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Perfluoroalkylation of azo compounds

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Abstract

Perfluoroalkyl azo dyes were prepared by the reaction of azo compounds with bis(perfluoroalkanoyl) peroxides The absorption spectra and melting points of the perfluoroalkyl azo dyes were also examined

Introduction

Much attention has been focused on the synthesis and characterization of functional dyes [1]. Bis(perfluoroalkanoyl) peroxides have been reported to be useful reagents for the introduction of a perfluoroalkyl group into a molecule under mild conditions [2]. Synthesis of perfluoroalkyl dyes is of interest because of their unique properties, *i.e.* good photostability, sublimation nature and solubility for organic solvents and plastics, *etc.* This paper describes the synthesis and some properties of perfluoroalkyl azo dyes.

Results and discussion

The reactions of 4-substituted azobenzenes with bis(heptafluorobutyryl) peroxide gave heptafluoropropylazobenzenes **2**, **3** and a mixture of NNO- and ONN-azoxybenzenes **4** (Scheme 1 and Table 1). In the cases of azobenzenes **1a–1d**, the heptafluoropropylation of azobenzenes to give **2** and **3** competed with the oxidation process to give **4** (runs 1–4). The higher the oxidation potential of the substrates, the greater the yields of azoxybenzenes **4**. The reactions of amino- and dialkylaminoazobenzenes **1e–1g** with the peroxide also afforded heptafluoropropylazobenzenes **2** and **3** (runs 5–7). In these cases, no azoxybenzenes were produced.

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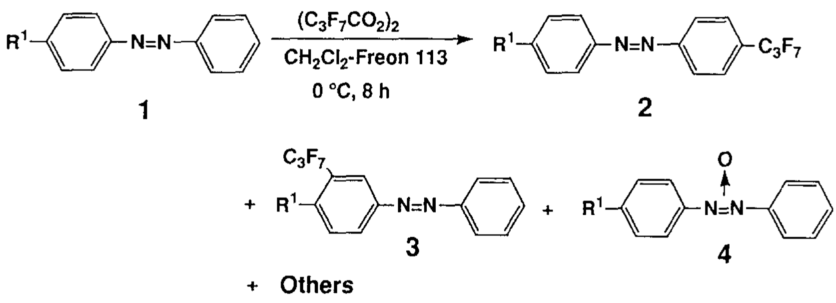


Scheme 1.

TABLE 1

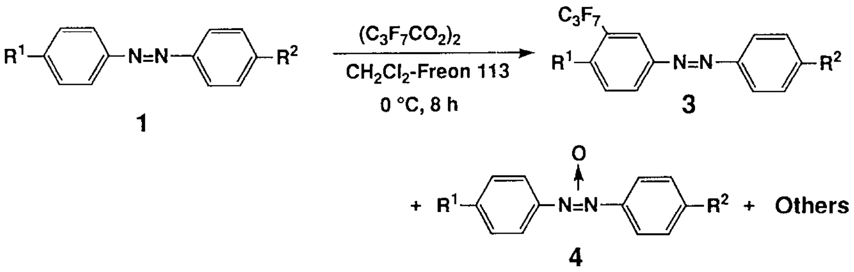
Reaction of 4-substituted azobenzenes with bis(heptafluorobutyryl) peroxide

Run	Comp.	R^1	E_{OX}[b]	Yield[a] (%)			Others
				2	**3**	**4**	
1	**a**	H	1.30	10	0	33	[c]
2	**b**	Cl	1.38	3	0	69	[d]
3	**c**	Me	1.22	10	21	20	
4	**d**	MeO	1.19	10	12	26	[e]
5	**e**	NH_2	0.56	6	11	0	
6	**f**	NMe_2	0.46	11	12	0	[f]
7	**g**	NEt_2	0.45	21	16	0	[g]

[a] Isolated yields.
[b] Oxidation potential of **1** (onset potential *vs.* Ag/Ag$^+$).
[c] 2-Heptafluoropropylazobenzene (**2′a**) was obtained in 15% yield.
[d] 4-Chloro-2′-heptafluoropropylazobenzene (**2′b**) was obtained in 3% yield.
[e] 2-Heptafluoropropyl-4′-methoxyazobenzene (**2′d**) was obtained in 10% yield.
[f] 4-Heptafluoropropyl-*N,N*-diemethylaniline was obtained in 21% yield.
[g] 4-Heptafluoropropyl-*N,N*-diethylaniline was obtained in 10% yield.

The reactions of 4,4′-disubstituted azobenzenes with the peroxide gave heptafluoropropylazobenzenes **3** and a mixture of NNO- and ONN-azobenzenes **4** (Scheme 2 and Table 2). In the reactions of 4,4′-disubstituted azobenzenes **1h–1l**, a heptafluoropropyl group was introduced preferentially into the *ortho* position to the more electron-releasing group (runs 1–5). In the cases of **1j–1l**, the azoxybenzenes were not formed (runs 3–5).

Perfluoroalkylation of 4-(2′-thiazolylazo)-*N,N*-dimethylaniline (**5**) is shown in Scheme 3 and Table 3. The thiazolylazo compound reacted more smoothly with the peroxides than did 4-dimethylaminoazobenzene (**1f**). The reaction with bis(trifluoroacetyl) peroxide gave an inseparable mixture of 4-(2′-thiazolylazo-5′-trifluoromethyl)- and 4-(2′-thiazolylazo)-2-trifluoromethyl-*N,N*-dimethylanilines (product distribution = 6:4) in 9%



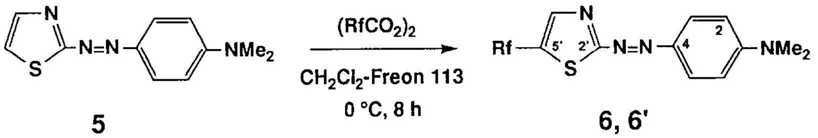
Scheme 2.

TABLE 2

Reaction of 4,4′-disubstituted azobenzenes with bis(heptafluorobutyryl) peroxide

Run	Comp.	R^1	R^2	E_{OX}[b]	Yield[a] (%)		Others
					3	4	
1	**h**	Me	Me	1.28	27	16	
2	**i**	Me	Cl	1.32	29	42	
3	**j**	NMe_2	NO_2	0.58	11	0	[c]
4	**k**	NMe_2	Cl	0.50	14	0	
5	**l**	NMe_2	Me	0.44	14	0	

[a] Isolated yield.
[b] Oxidation potential of **1** (onset potential *vs.* Ag/Ag$^+$).
[c] 4-Heptafluoropropyl-*N*,*N*-dimethylaniline was obtained in 17% yield.



Scheme 3.

TABLE 3

Synthesis of perfluoroalkyl thiazolyl azo dyes

Run	Comp.	R_f	Yield[a] (%)
1	–	CF_3	9[b]
2	**6**	C_3F_7	27
3	**6′**	C_7F_{15}	31

[a] Isolated yield.
[b] An inseparable mixture of 5′-trifluoromethyl and 2-trifluoromethyl derivatives was obtained in the ratio 6:4, which was determined on the basis of ^{1}H NMR spectroscopy.

yield (run 1). The reactions with bis(heptafluorobutyryl)- and bis(pentadecafluorooctanoyl) peroxides gave exclusively 4-(5′-perfluoroalkyl-2′-thiazolylazo)-*N*,*N*-dimethylanilines **6** and **6′** (runs 2, 3).

Absorption spectra and melting points of selected perfluoroalkyl azo dyes are summarized in Table 4. The absorption spectra of **2f**, **2g**, **6** and **6′** showed bathochromic shifts (*ca.* 20–30 nm) compared with the corresponding unperfluoroalkylated ones (runs 1–4, 10–12). This result supports an intramolecular charge-transfer chromophore system of azo dyes [3]. No remarkable differences in λ_{max} were observed between **1m** and **2f**, indicating that a hepafluoropropyl group showed electron-withdrawing ability similar to a trifluoromethyl group (runs 2, 9). On the other hand, those of 3-heptafluoropropyl-4-dimethylamino azo dyes **3j** and **3l** showed hypochromic shifts (*ca.* 60–90 nm) compared with the 3-unsubstituted azo dyes **1j** and **1l**, suggesting twisting of the dimethylamino moiety from the plane of the aromatic residue due to the steric effect of the perfluoroalkyl group at the 3-position (runs 5–8). Although the introduction of perfluoroalkyl groups into dye molecules was expected to lower their melting points, those of perfluoroalkyl azo dyes were not always low compared with the corresponding unperfluoroalkylated ones. For example, those of **2f**, **6** and **6′** were higher than **1f** and **5**, respectively (runs 1, 2, 10–12), while that of **2g** was lower than **1g** (runs 3, 4). The melting points of all 3-heptafluoropropylazobenzenes **3j** and **3l** were lower than the corresponding unperfluoroalkylated azobenzenes **1j** and **1l**, respectively (runs 5–8).

TABLE 4

Absorption spectra and thermal analysis of azo dyes

Run	Comp.	R^1	R^2	λ_{max}/NM[a] (log ε)	m.p. (°C)
1	**1f**	NMe_2	H	404 (4.37)	119
2	**2f**	NMe_2	C_3F_7	425 (4.48)	127
3	**1g**	NEt_2	H	414 (4.44)	100
4	**2g**	NEt_2	C_3F_7	434 (4.50)	83
5	**1j**	NMe_2	NO_2	470 (4.42)	234
6	**3j**	NMe_2	NO_2	377[b] (4.58)	63
7	**1l**	NMe_2	Me	402 (4.48)	173
8	**3l**	NMe_2	Me	340 (4.62)	oil
9	**1m**	NMe_2	CF_3	425 (4.45)	172
10	**5**	—	—	483 (4.45)	174
11	**6**	—	—	514 (4.59)	184[c]
12	**6′**			515 (4.54)	210[d]

[a] Measured in MeOH.

[b] Shoulder.

[c] Phase transformation was observed at 89.2 and 115.3 °C.

[d] Phase transformation was observed at 146.0 °C.

Experimental

Instruments

Melting points were measured with Yanagimoto micro-melting point and Seiko DSC-210 apparatus and are uncorrected. ^{1}H NMR spectra were obtained with a JEOL JUM GX-270 (270 MHz) spectrometer in deuterochloroform and chemical shifts were given as δ ppm relative to tetramethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were obtained with a Hitachi R-20B (56.45 MHz) instrument in deuterochloroform and chemical shifts were given as δ ppm relative to trifluoroacetic acid as an external standard. Mass and UV spectra were measured with Shimadzu QP-1000 and Jasco UVIDEC-410 spectrometers, respectively. Oxidation potentials were measured using a Nikkou Keisoku potential sweeper NIP-2 and a TOHO Technical Research potentiostat 2000.

Reagents

Bis(perfluoroalkanoyl) peroxides were synthesized as described in the literature [2j]. Azobenzene (**1a**), 4-aminoazobenzene (**1e**), 4-dimethylaminoazobenzene (**1f**), and azoxybenzene (**4a**) were purchased from Tokyo Kasei Kogyo Co. The other azo and azoxy compounds were prepared as described in the literature [4–12].

Synthesis of perfluoroalkyl azo dyes

As a general procedure, to a dichloromethane solution (40 ml) of an azo compound (2 mmol) was added bis(perfluoroalkanoyl) peroxide (2 mmol)-Freon 113 solution. The mixture was stirred for 8 h at 0 °C. After the reaction, the solution was washed with brine (40 ml), 10% aqueous sodium hydrogen carbonate (40 ml) and brine (40 ml). The organic layer was dried over sodium sulfate. After evaporation of the solvent, the products were separated by column chromatography (SiO_2, hexane–benzene = 3/1 (**1a–1f**), toluene–hexane = 1/1 or dichloromethane (**1g–1m**, 5)). Azoxybenzenes were identified by comparing their spectral data with those of authentic samples. Physical and spectra data of perfluoroalkyl azo dyes are shown below.

*4-Heptafluoropropylazobenzene (**2a**)*

Melting point 95.0–97.0 °C; ^{1}H NMR ($CDCl_3$): δ 7.53–7.56 (m, 3H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.94–7.98 (m, 2H), 8.02 (d, $J = 8.2$ Hz, 2H); EIMS (70 eV) m/z (rel. intensity) 350 (M^+, 37), 245 (17), 145 (15), 105 (33), 77 (100); Elemental analysis: found: C, 51.23; H, 2.53; N, 8.29%. Calcd. for $C_{15}H_9F_7N_2$: C, 51.44; H, 2.59; N, 8.00%.

*2-Heptafluoropropylazobenzene (**2′a**)*

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 7.52–7.71 (m, 5H), 7.76–7.80 (m, 2H), 7.92–7.96 (m, 2H); EIMS (70 eV) m/z (rel. intensity) 350 (M^+, 11), 145 (23), 105 (15), 77 (100); HRMS m/z 350.0631. Calcd. for $C_{15}H_9F_7N_2$: 350.0654.

4-Chloro-4′-heptafluoropropylazobenzene ***(2b)***

Melting point 88.5–91.0 °C; ^{1}H NMR ($CDCl_3$): δ 7.52 (d, $J = 8.9$ Hz, 2H), 7.57–7.82 (m, 4H), 7.88 (d, $J = 8.9$ Hz, 2H); EIMS (70 eV) m/z (rel. intensity) 384 (M^+, 19), 245 (24), 111 (100), 77 (5); Elemental analysis; found: C, 46.67; H, 2.08; N, 7.35%. Calcd. for $C_{15}H_8ClF_7N_2$: C, 46.84; H, 2.10; N, 7.28%.

4-Chloro-2′-heptafluoropropylazobenzene ***(2′b)***

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 7.51 (d, $J = 8.9$ Hz, 2H), 7.57–7.82 (m, 4H), 7.88 (d, $J = 8.9$ Hz, 2H); EIMS (70 eV) m/z (rel. intensity) 384 (M^+, 7) 111 (100), 77 (3); HRMS m/z 384.0297. Calcd. for $C_{15}H_8ClF_7N_2$: 384.0264.

4-Heptafluoropropyl-4′-methylazobenzene ***(2c)***

Melting point 91.0–92.0 °C; ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 8.6$ Hz, 2H), 7.87 (d, $J = 8.2$ Hz, 2H), 8.00 (d, $J = 8.6$ Hz, 2H); EIMS (70 eV) m/z (rel. intensity) 364 (M^+, 18), 245 (10), 91 (100), 77 (4); Elemental analysis: found: C, 52.46; H, 3.00; N, 7.76%. Calcd. for $C_{16}H_{11}F_7N_2$: C, 52.76; H, 3.04; N, 7.69%.

2-Heptafluoropropyl-4′-methoxyazobenzene ***(2d)***

Melting point 79.0–83.0 °C; ^{1}H NMR ($CDCl_3$): δ 3.91 (s, 3H), 7.03 (d, $J = 9.0$ Hz, 2H), 7.72 (d, $J = 9.0$ Hz, 2H), 7.96 (d, $J = 9.0$ Hz, 2H), 7.97 (d, $J = 9.0$ Hz, 2H); EIMS (70 eV) m/z (rel. intensity) 380 (M^+, 26), 245 (6), 107(100), 77 (55); Elemental analysis: found: C, 50.41; H, 2.88; N, 7.35%. Calcd. for $C_{16}H_{11}F_7N_2O$: C, 50.54; H, 2.92; N, 7.37%.

2-Heptafluoropropyl-4′-methoxyazobenzene ***(2′d)***

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 3.90 (s, 3H), 7.03 (d, $J =$ 8.9 Hz, 2H), 7.49–7.78 (m, 4H), 7.93 (d, $J = 8.9$ Hz, 2H); EIMS (70 eV) m/z (rel. intensity) 380 (M^+, 22), 245 (1), 107 (100), 77 (58); HRMS m/z 380.0731. Calcd. for $C_{16}H_{11}F_7N_2O$: 380.0759.

4-Amino-4′-heptafluoropropylazobenzene ***(2e)***

Melting point 94.0–96.0 °C; ^{1}H NMR ($CDCl_3$): δ 4.17 (s, 2H), 6.74 (d, $J = 9.2$ Hz, 2H), 7.69 (d, $J = 8.6$ Hz, 2H), 7.84 (d, $J = 9.2$ Hz, 2H), 7.93 (d, $J = 8.6$ Hz, 2H); EIMS (70 eV) m/z (rel. intensity) 365 (M^+ 21), 120 (27), 92 (100), 65 (41); HRMS m/z 365.0765. Calcd. for $C_{15}H_{10}F_7N_4$: 365.0763.

4-Dimethylamino-4′-hepafluoropropylazobenzene ***(2f)***

^{1}H NMR ($CDCl_3$): δ 3.12 (s, 6H), 6.77 (d, $J = 9.2$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 9.2$ Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH): δ −1.3 (t, $J = 9$ Hz, 3F), −32.8 (q, $J = 9$ Hz, 2F), −47.8 (s, 2F); EIMS (70 eV) m/z (rel. intensity) 393 (M^+, 33), 145 (25), 120 (100), 105 (32), 77 (60), 69 (44); Elemental analysis: found: C, 52.11; H, 3.71; N, 10.55%. Calcd. for $C_{17}H_{14}F_7N_3$: C, 51.89; H, 3.59; N, 10.69%.

*4-Diethylamino-4'-heptafluoropropylazobenzene (**2g**)*

^{1}H NMR ($CDCl_3$): δ 1.24 (t, $J = 6.7$ Hz, 6H), 3.47 (q, $J = 6.7$ Hz, 4H), 6.73 (d, $J = 9.2$ Hz, 2H), 7.67 (d, $J = 8.6$ Hz, 2H), 7.88 (d, $J = 9.2$ Hz, 2H), 7.91 (d, $J = 8.6$ Hz, 2H), EIMS (70 eV) m/z (rel. intensity) 421 (M^+, 46), 406 (42), 148 (100), 105 (30), 91 (31), 77 (33); Elemental analysis: found: C, 54.32; H, 4.28; N, 9.89%. Calcd. for $C_{19}H_{18}F_7N_3$: C, 54.14; H, 4.31; N, 9.98%.

*3-Heptafluoropropyl-4-methylazobenzene (**3c**)*

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 2.50 (s, 3H), 7.33 (d, $J = 8.2$ Hz, 1H), 7.44–7.54 (m, 3H), 7.55 (s, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.89–7.96 (m, 2H); EIMS (70 eV) m/z (rel. intensity) 364 (M^+, 10), 259 (3), 77 (100); HRMS m/z 364.0791. Calcd. for $C_{16}H_{11}F_7N_2$: 364.0810.

*3-Heptafluoropropyl-4-methoxyazobenzene (**3d**)*

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 3.93 (s, 3H), 7.17 (d, $J = 9.2$ Hz, 1H), 7.24 (s, 1H), 7.46–7.55 (m, 3H), 7.88–8.91 (m, 2H), 7.91 (d, $J = 9.2$ Hz, 1H); EIMS (70 eV) m/z (rel. intensity) 380 (M^+, 35), 275 (14), 77 (100); HRMS m/z 380.0781. Calcd. for $C_{16}H_{11}F_7N_2O$: 380.0760.

*4-Amino-3-heptafluoropropylazobenzene (**3e**)*

Melting point 45.0–53.0 °C; ^{1}H NMR ($CDCl_3$): δ 4.61 (s, 2H), 7.43–7.56 (m, 4H), 7.85–7.88 (m, 2H), 7.94 (dd, $J = 8.8$ and 2.2 Hz, 1H), 8.01 (d, $J = 2.2$ Hz, 1H); EIMS (70 eV) m/z (rel. intensity) 365 (M^+, 42), 260 (51), 171 (40), 77 (100), 51 (34); HRMS m/z 365.0795. Calcd. for $C_{15}H_{10}F_7N_3$: 365.0763.

*4-Dimethylamino-3-heptafluoropropylazobenzene (**3f**)*

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 2.73 (s, 6H), 7.47–7.53 (m, 4H), 7.90–7.94 (m, 2H), 8.07 (dd, $J = 8.6$ and 2.4 Hz, 1H), 8.16 (d, $J = 2.4$ Hz, 1H); EIMS (70 eV) m/z (rel. intensity) 393 (M^+, 39), 288 (45), 77 (100); HRMS m/z 393.1058. Calcd. for $C_{17}H_{14}F_7N_3$: 393.1076.

4-Heptafluoropropyl-N,N-dimethylaniline

Melting point 48.0–49.0 °C (lit [13] 52 °C); ^{1}H NMR ($CDCl_3$): δ 3.01 (s, 6H), 6.71 (d, $J = 9.2$ Hz, 2H), 7.39 (d, $J = 9.2$ Hz, 2H); EIMS (70 eV) m/z (rel. intensity) 289 (M^+, 31), 170 (100), 154 (20).

*4-Diethylamino-3-heptafluoropropylazobenzene (**3g**)*

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 1.95 (t, $J = 7.1$ Hz, 6H), 3.04 (q, $J = 7.1$ Hz, 4H), 7.43–7.54 (m, 4H), 7.90–7.94 (m, 2H), 8.05 (dd, $J = 8.5$ and 2.0 Hz, 1H), 8.19 (d, $J = 2.0$ Hz, 1H); EIMS (70 eV) m/z (rel. intensity) 421 (M^+, 29), 406 (100), 77 (41); HRMS m/z 421.1403. Calcd. for $C_{19}H_{18}F_7N_3$: 421.1388.

4-Heptafluoropropyl-N,N-diethylaniline

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 1.23 (t, $J = 7.3$ Hz, 6H), 3.46 (q, $J = 7.3$ Hz, 4H), 6.65 (d, $J = 9.2$ Hz, 2H), 7.96 (d, $J = 9.2$ Hz, 2H); EIMS

(70 eV) *m/z* (rel. intensity) 317 (M^+, 28), 302 (100), 274 (37); HRMS *m/z* 317.1031. Calcd. for $C_{13}H_{14}F_7N$: 317.1014.

4,4'-Dimethyl-3-heptafluoropropylazobenzene ***(3h)***

Melting point 44.0–45.5 °C; ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H), 2.49 (s, 3H), 7.31 (d, $J = 8.5$ Hz, 2H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.54 (s, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.82 (d, $J = 8.5$ Hz, 2H); EIMS (70 eV) *m/z* (rel. intensity) 378 (M^+, 65), 259 (10), 91 (100); Elemental analysis: found: C, 53.80; H, 3.41; N, 7.38%. Calcd. for $C_{17}H_{13}F_7N_2$: C, 53.98; H, 3.46; N, 7.40%.

4-Chloro-3'-heptafluoropropyl-4'-methylazobenzene ***(3i)***

Melting point 177.0–178.0 °C; ^{1}H-NMR ($CDCl_3$): δ 2.50 (s, 3H), 7.36 (s, 1H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 1H), 7.85 (d, $J = 8.6$ Hz, 1H), 7.86 (d, $J = 8.6$ Hz, 2H); EIMS (70 eV) *m/z* (rel. intensity) 398 (M^+, 56), 259 (15), 111, (100); Elemental analysis: found: C, 48.15; H, 2.41; N, 6.92%. Calcd. for $C_{16}H_{10}ClF_7N_2$: C, 48.20; H, 2.52; N, 7.03%.

4-Dimethylamino-3-heptafluoropropyl-4'-nitroazobenzene ***(3j)***

^{1}H NMR ($CDCl_3$): δ 2.76 (s, 6H), 7.52 (d, $J = 8.5$ Hz, 1H), 8.04 (d, $J = 8.9$ Hz, 2H), 8.12 (dd, $J = 8.5$ and 2.2 Hz, 1H), 8.21 (d, $J = 2.2$ Hz, 1H), 8.39 (d, $J = 8.9$ Hz, 2H); EIMS (70 eV) *m/z* (rel. intensity) 438 (M^+, 100), 316 (4), 288 (99), 169 (21), 150 (10), 122 (14); HRMS *m/z* 438.0923. Calcd. for $C_{17}H_{13}F_7N_4O_2$: 438.0926.

4-Chloro-4'-dimethylamino-3'-heptafluoropropylazobenzene ***(3k)***

Melting point oil; ^{1}H NMR ($CDCl_3$): δ 2.74 (s, 6H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.56 (d, $J = 9.2$ Hz, 1H), 7.83 (d, $J = 8.2$ Hz, 2H), 8.06 (dd, $J = 9.2$ and 2.4 Hz, 1H), 8.14 (d, $J = 2.4$ Hz, 1H); EIMS (70 eV) *m/z* (rel. intensity) 427 (M^+, 52), 288 (93), 274 (37), 139 (30), 111 (100); HRMS *m/z* 427. 0695. Calcd. for $C_{17}H_{13}ClF_7N_3$: 427.0686.

4-Dimethylamino-3-heptafluoropropyl-4'-methylazobenzene ***(3l)***

^{1}H NMR ($CDCl_3$): δ 2.50 (s, 3H), 2.75 (s, 6H), 7.32 (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 9.0$ Hz, 1H), 7.83 (d, $J = 8.5$ Hz, 2H), 8.05 (dd, $J = 9.0$ and 2.4 Hz, 1H), 8.13 (d, $J = 9.2$ Hz, 1H); EIMS (70 eV) *m/z* (rel. intensity) 407 (M^+, 57), 288 (86), 119 (33), 91 (100); HRMS *m/z* 407.1248. Calcd. for $C_{18}H_{16}F_7N_3$: 407.1232.

4-(5'-Heptafluoropropyl-2'-thiazolylazo)-N,N-dimethylaniline ***(6)***

^{1}H NMR ($CDCl_3$): δ 3.18 (s, 6H), 6.76 (d, $J = 9.2$ Hz, 2H), 7.95 (d, $J = 9.2$ Hz, 2H), 8.14 (s, 1H); EIMS (70 eV) *m/z* (rel. intensity) 400 (M^+, 32), 253 (14), 120 (100), 105 (33), 91 (23), 77 (44). Elemental analysis: found: C, 42.21; H, 2.78; N, 14.13%. Calcd. for $C_{14}H_{11}F_7N_4S$: C, 41.99; H, 2.77; N, 14.00%.

4-(5'-Pentadecafluoroheptyl-2'-thiazolylazo)-N,N-dimethylaniline (**6'**)

^{1}H NMR ($CDCl_3$): δ 3.18 (s, 6H), 6.76 (d, $J = 9.2$ Hz, 2H), 7.95 (d, $J = 9.2$ Hz, 2H), 8.14 (s, 1H); EIMS (70 eV) m/z (rel. intensity) 600 (M^+, 22), 253 (16), 120 (100), 105 (17), 91 (11), 77 (19), 69 (16). Elemental analysis: found: C, 36.00; H, 2.02; N, 9.56%. Calcd. for $C_{18}H_{11}F_{15}N_4S$: C, 36.00; H, 1.85; N, 9.33%.

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References

1 Z. Yoshida and T. Kitao, *Chemistry of Functional Dyes*, Mita Press, Tokyo, 1989.

2 (a) M. Yoshida, K. Moriya, H. Sawada and M. Kobayashi, *Chem. Lett.*, (1985) 755; (b) M. Yoshida, H. Aoyama, M. Kobayashi, H. Sawada, H. Hagii and K. Aoshima, *J. Chem. Soc. Chem. Commun.*, (1985) 234; (c) H. Sawada, M. Yoshida, H. Hagii, K. Aoshima and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, *59* (1986) 215; (d) M. Yoshida, T. Yoshida, N. Kamigata and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, *61* (1988) 3549; (e) M. Yoshida, T. Yoshida, M. Kobayashi and N. Kamigata, *J. Chem. Soc.*, *Perkin Trans. 1*, (1989) 909; (f) H. Sawada, M. Mitani, M. Nakayama, M. Yoshida and N. Kamigata, *Polym. Commun.*, *31* (1990) 63; (g) H. Sawada, M. Nakayama, M. Yoshida, T. Yoshida and N. Kamigata, *J. Fluorine Chem.*, *46* (1990) 423; (h) H. Sawada and M. Nakayama, *J. Fluorine Chem.*, *51* (1991) 117; (i) M. Matsui, K. Shibata, H. Muramatsu, H. Sawada and M. Nakayama, *Synlett*, (1991) 113; (j) C. Zhao, R. Zhao, H. Pan, X. Jin, Y. Qu, C. Wu and X. Jiang, *J. Org. Chem.*, *47* (1982) 2009.

3 J. Fabian and H. Hartmann, *Light Absorption of Organic Colorants*, Springer-Verlag, New York, 1980.

4 M. Matsui, Y. Iwata, T. Kato and K. Shibata, *Dyes Pigm.*, *9* (1988) 109.

5 E. Bamberger, *Chem. Ber.*, *29* (1896) 102.

6 J. Burns, H. McCombie and H. A. Scarborough, *J. Chem. Soc.*, (1928) 2828.

7 H. Boeke, E. Koppe and F. Staiger, *Chem. Ber.*, *41* (1908) 1156.

8 N. Nishimura, T. Sueyama, H. Yamamoto, E. Imai, S. Yamamoto and S. Hasegawa, *Bull. Chem. Soc. Jpn.*, *49* (1976) 1381.

9 F. Wreden, *Chem. Ber.*, *6* (1873) 556.

10 E. Bamberger and O. Baudisch, *Chem. Ber.*, *42* (1909) 3568.

11 M. Isaaks and H. H. Jaffe, *J. Am. Chem. Soc.*, *86* (1964) 2209.

12 M. Furuyama, *Anal. Chim. Acta*, *140* (1982) 281.

13 L. M. Yagupolskii, I. I. Maletina, N. V. Kondratenko and V. V. Orda, *Synthesis*, (1978) 835.