenes [3] have been proposed as positive dichroic dyes in guest-host liquid crystal displays. However, little is known about negative dichroic dyes. Only acylaminoanthraquinones [4], tetrazines [5] and azo dyes having long side chains [6] have been reported to show a negative dichroism. Although the acylamino-anthraquinones are the most interesting compounds among those reported, their solubilities in organic solvents and liquid crystals are low. The introduction of fluorine atoms and fluoroalkyl groups into organic molecules can change their properties; dichroic azo dyes containing a perfluoroalkyl group have been reported to show higher solubility than the corresponding alkyl derivatives [7]. In our continuing study of dichroic dyes in guest-host liquid crystal displays, fluorine-containing negative dichroic 1,4,-bis(acylamino)anthraquinone dyes are the subject of this report.



2. Results and discussion

2.1. *Synthesis*

4-(Perfluoroalkyl)benzoyl chlorides **7** and **8** were prepared as shown in scheme 1. 4-Iodotoluene (**2**) was reacted with perfluoroalkyl iodide in the presence of copper to give the 4-(perfluoroalkyl)toluenes **3** and **4**; this was followed by oxidation of the methyl group to afford the carboxylic acids **5** and **6**. The presence of acetic acid, in which the toluenes **3** and **4** were soluble, was necessary to allow the oxidation reaction to occur.

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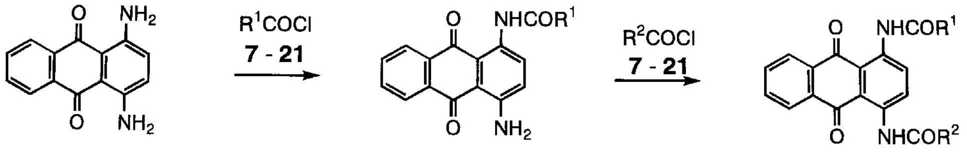
*Author for correspondence.



1 22 - 32 33 - 62

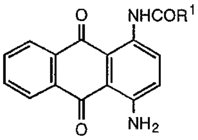
The carboxylic acids were finally treated with thionyl chloride to afford the acid chlorides **7** and **8**.

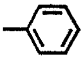
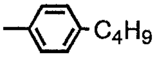
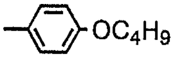
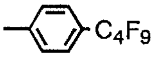
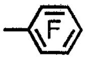
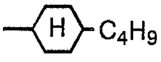
Scheme 2 shows the synthesis of the acylaminoanthraquinone dyes. 1-Acylamino-4-aminoanthraquinone dyes **22**–**32** were prepared by the reaction of 1,4-diaminoanthraquinone with an equivalent amount of the appropriate acid chlorides. The 4-bis(acylamino)anthraquinone dyes **33**–**62** were obtained by treating the 1-acylamino-4-aminoanthraquinone dyes **22**–**32** with acid chlorides.

2.2. *Absorption and fluorescence spectra*

Tables 1 and 2 summarize the physical properties of the acylaminoanthraquinone dyes **22**–**62**. In the series of 1-acylamino-4-amino- (**22**–**32**) and symmetrical 1,4-bis(acylamino)anthraquinone dyes (**33**, **37**, **41**, **44**, **45**,

Table 1. Physical properties of 1-acylamino-4-aminoanthraquinone dyes.



Compound	R^1	λ_{max}/nm[a]	ε[a]	λ_{em}/nm[b]	RFI[b]	Stokes shift nm[b]	Solubility g/100 ml (mol dm^{-3})[c]	λ_{max}/nm[d]	S[d]	l/d	θ/°
22		532	9500	597	0·18	65	0·6(0·018)	—[e]	—[e]	—[g]	—[g]
23		532	9800	593	0·15	61	11·5(0·289)	—[f]	—[f]	—[g]	—[g]
24		534	9700	599	0·21	65	9·3(0·225)	—[f]	—[f]	—[g]	—[g]
25		529	8300	596	0·20	67	6·7(0·120)	—[e]	—[e]	—[g]	—[g]
26		522	8800	587	0·27	65	0·2(0·006)	—[e]	—[e]	—[g]	—[g]
27	C_5H_{11}	526	9500	592	0·41	66	8·0(0·238)	—[f]	—[f]	—[g]	—[g]
28		527	13800	600	0·21	73	4·1(0·101)	—[f]	—[f]	—[g]	—[g]
29	$CF_2(CClFCF_2)_2Cl$	515	8900	581	0·28	66	5·9(0·101)	516	0·01	1·77	42·7
30	C_4F_9	514	8900	579	0·34	65	2·8(0·058)	471	0·25	1·56	46·6
31	C_7F_{15}	514	9200	580	0·27	66	1·3(0·021)	513	−0·03	1·92	45·1
32	C_9F_{19}	513	9100	581	0·33	68	0·5(0·007)	—[e]	—[e]	—[g]	—[g]

[a] Measured in chloroform.
[b] Measured in chloroform (1×10^{-5} mol dm^{-3}).
[c] Measured in chloroform at 25°C.
[d] Measured in ZLI-4792.
[e] Could not be measured due to low solubility in ZLI-4792.
[f] Not measured.
[g] Not calculated.

Table 2. Physical properties of 1,4-bis(acylamino)anthraquinone dyes.

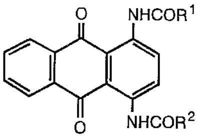
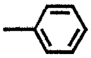
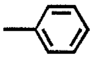
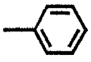
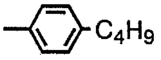
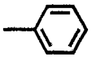
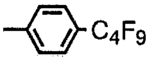
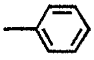
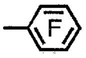
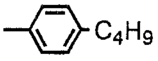
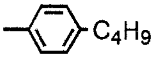
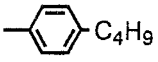
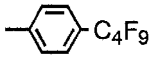
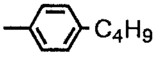
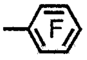
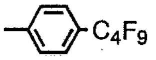
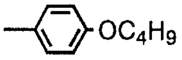
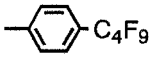
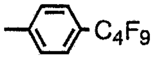
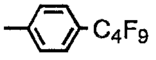
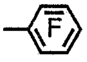
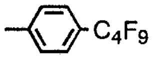
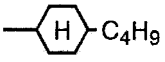
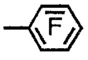


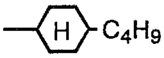
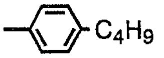
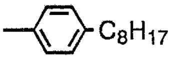
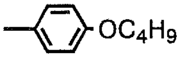
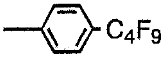
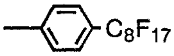
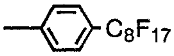
Table 2

Compound	R^1	R^2	λ_{max}/nm[a]	ε[a]	λ_{em}/nm[b]	RFI[b]	Stokes shift nm[b]	Solubility g/100 ml (mol dm^{-3})[c]	λ_{max}/nm[d]	S[d]	l/d	θ/°
33			494	8100	568	0·85	74	0·4(0·008)	—[e]	—[e]	—[f]	—[f]
34			495	7900	571	0·67	76	0·4(0·007)	—[e]	—[e]	—[f]	—[f]
35			490	5500	565	1·07	75	0·5(0·009)	—[e]	—[e]	—[f]	—[f]
36			479	8500	558	0·76	79	0·9(0·015)	—[e]	—[e]	—[f]	—[f]
37			499	8200	570	0·80	71	8·3(0·149)	506	−0·32	2·32	90·0
38			493	7800	567	1·00	74	0·9(0·013)	—[e]	—[e]	—[f]	—[f]
39			482	7900	560	0·90	78	2·8(0·047)	—[e]	—[e]	—[f]	—[f]
40			493	8400	567	0·83	74	1·0(0·014)	—[e]	—[e]	—[f]	—[f]
41			486	6200	561	1·02	75	0·1(0·001)	—[e]	—[e]	—[f]	—[f]
42			473	7500	554	1·23	81	2·3(0·031)	—[e]	—[e]	—[f]	—[f]
43			489	5900	564	1·06	75	2·1(0·029)	—[e]	—[e]	—[f]	—[f]
44			459	7600	544	1·01	85	0·7(0·010)	—[e]	—[e]	—[f]	—[f]
45	C_5H_{11}	C_5H_{11}	488	8900	564	1·00	76	26·1 (0·601)	497	−0·26	1·74	90·0
46	C_5H_{11}	$CF_2(CClFCF_2)_2Cl$	466	7300	548	1·43	82	53·9 (0·793)	475	−0·22	1·72	85·6
47	C_5H_{11}	C_4F_8H	463	7500	548	1·50	85	20·8 (0·369)	471	−0·17	1·62	87·3
48	C_5H_{11}	C_4F_9	463	8100	548	1·47	85	6·5 (0·112)	—[e]	—[e]	—[f]	—[f]
49	C_5H_{11}	C_7F_{15}	465	8700	548	1·45	83	5·0 (0·068)	473	−0·21	1·83	84·4
50	C_5H_{11}	C_9F_{19}	464	8400	547	1·56	83	1·7 (0·020)	—[e]	—[e]	—[f]	—[f]
51	$CF_2(CClFCF_2)_2Cl$	$CF_2(CClFCF_2)_2Cl$	444	7900	543	0·32	99	8·3 (0·089)	456	−0·29	1·71	90·0
52	$CF_2(CClFCF_2)_2Cl$	C_4F_9	443	7200	542	0·25	99	8·5 (0·103)	449	−0·26	1·65	88·0
53	C_4F_9	C_4F_9	441	7700	540	0·12	99	1·3 (0·018)	—[e]	—[e]	—[f]	—[f]
54	C_7F_{15}	C_7F_{15}	442	7400	539	0·19	97	0·1 (0·001)	—[e]	—[e]	—[f]	—[f]

51, **53** and **54**), the first absorption maximum based on an acyl moiety was hypsochromic in the order of perfluoroalkanoyl, 3,5,6-trichloro-octafluorohexanoyl > pentafluorobenzoyl > alkanoyl, 4-(perfluoroalkyl)benzoyl > benzoyl, 4-butylbenzoyl and 4-butoxybenzoyl. The first absorption band of 1,4-diaminoanthraquinone is

Table 2. (*Continued*).

Table 2

55	$CF_2(CClFCF_2)_2Cl$		478	8300	557	1·15	79	6·2 (0·083)	483	−0·28	1·87	88·8
56	$CF_2(CClFCF_2)_2Cl$		469	7200	545	0·76	76	5·5 (0·080)	—[e]	—[e]	—[f]	—[f]
57	$CF_2(CClFCF_2)_2Cl$		471	7000	552	1·34	81	17·6 (0·237)	483	−0·26	1·97	86·0
58	$CF_2(CClFCF_2)_2Cl$		471	7800	534	1·30	63	7·3 (0·091)	—[e]	—[e]	—[f]	—[f]
59	$CF_2(CClFCF_2)_2Cl$		467	8200	555	1·38	88	17·1 (0·226)	476	−0·29	2·05	85·3
60	$CF_2(CClFCF_2)_2Cl$		461	7600	546	1·33	85	1·8 (0·020)	—[e]	—[e]	—[f]	—[f]
61	$CF_2(CClFCF_2)_2Cl$		461	5200	544	1·09	83	0·6 (0·005)	—[e]	—[e]	—[f]	—[f]
62	$CF_2(CClFCF_2)_2Cl$		451	7500	538	1·62	87	3·7 (0·047)	—[e]	—[e]	—[f]	—[f]

[a] Measured in chloroform.
[b] Measured in chloroform (1×10^{-5} mol dm^{-3}).
[c] Measured in chloroform at 25°C.
[d] Measured in ZLI-4792.
[e] Could not be measured due to low solubility in ZLI-4792.
[f] Not measured.
[g] Not calculated.

attributed to an intramolecular charge-transfer from the amino groups to the naphthoquinone moiety [8]. Therefore, the stronger the electron-withdrawing nature of the acyl moiety, the more hypsochromic the absorption maximum. No remarkable differences in the absorption maxima among compounds **30**–**32** and between **53** and **54** were observed, suggesting the similar electron-withdrawing nature of the perfluoroalkanoyl substituents.

The acylaminoanthraquinone dyes **22**–**62** were fluorescent compounds; their emission maxima were observed at around 534–600 nm in chloroform. The Stokes shifts of the 1-acylamino-4-aminoanthraquinone dyes **22**–**32** were 61–73 nm, being slightly smaller than those of the 1,4-bis(acylamino)anthraquinone dyes **33**–**62** (63–99 nm). The relative fluorescence intensities (RFI) of dyes **33**–**62** (0·12–1·62) were mostly larger than those of **22**–**32** (0·15–0·41). Interestingly, for the hexanoyl, perfluoroalkanoyl, and 3,5,6-trichloro-octafluorohexanoyl derivatives **45**–**54**, the RFI were significantly affected by the combination of the two acyl substituents: hexanoyl plus perfluoroalkanoyl, hexanoyl plus 3,5,6-trichloro-octafluorohexanoyl > hexanoyl plus hexanoyl > 3,5,6-trichloro-octafluorohexanoyl plus 3,5,6-trichloro-octafluorohexanoyl, 3,5,6-trichloro-octafluorohexanoyl plus perfluorohexanoyl, perfluoroalkanoyl plus perfluoroalkanoyl.

2.3. *Solubility*

The solubilities of the 1-acylamino-4-aminoanthraquinone dyes **22**–**32** were in the order of the acyl group: alkanoyl, 4-butylbenzoyl and 4-butoxybenzoyl > 3,5,6-trichloro-octafluorohexanoyl, 4-(perfluorobutyl)-benzoyl > perfluoroalkanoyl, pentafluorobenzoyl, and benzoyl. A similar tendency was observed in the symmetrical 1,4-bis(acylamino)anthraquinone dyes **33**, **37**, **41**, **44**, **45**, **51**, **53** and **54**: hexanoyl > 4-butylbenzoyl > 3,5,6-trichloro-octafluorohexanoyl > perfluoroalkanoyl, 4-(perfluorobutyl)benzoyl, pentafluorobenzoyl, and benzoyl. Thus, the fluorine-containing acylamino-anthraquinone dyes were less soluble than non-fluorine-containing dyes. This could be attributed to the strong electron-withdrawing nature of the fluorine-containing acyl group(s) which decreased the electron density at the amido-nitrogen(s) to make the intermolecular hydrogen bond stronger. The longer the chain length in the perfluoroalkanoyl groups in **30**–**32**, **53** and **54**, the smaller the solubility of the dyes, probably due to the reduced lipophilicity of the long perfluoroalkyl moiety. The bulkiness of the 3,5,6-trichloro-octafluorohexanoyl group (van der Waals radius: F 1·35 Å, Cl 1·80 Å) might make the intermolecular interaction weak, resulting in the larger solubility of its derivatives, compared with the perfluoroalkanoyl derivatives. The solubilities of the unsymmetrical 1,4-bis(acylamino)anthraquinone dyes **35**, **36**, **42**, **46**, **52** and **57** were higher than the corresponding symmetrical ones **33**, **37**, **41**, **44**, **45**, **51** and **53**, respectively. To measure the order parameter (S) of the dyes in ZLI-4792, the value of the solubility in chloroform at 25°C was required to be larger than 0·5 mmol dm^{-3}.

1,4,5,8-Tetrakis[(3,5,6-trichloro-octafluorohexanoyl)-amino]anthraquinone (**63**, $\lambda_{max} = 514$ nm in $CHCl_3$) was less soluble (0·7 g/100 ml of $CHCl_3$; 0·004 mol dm^{-3}). Therefore, we could not measure its dichroism.

2.4. *Dichroism*

Dichroism (order parameter S) is defined as $S = (A_{\|} - A_{\perp})/(2A_{\|} + A_{\perp})$ where $A_{\|}$ and $A_{\perp}$ are the absorbances of light polarized parallel and perpendicular, respectively, to the direction of the alignment of the dye molecule in a liquid crystal medium. Theoretically maximal negative and positive S values are $-0{\cdot}50$ and 1·00, respectively.

Figure 1 depicts the typical negative dichroism of the acylaminoanthraquinone dyes in ZLI-4792. The S value of dye **46** was calculated to be $-0{\cdot}22$.

In the series of 1-acylamino-4-amino derivatives **29**–**31**, no significant negative dichroism ($S = 0{\cdot}25$ to $-0{\cdot}03$) was observed, while the S values of the 1,4-bis(acylamino)anthraquinone dyes **37**, **45**–**47**, **49**, **51**, **52**, **55**, **57** and **59** were measured to be $-0{\cdot}17$ to $-0{\cdot}32$.

A typical example for the MO calculation of the l/d ratio (where l and d represent the length of the long axis and diameter of the cylindrical dye molecule, respectively) and the deviation of angle θ between the direction of the transition moment and that of the long axis are shown in figure 2.

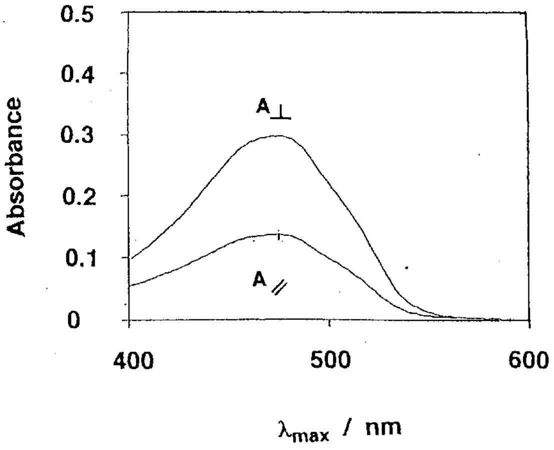


Figure 1. Dichroism of dye **46** in ZLI-4792.

For the calculation, the π-conjugated anthraquinone and aromatic moieties were assumed to be planar. The intramolecular hydrogen bond between the amido-hydrogen and the adjacent quinonoid-oxygen and the van der Waals radius were taken into account. The molecules were assumed to have Cs symmetry. The heat of all conformations of the molecules was calculated. The l and d values of dye **46** in the most stable conformation were calculated to be 23·9 and 13·9 Å, respectively, and l/d ratio being 1·72; θ was 85·6°. The relationship among S, l/d and θ values is indicated in figure 3. It is clear that the larger the l/d ratio and closer the θ value to 90°, the smaller the S value. This implies that the long and symmetrical 1,4-bis-(acylamino)anthraquinone derivatives can show a good negative dichroism. The 1,4-bis[(3,5,6-trichloro-octafluorohexanoyl)amino] derivative **51** showed a better negative dichroism than the 1,4-bis(hexanoylamino) derivative **45**, probably due to the rigidity of the chlorofluoroalkyl moieties in the dye **51**.

3. Conclusions

Fluorine-containing 1,4-bis(acylamino)anthraquinone dyes were less soluble in chloroform than the non-fluorine-containing derivatives. However, the 1,4-bis-(acylamino)anthraquinone dyes **51**, **52**, **55**, **57** and **59**, containing 3,5,6-trichloro-octafluorohexanoyl groups were sufficiently soluble. Their S values were $-0{\cdot}26$ to $-0{\cdot}29$ in ZLI-4792. The larger the l/d ratio and the closer the θ value to 90°, the more negative the dichroism of the 1,4-bis(acylamino)anthraquinone dyes.

4. Experimental

4.1. *Characterization*

Melting points were measured with a Yanagimoto MP-S2 micro melting point apparatus. NMR, mass, UV, and fluorescence spectra were obtained on Jeol α-400, Shimadzu 9020-DF, Shimadzu UV-160A and Hitachi F-4500 spectrometers, respectively.

4.2. *Materials*

1,4-Diaminoanthraquinone (**1**), 4-iodotoluene (**2**), benzoyl chloride (**9**) and pentafluorobenzoyl chloride (**14**) were purchased from Tokyo Kasei Co., Ltd. 3,5,6-Trichloro-octafluorohexanoyl chloride (**17**) and 5*H*-perfluorovaleryl chloride (**19**) were obtained from Daikin Fine Chemical Co., Ltd. 4-Butylbenzoyl chloride (**10**), 4-octylbenzoyl chloride (**11**), 4-butoxybenzoyl chloride (**12**), 4-octyloxybenzoyl chloride (**13**), valeroyl chloride (**15**), *trans*-4-butylcyclohexanecarbonyl chloride

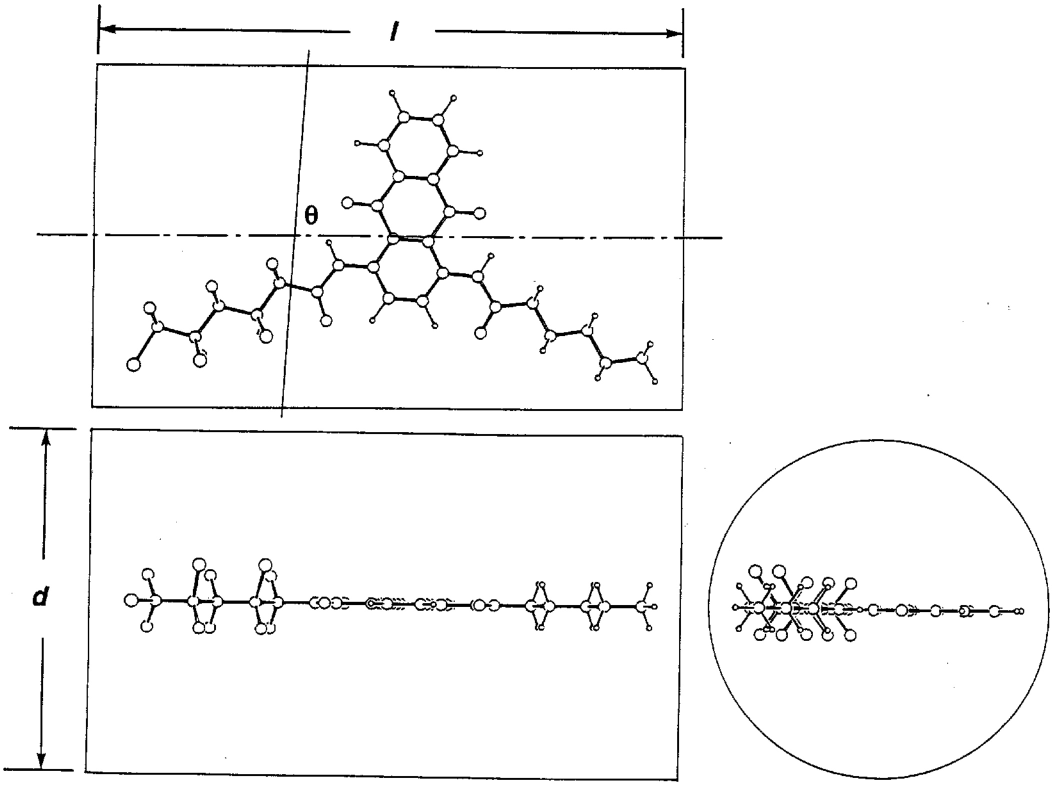


Figure 2. Calculation of *l*/*d* ratio and *θ* value of dye **46**.

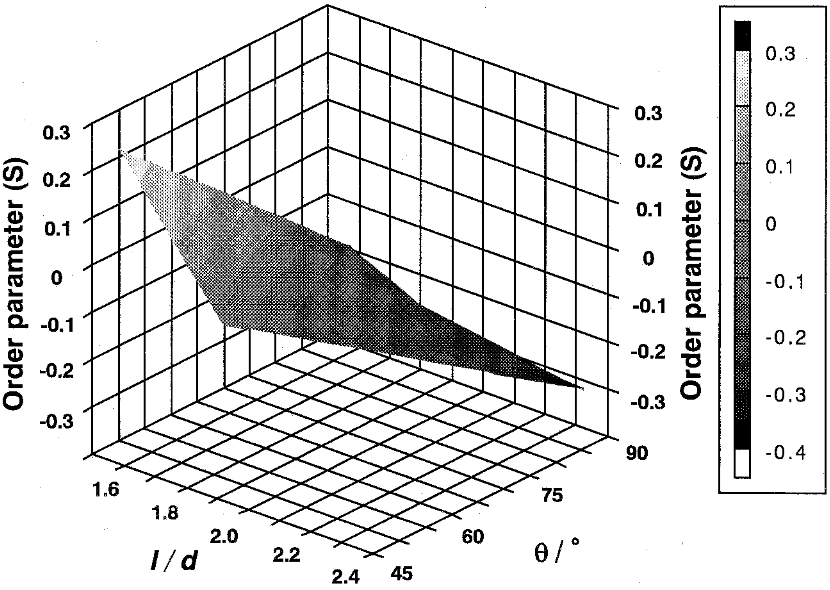


Figure 3. Relationship among *S*, *l*/*d* ratio and *θ* value.

(**16**), perfluorovaleryl chloride (**18**), perfluoro-octanoyl chloride (**20**), and perfluorodecanoyl chloride (**21**) were prepared by the reaction of the corresponding carboxylic acid with thionyl chloride.

4.3. *Synthesis of* 4-*(perfluoroalkyl) toluenes* (**3**, **4**)

To a DMSO solution (40 ml) of 4-iodotoluene (4·36 g, 20 mmol) were added copper powder (3·0 g) and the perfluoroalkyl iodide (20 mmol); the mixture was heated at 110°C overnight. When the reaction was complete, the mixture was poured into water (40 ml); the product was then extracted with ether (40 ml × 2), washed several times with water, dried over sodium sulphate and distilled under reduced pressure. The physical and spectral data are given below.

4.3.1. 4-*(Perfluorobutyl)toluene* (**3**)

Yield 42%; b.p. 67°C/2530 Pa. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2{\cdot}28$ (s, 3H), 7·02 (d, $J = 8{\cdot}1$ Hz, 2H), 7·60 (d, $J = 8{\cdot}1$ Hz, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 310 $[M]^+$ (10), 141 (100).

4.3.2. 4-*(Perfluoro-octyl)toluene* (**4**)

Yield 50%; b.p. 123°C/2400 Pa. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2{\cdot}28$ (s, 3H), 7·23 (d, $J = 7{\cdot}9$ Hz, 2H), 7·45 (d, $J = 7{\cdot}9$ Hz, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 510 $[M]^+$ (5), 141 (100).

4.4. *Synthesis of* 4-*(perfluoroalkyl)benzoic acids* (**5**, **6**)

To an aqueous solution (30 ml) of sodium dichromate dihydrate (14·9 g, 50 mmol) was added an acetic acid solution (150 ml) of the 4-(perfluoroalkyl)toluene (37 mmol). To this was added concentrated sulphuric acid (37·2·g) with stirring, and the mixture boiled under reflux for 2 h. After cooling, the reaction mixture was poured into water (50 ml), and the resulting precipitate was filtered and washed with water. The products were pure enough for the next step; physical and spectral data are given below.

4.4.1. 4-*(Perfluorobutyl)benzoic acid* (**5**)

Yield 82%; m.p. 143–144°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}73$ (d, $J = 8{\cdot}8$ Hz, 2H), 8·25 (d, $J = 8{\cdot}8$ Hz, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 340 $[M]^+$ (10), 171 (100), 143 (25).

4.4.2. 4-*(Perfluoro-octyl)benzoic acid* (**6**)

Yield 82%; m.p. 206–208°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}31$ (d, $J = 7{\cdot}9$ Hz, 2H), 7·47 (d, $J = 7{\cdot}9$ Hz, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 540 $[M]^+$ (3), 248 (61), 171 (86), 149 (100), 57 (21).

4.5. *Synthesis of acyl chlorides* (**7**, **8**)

To the 4-(perfluoroalkyl)benzoic acid (10 mmol) was added thionyl chloride (69 mmol) and the mixture was heated under reflux for 4 h. After cooling, excess thionyl chloride was removed and the product distilled under reduced pressure. Physical and spectral data are given below.

4.5.1. 4-*(Perfluorobutyl)benzoyl chloride* (**7**)

Yield 49%; b.p. 109°C/2530 Pa. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}77$ (d, $J = 8{\cdot}2$ Hz, 2H), 8·27 (d, $J = 8{\cdot}2$ Hz, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 323 $[M\text{–}Cl]^+$ (100), 126 (25).

4.5.2. 4-*(Perfluoro-octyl)benzoyl chloride* (**8**)

Yield 94%; b.p. 150–152°C/2400 Pa. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}77$ (d, $J = 8{\cdot}6$ Hz, 2H), 8·27 (d, $J = 8{\cdot}6$ Hz, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 523 $[M\text{–}Cl]^+$ (100), 126 (50).

4.6. *Synthesis of acylaminoanthraquinone dyes* (**22**–**63**, **64**–**72**, *and* **74**)

To a pyridine solution (80 ml) of a diaminoanthraquinone (5 mmol) was added an acid chloride in small portions at 0°C, and the mixture stirred overnight. When the reaction was complete, the mixture was washed with brine (80 ml), 5% aqueous sodium hydrogencarbonate (80 ml), and again brine (80 ml). The product was purified by column chromatography and crystallized from a chloroform–hexane mixture. Physical and spectral data are given below.

4.6.1. 1-*Amino*-4-*(*4-*benzoylamino)anthraquinone* (**22**)

Yield 41%; m.p. 282–284°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}14$ (d, $J = 9{\cdot}5$ Hz, 1H), 7·78–7·83 (m, 5H), 8·28–8·35 (m, 4H), 9·16 (d, $J = 9{\cdot}5$ Hz, 1H), 13·72 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 342 $[M]^+$ (62), 106 (100), 77 (93).

4.6.2. 1-*Amino*-4-*(*4-*butylbenzoylamino)anthraquinone* (**23**)

Yield 76%; m.p. 226–227°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}96$ (t, $J = 7{\cdot}3$ Hz, 3H), 1·39 (sextet, $J = 7{\cdot}3$ Hz, 2H), 1·67 (quintet, $J = 7{\cdot}3$ Hz, 2H), 2·72 (t, $J = 7{\cdot}3$ Hz, 2H), 7·12 (d, $J = 9{\cdot}2$ Hz, 1H), 7·16 (br s, 2H), 7·37 (d, $J = 8{\cdot}2$ Hz, 2H), 7·75–7·80 (m, 2H), 8·07 (d, $J = 8{\cdot}2$ Hz, 2H), 8·31–8·35 (m, 2H), 9·19 (d, $J = 9{\cdot}2$ Hz, 1H), 13·54 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 398 $[M]^+$ (39), 161 (100), 91 (34).

4.6.3. 1-*Amino*-4-*(*4-*butoxybenzoylamino)anthraquinone* (**24**)

Yield 58%; m.p. 237–239°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}01$ (t, $J = 7{\cdot}3$ Hz, 3H), 1·51 (sextet, $J = 7{\cdot}3$ Hz, 2H), 1·83 (quintet, $J = 7{\cdot}3$ Hz, 2H), 4·06 (t, $J = 7{\cdot}3$ Hz, 2H), 7·04 (d, $J = 8{\cdot}9$ Hz, 2H), 7·07 (d, $J = 9{\cdot}7$ Hz, 1H), 7·15 (br s, 2H), 7·72–7·77 (m, 2H), 8·10 (d, $J = 8{\cdot}9$ Hz, 2H), 8·27–8·32 (m, 2H), 9·14 (d, $J = 9{\cdot}7$ Hz, 1H), 13·49 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 414 $[M]^+$ (29), 177 (78), 121 (100).

4.6.4. 1-*Amino*-4-*[*4-*(perfluorobutyl)benzoylamino]*-*anthraquinone* (**25**)

Yield 43%; m.p. 187–189°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}11$ (d, $J = 9{\cdot}5$ Hz, 1H), 7·75–7·81 (m, 2H), 7·81 (d, $J = 8{\cdot}2$ Hz, 2H), 8·28 (d, $J = 8{\cdot}2$ Hz, 2H), 8·30–8·33 (m, 2H), 9·13 (d, $J = 9{\cdot}5$ Hz, 1H), 13·70 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 560 $[M]^+$ (100), 323 (31), 237 (40).

4.6.5. 1-*Amino*-4-*[(pentafluorobenzoyl)amino]*-*anthraquinone* (**26**)

Yield 54%; m.p. 265–267°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}13$ (d, $J = 9{\cdot}2$ Hz, 1H), 7·72–7·84 (m, 2H), 8·23–8·33 (m, 2H), 9·02 (d, $J = 9{\cdot}2$ Hz, 1H), 13·26 (br s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 432 $[M]^+$ (90), 323 (25), 237 (100).

4.6.6. 1-*Amino*-4-*(hexanoylamino)anthraquinone* (**27**)

Yield 29%; m.p. 88–90°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}93$ (t, $J = 7{\cdot}6$ Hz, 3H), 1·39–1·44 (m, 4H), 1·81 (quintet, $J = 7{\cdot}6$ Hz, 2H), 2·51 (t, $J = 7{\cdot}6$ Hz, 2H), 7·04 (d, $J = 9{\cdot}8$ Hz, 1H), 7·10 (br s, 2H), 7·73–7·78 (m, 2H), 8·25–8·31 (m, 2H), 8·96 (d, $J = 9{\cdot}8$ Hz, 1H), 12·60 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 336 $[M]^+$ (18), 238 (100).

4.6.7. 1-*Amino*-4-*(*4-*butylcyclohexylcarbonylamino)*-*anthraquinone* (**28**)

Yield 72%; m.p. 227–228°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}88$ (t, $J = 7{\cdot}3$ Hz, 3H), 0·93–2·36 (m, 16H), 7·04 (d, $J = 9{\cdot}8$ Hz, 1H), 7·15 (br s, 2H), 7·74–7·79 (m, 2H), 8·23–8·31 (m, 2H), 8·99 (d, $J = 9{\cdot}8$ Hz, 1H), 12·60 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 404 $[M]^+$ (53), 238 (100), 83 (5).

4.6.8. 1-*Amino*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)*-*amino]anthraquinone* (**29**)

Yield 50%; m.p. 192–193°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}09$ (d, $J = 9{\cdot}5$ Hz, 1H), 7·13 (br s, 2H), 7·75 (td, $J = 7{\cdot}3$ and 1·5 Hz, 1H), 7·81 (td, $J = 7{\cdot}3$ and 1·5 Hz, 1H), 8·27–8·32 (m, 2H), 8·84 (d, $J = 9{\cdot}5$ Hz, 1H), 13·72 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 586 $[M+4]^+$ (10), 584 $[M+2]^+$ (27), 582 $[M]^+$ (28), 265 (100), 237 (60). Elemental analysis: calculated for $C_{20}H_9Cl_3F_8N_2O_3$, C 41·16, H 1·55, N 4·80; found, C 41·03, H 1·75, N 4·75%.

4.6.9. 1-*Amino*-4-*[(perfluorovaleryl)amino]*-*anthraquinone* (**30**)

Yield 20%; m.p. 181–183°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}06$ (d, $J = 9{\cdot}5$ Hz, 1H), 7·12 (br s, 2H), 7·74 (td, $J = 7{\cdot}3$ and 1·8 Hz, 1H), 7·81 (td, $J = 7{\cdot}3$ and 1·8 Hz, 1H), 8·30–8·34 (m, 2H), 8·86 (d, $J = 9{\cdot}5$ Hz, 1H), 13·80 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 484 $[M]^+$ (77), 265 (100), 237 (70). Elemental analysis: calculated for $C_{19}H_9F_9N_2O_3$, C 47·12, H 1·87, N 5·78; found, C 47·35, H 1·74, N 5·88%.

4.6.10 1-*Amino*-4-*[(perfluoro-octanoyl)amino]*-*anthraquinone* (**31**)

Yield 40%; m.p. 150–152°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}11$ (d, $J = 9{\cdot}5$ Hz, 1H), 7·13 (br s, 2H), 7·77 (td, $J = 7{\cdot}3$ and 1·5 Hz, 1H), 7·83 (td, $J = 7{\cdot}3$ and 1·5 Hz, 1H), 8·30–8·34 (m, 2H), 8·85 (d, $J = 9{\cdot}5$ Hz, 1H), 13·80 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 634 $[M]^+$ (55), 265 (100), 237 (57). Elemental analysis: calculated for $C_{22}H_9F_{15}N_2O_3$, C 41·66, H 1·43, N 4·42; found, C 41·83, H 1·23, N 4·41%.

4.6.11. 1-*Amino*-4-*[(perfluorodecanoyl)amino]*-*anthraquinone* (**32**)

Yield 44%; m.p. 177–178°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}11$ (d, $J = 9{\cdot}5$ Hz, 1H), 7·12 (br s, 2H), 7·77 (td, $J = 7{\cdot}3$ and 1·5 Hz, 1H), 7·83 (td, $J = 7{\cdot}3$ and 1·5 Hz, 1H), 8·30–8·34 (m, 2H), 8·86 (d, $J = 9{\cdot}5$ Hz, 1H), 13·80 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 734 $[M]^+$ (38), 265 (100), 237 (54).

4.6.12. 1,4,-*bis(benzoylamino)anthraquinone* (**33**)

Yield 69%; m.p. 296–298°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}59$–7·63 (m, 6H), 7·84 (dd, $J = 5{\cdot}8$ and 3·4 Hz, 2H), 8·19 (dd, $J = 7{\cdot}6$ and 1·8 Hz, 4H), 8·36 (dd, $J = 5{\cdot}8$ and 3·4 Hz, 2H), 9·46 (s, 2H), 13·54 (s, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 446 $[M]^+$ (24), 106 (100), 77 (51).

4.6.13. 1-*(Benzoylamino)*-4-*(*4-*butylbenzoylamino)*-*anthraquinone* (**34**)

Yield 74%; m.p. 210–212°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}96$ (t, $J = 7{\cdot}3$ Hz, 3H), 1·40 (sextet, $J = 7{\cdot}3$ Hz, 2H), 1·67 (quintet, $J = 7{\cdot}3$ Hz, 2H), 2·73 (t, $J = 7{\cdot}3$ Hz, 2H), 7·39 (d, $J = 8{\cdot}3$ Hz, 2H), 7·53–7·65 (m, 3H), 7·82–7·86 (m, 2H), 8·09 (d, $J = 8{\cdot}3$ Hz, 2H), 8·18 (dd, $J = 7{\cdot}6$ and 1·5 Hz, 2H), 8·33–8·38 (m, 2H), 9·45 (d, $J = 9{\cdot}8$ Hz, 1H), 9·46 (d, $J = 9{\cdot}8$ Hz, 1H), 13·52 (s, 1H), 13·56 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 502 $[M]^+$ (39), 163 (100).

4.6.14. 1-*(Benzoylamino)*-4-*[*4-*(perfluorobutyl)*-*benzoylamino]anthraquinone* (**35**)

Yield 82%; m.p. 250–252°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}60$–7·67 (m, 3H), 7·84 (d, $J = 8{\cdot}5$ Hz, 2H), 7·87–7·90 (m, 2H), 8·18 (dd, $J = 7{\cdot}6$ and 2·1 Hz, 2H), 8·31 (d, $J = 8{\cdot}5$ Hz, 2H), 8·35–8·39 (m, 2H), 9·43 (d, $J = 9{\cdot}8$ Hz, 1H), 9·48 (d, $J = 9{\cdot}8$ Hz, 1H), 13·56 (s, 1H), 13·70 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 664 $[M]^+$ (3), 323 (6), 105 (100), 77 (34).

4.6.15. 1-*(Benzoylamino)*-4-[4-*(pentafluorobenzoyl)amino]anthraquinone* (**36**)

Yield 85%; m.p. 256–258°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7·56–7·65 (m, 3H), 7·81–7·89 (m, 2H), 8·18 (dd, J = 7·6 and 2·1 Hz, 2H), 8·26–8·30 (m, 1H), 8·34–8·39 (m, 1H), 9·27 (d, J = 9·8 Hz, 1H), 9·50 (d, J = 9·8 Hz, 1H), 13·25 (s, 1H), 13·53 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 536 $[M]^+$ (11), 195 (14), 105 (100).

4.6.16. 1,4-*Bis(*4-*butylbenzoylamino)anthraquinone* (**37**)

Yield 78%; m.p. 229–231°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0·96 (t, J = 7·3 Hz, 6H), 1·40 (sextet, J = 7·3 Hz, 4H), 1·68 (quintet, J = 7·3 Hz, 4H), 2·73 (t, J = 7·3 Hz, 4H), 7·39 (d, J = 8·5 Hz, 4H), 7·84 (dd, J = 5·8 and 3·4 Hz, 2H), 8·09 (d, J = 8·5 Hz, 4H), 8·36 (dd, J = 5·8 and 3·4 Hz, 2H), 9·45 (s, 2H), 13·51 (s, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 558 $[M]^+$ (19), 161 (100), 91 (40).

4.6.17 1-*(*4-*Butylbenzoylamino)*-4-[4-*(perfluorobutyl)benzoylamino]anthraquinone* (**38**)

Yield 79%; m.p. 265–267°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0·97 (t, J = 7·3 Hz, 3H), 1·40 (sextet, J = 7·3 Hz, 2H), 1·68 (quintet, J = 7·3 Hz, 2H), 2·73 (t, J = 7·3 Hz, 2H), 7·39 (d, J = 8·5 Hz, 2H), 7·82 (d, J = 8·5 Hz, 2H), 7·82–7·89 (m, 2H), 8·08 (d, J = 8·5 Hz, 2H), 8·31 (d, J = 8·5 Hz, 2H), 8·33–8·38 (m, 2H), 9·40 (d, J = 9·8 Hz, 1H), 9·48 (d, J = 9·8 Hz, 1H), 13·50 (s, 1H), 13·69 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 720 $[M]^+$ (33), 161 (100), 91 (21).

4.6.18. 1-*(*4-*Butylbenzoylamino)*-4-*[(pentafluorobenzoyl)amino]anthraquinone* (**39**)

Yield 87%; m.p. 218–220°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ=0·79 (t, J=7·3 Hz, 3H), 1·40 (sextet, J=7·3 Hz, 2H), 1·68 (quintet, J = 7·3 Hz, 2H), 2·73 (t, J = 7·3 Hz, 2H), 7·40 (d, J = 8·1 Hz, 2H), 7·81–7·88 (m, 2H), 8·09 (d, J = 8·1 Hz, 2H), 8·26–8·37 (m, 2H), 9·29 (d, J = 9·8 Hz, 1H), 9·50 (d, J = 9·8 Hz, 1H), 13·25 (s, 1H), 13·49 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 592 $[M]^+$ (6), 195 (11), 161 (100).

4.6.19. 1-*(*4-*Butoxybenzoylamino)*-4-[4-*(perfluorobutylbenzoyl)amino]anthraquinone* (**40**)

Yield 20%; m.p. 291–292°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ=1·02 (t, J=7·9 Hz, 3H), 1·54 (sextet, J=7·9 Hz, 2H), 1·83 (quintet, J = 7·9 Hz, 2H), 4·07 (t, J = 7·9 Hz, 2H), 7·05 (d, J = 8·9 Hz, 2H), 7·81–7·86 (m, 2H), 7·83 (d, J = 8·2 Hz, 2H), 8·11 (d, J = 8·9 Hz, 2H), 8·30 (d, J = 8·2 Hz, 2H), 8·31–8·37 (m, 2H), 9·37 (d, J = 9·8 Hz, 1H), 9·45 (d, J = 9·8 Hz, 1H), 13·45 (s, 1H), 13·68 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 736 $[M]^+$ (21), 323 (16), 177 (100), 121 (68).

4.6.20. 1,4-*Bis[*4-*(perfluorobutyl)benzoylamino]anthraquinone* (**41**)

Yield 28%; m.p. 299–300°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7·84 (d, J = 8·2 Hz, 4H), 7·87–7·99 (m, 2H), 8·32 (d, J = 8·2 Hz, 4H), 8·37–8·39 (m, 2H), 9·47 (s, 2H), 13·69 (s, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 882 $[M]^+$ (54), 323 (100), 176 (16), 154 (15), 126 (16).

4.6.21. 1-*[(Pentafluorobenzoyl)amino]*-4-[4-*(perfluorobutyl)benzoylamino]anthraquinone* (**42**)

Yield 92%; m.p. 226–228°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7·84 (d, J = 8·1 Hz, 2H), 7·83–7·89 (m, 2H), 8·27–8·42 (m, 2H), 8·31 (d, J = 8·1 Hz, 2H), 9·33 (d, J = 9·8 Hz, 1H), 9·42 (d, J = 9·8 Hz, 1H), 13·24 (s, 1H), 13·65 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 754 $[M]^+$ (59), 323 (100), 195 (48).

4.6.22. 1-*(*4-*Butylcyclohexylcarbonylamino)*-4-[4-*(perfluorobutyl)benzoylamino]anthraquinone* (**43**)

Yield 60%; m.p. 265–267°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0·92 (t, J = 7·0 Hz, 3H), 0·98–2·40 (m, 16H), 7·82–7·86 (m, 2H), 7·83 (d, J = 8·2 Hz, 2H), 8·23–8·35 (m, 2H), 8·29 (d, J = 8·2 Hz, 2H), 9·28 (d, J = 9·8 Hz, 1H), 9·34 (d, J = 9·8 Hz, 1H), 12·59 (s, 1H), 13·65 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 726 $[M]^+$ (50), 560 (100), 323 (42), 237 (22).

4.6.23. 1,4-*Bis[(pentafluorobenzoyl)amino]anthraquinone* (**44**)

Yield 67%; m.p. >300°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7·86 (dd, J = 5·9 and 3·4 Hz, 2H), 8·18 (dd, J = 5·9 and 3·4 Hz, 2H), 9·34 (s, 2H), 13·21 (s, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 626 $[M]^+$ (39), 195 (100), 167 (23).

4.6.24. 1,4-*Bis(hexanoylamino)anthraquinone* (**45**)

Yield 68%; m.p. 183–184°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0·94 (t, J = 7·3 Hz, 6H), 1·39–1·46 (m, 8H), 1·82 (quintet, J = 7·3 Hz, 4H), 2·54 (t, J = 7·3 Hz, 4H), 7·82 (dd, J = 5·8 and 3·4 Hz, 2H), 8·29 (dd, J = 5·8 and 3·4 Hz, 2H), 9·19 (s, 2H), 12·54 (s, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 434 $[M]^+$ (17), 336 (31), 238 (100). Elemental analysis: calculated for $C_{26}H_{30}N_2O_4$, C 71·87, H 6·96, N 6·45; found C 71·56, H 6·86, N 6·43%.

4.6.25. 1-*(Hexanoylamino)*-4-*[(*3,5,6-*trichlorooctafluorohexanoyl)amino]anthraquinone* (**46**)

Yield 76%; m.p. 168–170°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0·94 (t, J = 7·3 Hz, 3H), 1·40–1·45 (m, 4H), 1·83 (quintet, J = 7·3 Hz, 2H), 2·56 (t, J = 7·3 Hz, 2H), 7·81–7·89 (m, 2H), 8·28–8·34 (m, 2H), 9·07 (d, J = 9·8 Hz, 1H), 9·28 (d, J = 9·8 Hz, 1H), 12·54 (s, 1H), 13·70 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 680 $[M]^+$ (7), 586 (16), 584 (49), 582 (48), 265 (100), 237 (8). Elemental analysis: calculated for $C_{26}H_{19}Cl_3F_8N_2O_4$, C 45·80, H 2·81, N 4·11; found, C 45·93, H 2·56, N 3·93%.

4.6.26. 1-*(Hexanoylamino)*-4-*[5H-(octafluorovaleryl)amino]anthraquinone* (**47**)

Yield 74%; m.p. 188–189°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0·95$ (t, $J = 7·3$ Hz, 3H), 1·40–1·43 (m, 4H), 1·83 (quintet, $J = 7·3$ Hz, 2H), 2·55 (t, $J = 7·3$ Hz, 2H), 6·20 (tt, $J = 51·9$ and 5·5 Hz, 1H), 7·81–7·86 (m, 2H), 8·22–8·28 (m, 2H), 8·95 (d, $J = 9·8$ Hz, 1H), 9·20 (d, $J = 9·8$ Hz, 1H), 12·47 (s, 1H), 13·68 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 564 $[M]^+$ (23), 466 (100), 265 (50), 237 (18). Elemental analysis: calculated for $C_{25}H_{20}F_8N_2O_4$, C 53·20, H 3·57, N 4·96; found, C 53·25, H 3·67, N 5·01%.

4.6.27. 1-*(Hexanoylamino)*-4-*[(perfluorovaleryl)amino]anthraquinone* (**48**)

Yield 66%; m.p. 186–188°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0·93$ (t, $J = 7·3$ Hz, 3H), 1·40–1·43 (m, 4H), 1·83 (quintet, $J = 7·3$ Hz, 2H), 2·56 (t, $J = 7·3$ Hz, 2H), 7·81–7·88 (m, 2H), 8·25–8·31 (m, 2H), 9·00 (d, $J = 9·7$ Hz, 1H), 9·24 (d, $J = 9·7$ Hz, 1H), 12·47 (s, 1H), 13·68 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 582 $[M]^+$ (15), 484 (100), 265 (40), 237 (18).

4.6.28. 1-*(Hexanoylamino)*-4-*[(perfluorooctanoyl)amino]anthraquinone* (**49**)

Yield 72%; m.p. 175–176°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0·94$ (t, $J = 7·3$ Hz, 3H), 1·40–1·43 (m, 4H), 1·83 (quintet, $J = 7·3$ Hz, 2H), 2·56 (t, $J = 7·3$ Hz, 2H), 7·84–7·88 (m, 2H), 8·29–8·35 (m, 2H), 9·06 (d, $J = 9·8$ Hz, 1H), 9·29 (d, $J = 9·8$ Hz, 1H), 12·52 (s, 1H), 13·74 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 732 $[M]^+$ (33), 634 (100), 265 (73), 237 (27). Elemental analysis: calculated for $C_{28}H_{19}F_{15}N_2O_4$, C 45·92, H 2·61, N 3·82; found, C 45·81, H 2·62, N 3·81%.

4.6.29. 1-*(Hexanoylamino)*-4-*[(perfluorodecanoyl)amino]anthraquinone* (**50**)

Yield 83%; m.p. 179–180°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0·94$ (t, $J = 7·3$ Hz, 3H), 1·41–1·45 (m, 4H), 1·82 (quintet, $J = 7·3$ Hz, 2H), 2·56 (t, $J = 7·3$ Hz, 2H), 7·85–7·88 (m, 2H), 8·29–8·35 (m, 2H), 9·07 (d, $J = 9·8$ Hz, 1H), 9·30 (d, $J = 9·8$ Hz, 1H), 12·54 (s, 1H), 13·77 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 832 $[M]^+$ (29), 734 (100), 265 (77), 237 (24).

4.6.30. 1,4-*Bis[(*3,5,6-*trichloro-octafluorohexanoyl)amino]anthraquinone* (**51**)

Yield 79%; m.p. 238–240°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7·90$ (dd, $J = 5·9$ and 3·4 Hz, 2H), 8·36 (dd, $J = 5·9$ and 3·4 Hz, 2H), 9·20 (s, 2H), 13·68 (s, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 932 $[M+6]^+$ (8), 930 $[M+4]^+$ (16), 928 $[M+2]^+$ (19), 926 $[M]^+$ (10), 611 (71), 609 (70), 292 (100). Elemental analysis: calculated for $C_{26}H_8Cl_6F_{16}N_2O_4$, C 33·61, H 0·87, N 3·02; found, C 33·72, H 1·09, N 3·13%.

4.6.31. 1-*[(Perfluorovaleryl)amino]*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]anthraquinone* (**52**)

Yield 97%; m.p. 219–220°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7·90$ (dd, $J = 5·8$ and 3·4 Hz, 2H), 8·34 (dd, $J = 5·8$ and 3·4 Hz, 2H), 9·14–9·18 (m, 2H), 13·66 (s, 1H), 13·73 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 830 $[M+2]^+$ (26), 828 $[M]^+$ (26), 611 (19), 609 (19), 511 (100), 292 (58). Elemental analysis: calculated for $C_{25}H_8Cl_3F_{17}N_2O_4$, C 36·19, H 0·97, N 3·38; found, C 36·09, H 1·15, N 3·57%.

4.6.32. 1,4-*Bis[(perfluorovaleryl)amino]anthraquinone* (**53**)

Yield 64%; m.p. 241–243°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7·91$ (dd, $J = 5·9$ and 3·3 Hz, 2H), 8·36 (dd, $J = 5·9$ and 3·3 Hz, 2H), 9·18 (s, 2H), 13·68 (s, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 730 $[M]^+$ (13), 511 (100), 292 (40), 264 (17).

4.6.33. 1,4-*Bis[(perfluoro-octanoyl)amino]anthraquinone* (**54**)

Yield 40%; m.p. 245–246°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7·91$ (dd, $J = 5·8$ and 3·4 Hz, 2H), 8·37 (dd, $J = 5·8$ and 3·4 Hz, 2H), 9·19 (s, 2H), 13·75 (s, 2H). EI MS (70 eV) *m/z* (relative intensity, %): 1030 $[M]^+$ (28), 661 (100), 292 (53), 264 (20), 146 (34).

4.6.34. 1-*(*4-*Butylcyclohexylcarbonylamino)*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]anthraquinone* (**55**)

Yield 78%; m.p. 226–227°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0·91$ (t, $J = 7·0$ Hz, 3H), 1·03–2·44 (m, 16H), 7·84–7·87 (m, 2H), 8·30–8·35 (m, 2H), 9·07 (d, $J = 9·8$ Hz, 1H), 9·40 (d, $J = 9·8$ Hz, 1H), 12·55 (s, 1H), 13·70 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 750 $[M+2]^+$ (43), 748 $[M]^+$ (40), 584 (100), 582 (97), 265 (82). Elemental analysis: calculated for $C_{31}H_{27}Cl_3F_8N_2O_4$, C 49·65, H 3·63, N 3·74; found, C 49·63, H 3·75, N 3·79%.

4.6.35. 1-*(Benzoylamino)*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]anthraquinone* (**56**)

Yield 48%; m.p. 205–207°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7·58–7·64$ (m, 3H), 7·85–7·89 (m, 2H), 8·17 (dd, $J = 6·6$ and 1·7 Hz, 2H), 8·35–8·38 (m, 2H), 9·17 (d, $J = 9{\cdot}8$ Hz, 1H), 9·50 (d, $J = 9{\cdot}8$ Hz, 1H), 13·50 (s, 1H), 13·73 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 688 $[M+2]^+$ (52), 686 $[M]^+$ (51), 369 (19), 105 (100), 77 (68).

4.6.36. 1-*(4-Butylbenzoylamino)*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]anthraquinone* (**57**)

Yield 82%; m.p. 227–229°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}96$ (t, $J = 7{\cdot}3$ Hz, 3H), 1·40 (sextet, $J = 7{\cdot}3$ Hz, 2H), 1·67 (quintet, $J = 7{\cdot}3$ Hz, 2H), 2·73 (t, $J = 7{\cdot}3$ Hz, 2H), 7·39 (d, $J = 8{\cdot}3$ Hz, 2H), 7·85–7·88 (m, 2H), 8·07 (d, $J = 8{\cdot}3$ Hz, 2H), 8·34–8·38 (m, 2H), 9·14 (d, $J = 9{\cdot}8$ Hz, 1H), 9·48 (d, $J = 9{\cdot}8$ Hz, 1H), 13·46 (s, 1H), 13·73 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 744 $[M+2]^+$ (23), 742 $[M]^+$ (22), 161 (100), 91 (51). Elemental analysis: calculated for $C_{31}H_{21}Cl_3F_8N_2O_4$, C 50·06, H 2·85, N 3·77; found, C 49·95, H 2·60, N 3·55%.

4.6.37. 1-*(4-Octylbenzoylamino)*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]anthraquinone* (**58**)

Yield 60%; m.p. 213–215°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0{\cdot}89$ (t, $J = 7{\cdot}3$ Hz, 3H), 1·14–1·41 (m, 10H), 1·68 (quintet, $J = 7{\cdot}3$ Hz, 2H), 2·72 (t, $J = 7{\cdot}3$ Hz, 2H), 7·39 (d, $J = 8{\cdot}2$ Hz, 2H), 7·82–7·90 (m, 2H), 8·08 (d, $J = 8{\cdot}2$ Hz, 2H), 8·33–8·37 (m, 2H), 9·14 (d, $J = 9{\cdot}8$ Hz, 1H), 9·58 (d, $J = 9{\cdot}8$ Hz, 1H), 13·46 (s, 1H), 13·73 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 800 $[M+2]^+$ (12), 798 $[M]^+$ (11), 217 (100), 91 (29).

4.6.38. 1-*(4-Butoyxbenzoylamino)*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]anthraquinone* (**59**)

Yield 83%; m.p. 278–280°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1{\cdot}01$ (t, $J = 7{\cdot}3$ Hz, 3H), 1·52 (sextet, $J = 7{\cdot}3$ Hz, 2H), 1·83 (quintet, $J = 7{\cdot}3$ Hz, 2H), 4·06 (t, $J = 7{\cdot}3$ Hz, 2H), 7·06 (d, $J = 8{\cdot}5$ Hz, 2H), 7·85–7·87 (m, 2H), 8·12 (d, $J = 8{\cdot}5$ Hz, 2H), 8·34–8·36 (m, 2H), 9·13 (d, $J = 9{\cdot}8$ Hz, 1H), 9·47 (d, $J = 9{\cdot}8$ Hz, 1H), 13·42 (s, 1H), 13·72 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 760 $[M+2]^+$ (41), 758 $[M]^+$ (39), 177 (100), 121 (84). Elemental analysis: calculated for $C_{31}H_{21}Cl_3F_8N_2O_5$, C 49·00, H 2·79, N 3·69; found, C 49·01, H 2·54, N 3·50%.

4.6.39. 1-*[4-Perfluorobutyl)benzoylamino]*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]-anthraquinone* (**60**)

Yield 64%; m.p. 235–237°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}85$ (d, $J = 8{\cdot}5$ Hz, 2H), 7·88–7·91 (m, 2H), 8·31 (d, $J = 8{\cdot}5$ Hz, 2H), 8·35–8·39 (m, 2H), 9·19 (d, $J = 9{\cdot}8$ Hz, 1H), 9·46 (d, $J = 9{\cdot}8$ Hz, 1H), 13·65 (s, 1H), 13·74 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 906 $[M+2]^+$ (48), 904 $[M]^+$ (46), 587 (68), 323 (100).

4.6.40. 1-*[4-Perfluoro-octyl)benzoylamino]*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]-anthraquinone* (**61**)

Yield 53%; m.p. 239–241°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}86$ (d, $J = 8{\cdot}5$ Hz, 2H), 7·87–7·90 (m, 2H), 8·30 (d, $J = 8{\cdot}5$ Hz, 2H), 8·36–8·39 (m, 2H), 9·19 (d, $J = 9{\cdot}8$ Hz, 1H), 9·46 (d, $J = 9{\cdot}8$ Hz, 1H), 13·64 (s, 1H), 13·72 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 1106 $[M+2]^+$ (17), 1104 $[M]^+$ (16), 787 (33), 523 (100), 209 (18).

4.6.41. 1-*(Pentafluorobenzoylamino)*-4-*[(*3,5,6-*trichloro-octafluorohexanoyl)amino]-anthraquinone* (**62**)

Yield 27%; m.p. 226–227°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7{\cdot}84$–7·89 (m, 2H), 8·25–8·38 (m, 2H), 9·19 (d, $J = 9{\cdot}4$ Hz, 1H), 9·33 (d, $J = 9{\cdot}4$ Hz, 1H), 13·19 (s, 1H), 13·67 (s, 1H). EI MS (70 eV) *m/z* (relative intensity, %): 778 $[M+2]^+$ (35), 776 $[M]^+$ (35), 459 (100), 195 (77).

4.6.42. 1,4,5,8-*Tetrakis-[(*3,5,6-*trichloro-octafluorohexanoyl)amino]anthraquinone* (**63**)

Yield 53%; m.p. 249–251°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 9{\cdot}11$ (s, 4H), 12·83 (s, 4H). EI MS (70 eV) *m/z* (relative intensity, %): 1654 $[M+10]^+$ (13), 1652 $[M+8]^+$ (21), 1650 $[M+6]^+$ (34), 1648 $[M+4]^+$ (48), 1646 $[M+2]^+$ (40), 1644 $[M]^+$ (23), 320 (100), 151 (69), 85 (61).

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

Both these values were calculated from the geometry of the most stable conformer optimized by the MOPAC93 program [9] by the MNDO-PM3 method [10]. Transition moments of the dyes were calculated by the CNDO/S method [11] (singlet excitation, Nishimoto–Mataga equation, and 60 CI) using a geometry obtained by the MNDO-PM3 calculation.

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