Complexation and Photoinduced Electron-transfer Reaction between Perfluoroalkyl Iodides and *N,N,N',N'*-Tetramethylphenylene-1,4-diamine, Anilines and Piperazines

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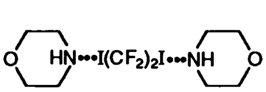
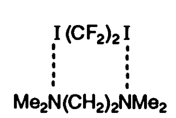
Treatment of tetrafluoro-1,2-diiodoethane **1a** or dodecafluoro-1,6-diiodohexane **1b** with *N,N,N',N'*-tetramethylphenylene-1,4-diamine **2** gave 1 + 1 solid complexes **3a** or **3b** in high yields. Complex **3a** decomposed to give tetrafluoroethylene, iodine and **2** when irradiated with UV or heated. Complex **3b** was converted into 6*H*-dodecafluorohexyl-*N,N,N',N'*-tetramethylphenylene-1,4-diamine **4** when irradiated with UV. On treatment of **1a** and **1b** with piperazine **6a** and *N,N'*-dimethylpiperazine **6b**, 1 + 1 solid complexes **7** were similarly obtained. However, heating or irradiating **7** gave no perfluoroalkylated products. Irradiating a mixture of **2** or anilines **13** and perfluoroalkyl iodides **10** in dimethylformamide also gave perfluoroalkylated products. The photoinduced electron transfer reaction involved radical cation $2^{\bullet+}$ as a reactive intermediate which was detected by EPR techniques.

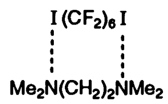
In 1965, it was first reported that charge-transfer complexes are formed between perfluoroalkyl iodides and amines based on the phase change diagram of the solution.[1] The complexation also resulted in the appearance in the IR and far-IR spectra of broad absorption at *ca.* 100 cm^{-1} characteristic of the nitrogen–iodine stretching mode and a marked upfield chemical shift for CF_3I or R_fCF_2I (R_f = perfluoroalkyl) in ^{19}F NMR spectra.[2] In 1978, Gutman proposed that such complexation occurs between perfluoroalkyl iodides and a variety of Lewis bases.[3] Our work has shown that the ^{19}F NMR upfield chemical shifts for the $-CF_2I$ of perfluoroalkyl iodides resulted from the complexation of perfluoroalkyl iodides with various solvents in a linear relationship with the DN (donor number) values of the solvents.[4] We have also reported that solid charge-transfer complexes are produced between tetrafluoro-1,2-diiodoethane or dodecafluoro-1,6-diiodohexane and morpholine, *N,N,N',N'*-tetramethylethylenediamine or 1,4-dioxane.[5]



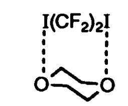
m.p. 90–91 °C



m.p. 106.5 °C



m.p. 103 °C



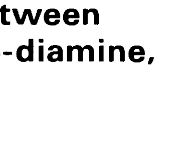
m.p. 50–51 °C

Recently, a number of reactions of perfluoroalkyl iodides acting as electron acceptors have been developed for the synthesis of fluorine-containing organic compounds of interest medicinally and biochemically.[6] In connection with our study of the photoinduced electron-transfer (PET) reaction of R_fI and CF_2I_2 with heterocyclic compounds (*e.g.* pyrroles, indoles, imidazoles and aminopyridines) to give perfluoroalkylated products,[7] here, we describe related work with *N,N,N',N'*-tetramethylphenylene-1,4-diamine, piperazines and anilines.

Results and Discussion

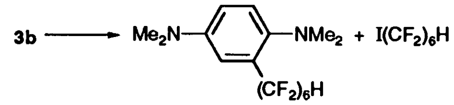
Tetrafluoro-1,2-diiodoethane **1a** or dodecafluoro-1,6-diiodohexane **1b** and *N,N,N',N'*-tetramethylphenylene-1,4-diamine (TMDP) **2** when mixed in chloroform at room temperature readily gave high yield of the solid products **3**, elemental analyses of which indicated that they comprised equimolar proportions of **1** and **2**. The ^{19}F NMR spectra showed that the chemical shifts of the CF_2I signal in **3a** and **3b** had moved

m.p. 85–88 °C
3a



m.p. 65 °C
3b

upfield (4.5 ppm for **3a** and 3.2 ppm for **3b**). When heated directly or irradiated with UV in acetonitrile or dimethylformamide (DMF), **3a** decomposed to afford tetrafluoroethylene, iodine and **2** (Scheme 1). When heated, compound **3b** began

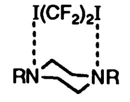


4 (45%) **5** (10%)

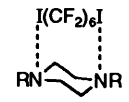
$$\mathbf{3a} \longrightarrow \mathbf{2} + CF_2{=}CF_2 + I_2$$

Scheme 1 *Conditions: hν* for **3b** and 85 °C or *hν* for **3a**

to melt at 65 °C and regenerate **1b** and **2**, none of the new compounds being produced; when irradiated with UV light in DMF or acetonitrile its temperature rose to 60 °C and it gave a moderate yield of 6*H*-perfluorohexylated product **4** and a small amount of the hydrogen-abstraction product **5** (Scheme 1). No



7a R = H m.p. 85 °C
7b R = Me m.p. 66 °C



7c R = H m.p. 55 °C
7d R = Me m.p. 77 °C

Scheme 2 *Reagents and conditions: hν*, DMF or MeCN, 60 °C, 6 h

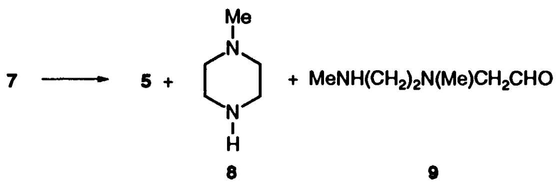
dodecafluoro-6-iodohexylated product was produced. Similarly, treatment of **1** with piperazine **6a** or *N,N'*-dimethylpiperazine **6b** gave solid 1:1 complexes **7** in high yields.

Table 1 Results of the reaction between **2** and **10**

Entry[a]	**10**[b]	Time (h)	**11**	Yield (%)[c]	R_fH (%)[d]
1	**10a**	4	**11a**	65	12
2	**10a** (1:3)	4	**11a**	70	13
3	**10b**	5	**11b**	66	18
4[e]	**10b**	8	**11b**	62	2
5	**10c**	4.5	**11c**	74	15
6[e]	**10c**	7	**11c**	70	2
7	**10d**	6.5	**11d**	64	12

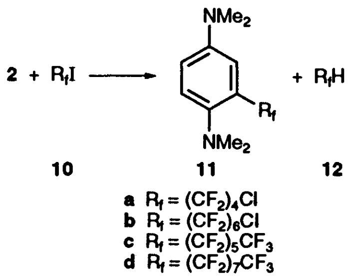
[a] Using DMF as solvent unless otherwise noted. [b] **2**:**10** = 1:2 unless otherwise noted. [c] Isolated yields based on **2**. [d] Determined by ^{19}F NMR. [e] Using acetonitrile as the solvent.

Compounds **7a** and **7b** decomposed to produce tetrafluoroethylene, iodine and **6a** or **6b**. When a solution of **7d** in acetonitrile was irradiated with UV light, compound **5**, *N*-methylpiperazine **8** and compound **9** were generated in low yields after treatment with water (Scheme 3). Although



Scheme 3 *Reagents and conditions: hv*, MeCN, 5 h; ii, H_2O

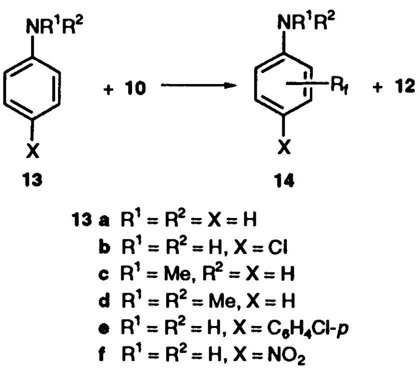
treatment of **2** with perfluoroalkyl iodides **10** in a similar manner gave no solid complexes, the corresponding perfluoroalkylated products **11** were generated in good yields when a mixture of **2** and **10** in DMF was irradiated (Scheme 4).



Scheme 4 *Reagents and conditions: hv*, DMF, K_2CO_2, 65 °C, 4–8 h

Potassium carbonate was added to neutralize the HI produced. Small amounts of compounds **12** were also generated but no diperfluoroalkylated products were detected. The results of the reactions are listed in Table 1.

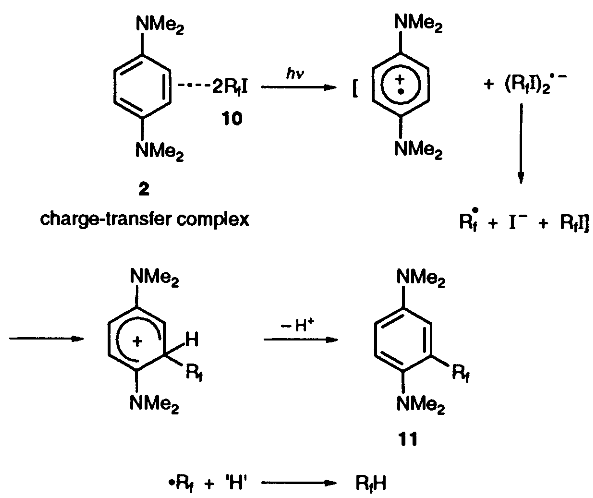
When an excess of anilines **13** was allowed to react with **10** (ratio 3:1) in DMF under similar conditions, the reaction temperature rose to 80 °C and mixtures of perfluoroalkylated products **14** in good yields with a small amount of compounds



Scheme 5 *Reagents and conditions: hv*, DMF, K_2CO_3, 80 °C, 12–20 h

12 were obtained (Scheme 5). Only *ortho*- and *para*-substituted products and no perfluoroalkylamino-substituted derivatives were produced. The reaction of *p*-nitroaniline **13f** afforded a very low yield, indicating that the presence of strong electron-withdrawing groups in the benzene ring of **13** was unprofitable to the reaction. The results of the reaction are listed in Table 2.

Aromatic amines are known as electron donors in photochemical reactions[8,9] and perfluoroalkyl iodides are recognized as electron acceptors.[6] As mentioned above, the upfield $-CF_2I$ ^{19}F NMR signal shifts of **1a** and **1b** in **3a** and **3b** are an indication of charge-transfer between **1** and **2**. In order to confirm the reaction mechanism, an electron paramagnetic resonance (EPR) spectroscopic study was carried out. Without irradiation, both complex **3a** and complex **3b** in DMF gave a signal with no hyperfine lines probably because of the strong polarity of DMF. In acetonitrile at room temperature, no EPR spectra of perfluoroalkyl radicals were observed even in the presence of 2-methyl-2-nitrosopropane.[10] However, the signals of the radical cation $TMPD^{\bullet+}$, similar to those reported by Lui *et al.*,[11] were seen for both **3a** ($g = 2.0031$, $a = 7.08 \times 10^{-4}$ T) and **3b** ($g = 2.0029$, $a = 7.24 \times 10^{-4}$ T), seemingly indicating the existence of the radical anions $\mathbf{1a}^{\bullet-}$ and $\mathbf{1b}^{\bullet-}$, because the ^{19}F NMR spectra showed that no reaction took place. Without UV irradiation, the solution of **2** and perfluoroalkyl iodides **10** in DMF or MeCN gave no EPR spectra. Under UV irradiation, the signals of $\mathbf{2}^{\bullet+}$ were also seen (for the solution of **2** and **10a**, $g = 2.0029$, $a = 7.11 \times 10^{-4}$ T). Therefore, we propose the mechanism shown in Scheme 6 for



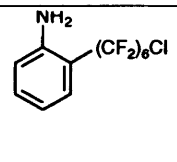
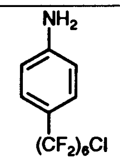
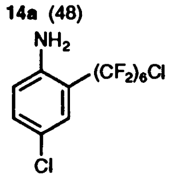
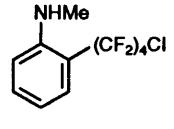
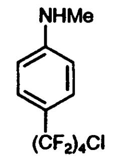
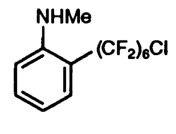
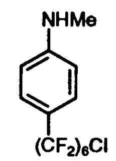
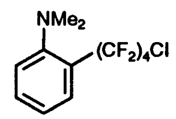
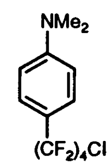
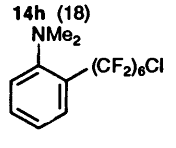
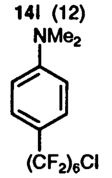
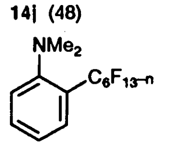
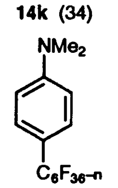
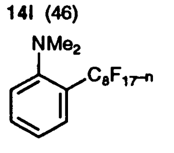
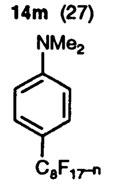
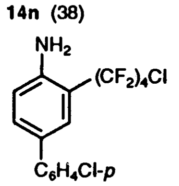
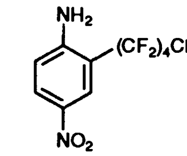
Scheme 6

the reaction between **2** and **1** or **10**. The radical anion, formed from electron-transfer between **2** and **10**, underwent carbon-iodine bond cleavage to give the perfluoroalkyl radical $R_f^{\bullet}$ which might couple with $\mathbf{2}^{\bullet+}$ forming the perfluoroalkylated product **11** or abstract hydrogen from the solvent affording R_fH.

In the irradiation-induced decomposition of **3a**, evolving tetrafluoroethylene, the radical anion $\mathbf{1a}^{\bullet-}$ formed after electron transfer from **2** to **1a**, preferentially underwent carbon–iodine bond cleavage. Similar results have been found for the reactions of $I(CF_2)_2X$ (X = I, Cl) and amines such as triethylamine, morpholine and *N*,*N*,*N*′,*N*′-tetramethylethylene-1,4-diamine.[12] While the thermal decomposition of **3a**, evolving tetrafluoroethylene, might involve both single electron-transfer and halophilic mechanisms similar to that of the reaction of $I(CF_2)_2X$ (X = I, Cl) with dialkyl malonate carbanions and other nucleophiles.[12]

In the reaction of **10** and **13**, addition of single electron-transfer scavengers, *p*-dinitrobenzene (DNB) and di-*tert*-

Table 2 Results of the reaction between **10** and **13**

Entry	10	13 (13:10)[a]	Time (h)	14(%)[b]		Yield of 12 (%)[c]
1	**10b**	**13a**	16	 **14a** (48)	 **14b** (28)	8
2	**10b**	**13b** (1.5:1)	20	 **14c** (51)		10
3	**10b**	**13b**	20	**14c** (60)		
4	**10a**	**13c**	12	 **14d** (54)	 **14e** (26)	12
5	**10b**	**13c**	14	 **14f** (52)	 **14g** (25)	11
6	**10a**	**13d**	12	 **14h** (55)	 **14i** (32)	10
7	**10a**	**13d** (1:1)	12	**14h** (24)	**14i** (18)	8
8[d]	**10a**	**13d**	12	**14h** (24)	**14i** (10)	5
9[e]	**10a**	**13d**	12	**14h** (28)	**14i** (14)	8
10[f]	**10a**	**13d**	12	**14h** (18)	**14i** (12)	4
11	**10b**	**13d**	14	 **14j** (48)	 **14k** (34)	12
12	**10c**	**13d**	14	 **14l** (46)	 **14m** (27)	18
13	**10d**	**13d**	18	 **14n** (38)	 **14o** (22)	10
14	**10a**	**13e**	12	 **14p** (60)		8
15[c]	**10a**	**13f**	20	 **14q** (10)		20

[a] **10**:**13** = 1:3 unless otherwise noted. [b] Isolated yields based on **10**. [c] Determined by ^{19}F NMR except entry 6. [d] 20 mol% of *p*-DNB was added. [e] 20 mol% of Bu^t_2NO was added. [f] 20 mol% of HQ was added.

butylaminooxyl or free radical inhibitor, hydroquinone (HQ) to the reaction mixtures significantly suppressed the reaction (entries 8–10 in Table 2), an indication that this reaction might also proceed by a PET mechanism.

The formation of compounds **8** and **9** should be the result of hydrogen abstraction of radical $I(CF_2)_6^{\bullet}$ produced in the reaction from the methyl or methylene group of **6b**.

Experimental

M.p.s are uncorrected. IR spectra were obtained on a Schimadzu-440 instrument in potassium bromide pellets for all solid samples and in films for all liquid samples. ^1H NMR spectra were recorded on a JEOL FX-90Q instrument or a Varian XL-200 instrument using tetramethylsilane or chloroform as an internal standard. ^{19}F NMR spectra were recorded on a Varian EM-360 instrument at 56.4 MHz using CF_3CO_2H as an external standard and chemical shifts in ppm were positive upfield. *J*-Values are given in Hz. Mass spectra were obtained on a Finnigan-4041 instrument. Silica gel (50 μm) was used for column chromatography.

Generation of Solid Complexes **3**.—Under a nitrogen atmosphere, **1a** (1.77 g, 5 mmol) and **2** (0.82 g, 5 mmol) were added to chloroform (10 cm^3) and the mixture was allowed to stand overnight at room temp., to give a precipitate which, after being filtered off and recrystallized from diethyl ether, gave 2.15 g (83%) of **3a** (2.15 g, 83%). M.p. 85–88 °C (decomposed to evolve $CF_2{=}CF_2$ quantitatively) (Found: C, 27.8; H, 3.1; N, 5.4; F, 14.4; I, 48.7. Calc. for $C_{12}H_{16}F_4I_2N_2$: C, 27.82; H, 3.12; N, 5.41; F, 14.67; I, 48.99%); ν_{max}/cm^{-1} 2860, 1615, 1510, 1500, 1470, 1450, 1295, 1110, 1065, 930 and 810; $\delta_H(CDCl_3)$ 2.45 (12 H, s, CH_3) and 6.60 (4 H, ArH); $\delta_F(CDCl_3)$ −23.8 (s); *m/z* 354 (**1a**$^+$, 32), 254 (37), 227 ($ICF_2CF_2^+$, 47), 208 (13), 177 (ICF_2^+, 16), 164 (**2**$^+$, 100), 149 (43), 127 (I^+, 24) and 100 ($CF_2CF_2^+$, 23).

Complex **3b**. 81% Yield; m.p. 65 °C (Found: C, 26.5; H, 1.2; N, 3.9; F, 31.6; I, 36.1. Calc. for $C_{16}H_{16}F_{12}I_2N_2$: C, 26.74; H, 2.23; N, 3.90; F, 31.75; I, 31.38%); ν_{max}/cm^{-1} 2960, 1855, 1515, 1475, 1300, 1210, 1160, 1075, 935, 820 and 785; $\delta_H(CDCl_3)$ 2.50 (12 H, s, CH_3) and 6.80 (4 H, s, Ar-H); $\delta_F(CDCl_3)$ −17.3 (4 F, s), 35.7 (4 F, s) and 44.0 (4 F, s); *m/z* 554 (**1b**$^+$, 5), 427 ($M^+ - I$, 12), 227 ($ICF_2CF_2^+$, 8), 181 (17), 177 (ICF_2^+, 100), 131 (66), 127 (I^+, 53), 100 ($CF_2CF_2^+$, 28) and 69 (67).

Photolysis of **3b**.—Under a nitrogen atmosphere, a solution of **3b** (3.60 g, 5 mmol) in DMF (10 cm^3) was irradiated and stirred, in a Pyrex flask, connected to a solid-CO_2 cooler, with a high-pressure mercury lamp (450 W) at a distance of 10 cm for 6 h. The temperature rose to about 60 °C as a result of the irradiation. ^{19}F NMR spectroscopy indicated that 10% of $I(CF_2)_6H$ **4** was produced. The solution was then poured into water (30 cm^3) and extracted with dichloromethane (3 × 10 cm^3). The chloromethane phase was washed with water (3 × 5

cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was then subjected to column chromatography on silica gel using diethyl ether–light petroleum (1:3) as eluent, to give 2-(6*H*-perfluorohexyl)-*N*,*N*,*N'*,*N'*-tetramethylphenylene-1,4-diamine **4** as an oil (1.04 g, 45%) (Found: C, 41.3; H, 3.3; N, 6.2; F, 48.8. Calc. for $C_{16}H_{16}F_{12}N_2$: C, 41.38; H, 3.45; N, 6.03; F, 49.14%); ν_{max}/cm^{-1} 2950, 1615, 1545, 1500, 1480, 1445, 1350, 1240, 1185, 985 and 895; $\delta_H(CDCl_3)$ 2.04 (6 H, s, CH_3), 2.43 (6 H, s, CH_3), 6.20 (1 H, tt, *J* 56, 8) and 6.32–6.98 (3 H, m); $\delta_F(CDCl_3)$ 28.0 (2 F, s), 43.3 (2 F, s), 45.4 (2 F, s), 46.3 (2 F, s), 53.4 (2 F, s) and 61.9 (2 F, d, *J* 56); *m/z* 464 (M^+, 100), 449 ($M^+ - CH_3$, 20), 448 ($M^+ - CH_4$, 16) and 213 [$M^+ - (CF_2)_5H$, 14].

Generation of Solid Complexes **7**.—Solid complexes **7** were produced in a procedure similar to that described for **3**. **7a** (in 85% yield); m.p. 85 °C (decomp.) (Found: C, 16.2; H, 2.1; N, 6.7; F, 15.3; I, 57.4. Calc. for $C_6H_{10}F_4I_2N_2$: C, 16.36; H, 2.27; N, 6.36; F, 15.27; I, 57.73%); ν_{max}/cm^{-1} 3250 (NH), 2830, 1450, 1365, 1315, 1100, 1060, 940 and 825; $\delta_H(CDCl_3)$ 2.65 (8 H, s, CH_2) and 3.10 (2 H, NH); $\delta_F(CDCl_3)$ −20.0 (s); *m/z* 354 (**1a**$^+$, 51), 254 (70), 227 ($ICF_2CF_2^+$, 100), 208 (21), 177 (ICF_2^+, 33) and 100 ($CF_2CF_2^+$, 40).

Complex **7c**. 75% Yield; m.p. 55 °C (Found: C, 18.5; H, 1.3; N, 4.2; F, 35.6; I, 39.4. Calc. for $C_{10}H_{10}F_{12}I_2N_2$: C, 18.75; H, 1.56; N, 4.36; F, 35.63; I, 39.69%); ν_{max}/cm^{-1} 3300 (NH), 2850, 1445, 1380, 1365, 1320, 1180, 1065, 990, 885 and 760; $\delta_H(CDCl_3)$ 2.64 (8 H, s, CH_2) and 3.05 (2 H, s, NH); $\delta_F(CDCl_3)$ −15.5 (4 F, s), 35.6 (4 F, s) and 43.5 (4 F, s); *m/z* 554 (**1b**$^+$, 17), 427 (**1b**$^+$ − I, 100), 281 (18), 254 (8), 227 ($ICF_2CF_2^+$, 15), 177 (ICF_2^+, 98), 181 (17), 131 (61), 100 (25) and 69 (53).

Complex **7b**. 79% Yield; m.p. (decomp.) 66 °C (Found: C, 20.8; H, 2.7; N, 6.2; F, 16.1; I, 54.0. Calc. for $C_8H_{14}F_4I_2N_2$: C, 20.51; H, 2.99; N, 5.98; F, 16.24; I, 54.27%); ν_{max}/cm^{-1} 2850, 1445, 1350, 1290, 1140, 985, 935 and 880; $\delta_H(CDCl_3)$ 2.24 (6 H, s, CH_3) and 2.66 (8 H, s, CH_2); $\delta_F(CDCl_3)$ −20.1 (4 F, s); *m/z* 354 (**1a**$^+$, 677), 227 ($ICF_2CF_2^+$, 76), 177 (ICF_2^+, 100), 127 (I^+, 24) and 100 ($CF_2CF_2^+$, 10).

Complex **7d**. 71% Yield; m.p. 77 °C (Found: C, 21.2; H, 1.7; N, 3.9; F, 34.2; I, 37.8. Calc. for $C_{12}H_{14}F_{12}I_2N_2$: C, 21.56; H, 2.10; N, 4.20; F, 34.13; I, 38.08%); ν_{max}/cm^{-1} 2950, 2850, 1450, 1360, 1250, 1140, 980, 940 and 890; $\delta_H(CDCl_3)$ 2.20 (6 H, s, CH_3) and 2.64 (8 H, s, CH_2); $\delta_F(CDCl_3)$ −16.0 (4 F, s), 35.6 (4 F, s) and 44.0 (4 F, s); *m/z* 554 (**1b**$^+$, 15), 427 (**1b**$^+$ − I, 60), 227 ($ICF_2CF_2^+$, 11), 117 (ICF_2^+, 58), 131 (41), 127 (I^+, 33), 115 (**11b**$^+$ + 1, 100), 100 ($CF_2CF_2^+$, 19) and 69 (28).

Photolysis of **7d**.—Under a nitrogen atmosphere, a solution of **7d** (1.54 g, 2 mmol) in acetonitrile (10 cm^3) was irradiated for 5 h. ^{19}F NMR spectroscopy indicated that 10% of $I(CF_2)_6H$ **5** had been produced. After work-up as described above, **8** (0.01 g, 5%) and **9** (0.013 g, 5%) were obtained. **8**: $\delta_H(CDCl_3)$ 2.28 (3 H, s, CH_3), 2.58–2.70 (8 H, m, CH_2) and 3.15 (1 H, s, NH); *m/z* 101 (M^+ + 1, 100) and 84 ($M^+ - CH_4$, 48). **9** oil (Found: C, 55.0; H, 10.7; N, 21.7. Calc. for $C_6H_{14}N_2O$: C, 55.34; H, 10.86; N, 21.52%); $\delta_H(CDCl_3)$ 2.15 (3 H, s, CH_3), 2.22 (3 H, s, CH_3), 2.63 (4 H, m, CH_2), 3.04 (1 H, s, NH), 3.82 (2 H, d, *J* 2.5, CH_2CO) and 9.80 (1 H, d, *J* 2.5, CHO); *m/z* 130 (M^+ + 1, 20) and 43 ($CH_3N{=}CH_2^{\bullet +}$).

Photoinduced Reaction of N,N,N',N'*-Tetramethylphenylene-*1,4*-diamine* **2** *and Perfluoroalkyl Iodides* **10**.—*Typical procedure.* Under a nitrogen atmosphere, a solution of **2** (0.82 g, 5 mmol), **10b** (4.65 g, 10 mmol), and K_2CO_3 (0.70 g, 5 mmol) in DMF (10 cm^3) was irradiated for 4 h. ^{19}F NMR spectroscopy indicated that about 18% of compound **12b** was formed. Work-up as described above gave 2-(6-chlorododecafluorohexyl)-*N*,*N*,*N'*,*N'*-tetramethylphenylene-1,4-*diamine* **11b** as an oil (1.65 g, 66%) (Found: C, 38.0; H, 2.7; N, 3.55; F, 45.6. Calc. for $C_{16}H_{16}ClF_{12}N_2$: C, 38.52; H, 3.01; N, 3.62; F, 45.70%); ν_{max}/cm^{-1} 2945, 2810, 1615, 1515, 1435, 1355, 1200, 1080, 990 and 770; $\delta_H(CDCl_3)$ 2.19 (6 H, s, CH_3), 2.42 (6 H, s, CH_3) and 6.36–7.02 (3 H, m); $\delta_F(CDCl_3)$ −8.2 (2 F, s), 28.0 (2 F, s) and 44.5 (4 F, s); *m/z* 501 (M^+ + 1, 36), 500 (M^+, 17), 499 (M^+ + 1, 100), 498 (M^+, 54), 483 (9) and 213 [$M^+ - (CF_2)_5Cl$, 19].

2-(4-*Chlorooctafluorobutyl*)-N,N,N',N'*-tetramethylphenylene-*1,4*-diamine* **11a**. Oil (Found: C, 42.2; H, 3.6; N, 6.7; F, 38.3. Calc. for $C_{14}H_{15}ClF_8N_2$: C, 42.16; H, 3.76; N, 7.03; F, 38.14%); ν_{max}/cm^{-1} 2950, 1620, 1500, 1455, 1360, 1310, 1190, 1080, 985 and 785; $\delta_H(CDCl_3)$ 2.29 (6 H, s, CH_3), 2.51 (6 H, s, CH_3) and 6.46–7.13 (3 H, m); $\delta_F(CDCl_3)$ −8.6 (2 F, s), 27.8 (2 F, s), 44.5 (2 F, s) and 45.7 (2 F, s); *m/z* 400 (M^+, 26), 298 (M^+, 100), 383 (23), 363 (8), 213 [$M^+ - (CF_2)_3Cl$, 24] and 198 (12).

2-*Perfluorohexyl*-N,N,N',N'*-tetramethylphenylene-*1,4*-diamine* **11c**. Oil (Found: C, 39.8; H, 3.1; N, 5.8; F, 52.2. Calc. for $C_{16}H_{15}F_{13}N_2$: C, 39.71; H, 3.37; N, 6.04; F, 52.33%); ν_{max}/cm^{-1} 2950, 1615, 1545, 1495, 1410, 1395, 1200, 1145, 985 and 785; δ_H([$^2H_6$]acetone) 2.05 (6 H, s, CH_3), 2.41 (6 H, s, CH_3) and 6.35–6.79 (3 H, m); δ_F([$^2H_6$]acetone) 4.9 (3 F, s), 27.7 (2 F, s), 43.2 (2 F, s), 45.1 (2 F, s), 45.9 (2 F, s) and 49.6 (2 F, s); *m/z* 482 (M^+, 100), 467 ($M^+ - CH_3$, 15), 466 (13), 213 ($M^+ - C_5H_{11}$, 10), 198 (15) and 69 (12).

2-*Perfluorooctyl*-N,N,N',N'*-tetramethylphenylene-*1,4*-diamine* **11d**. Oil (Found: C, 36.85; H, 2.5; N, 4.9; F, 56.0. Calc. for $C_{18}H_{15}F_{17}N_2$: C, 37.11; H, 2.58; N, 4.98; F, 55.50%); ν_{max}/cm^{-1} 2965, 1620, 1595, 1545, 1450, 1400, 1345, 1200, 985 and 780; δ_H([$^2H_6$]acetone) 2.04 (6 H, s, CH_3), 2.42 (6 H, s, CH_3) and 6.50–6.94 (3 H, m); δ_F([$^2H_6$]acetone) 5.1 (3 F, s), 27.8 (2 F, s), 43.3 (2 F, s), 45.3 (8 F, s) and 49.8 (2 F, s); *m/z* 582 (M^+, 100), 567 ($M^+ - CH_3$, 6), 213 ($M^+ - C_7F_{15}$, 6) and 69 (14).

Photoinduced Reaction of Perfluoroalkyl Iodides **10** *and Anilines* **13**.—*Typical procedure.* **10a** (1.82 g, 5 mmol), **13d** (1.82 g, 15 mmol), K_2CO_3 (0.69 g, 5 mmol) and DMF (10 cm^3) were added to a Pyrex flask under a nitrogen atmosphere. The system was connected to a solid-CO_2 cooler and then exposed, whilst being stirred, to a high-pressure mercury lamp (450 W) at a distance of *ca.* 8 cm for 12 h. Distillation gave **12a** (0.12 g, 10%). The residue was then poured into water (30 cm^3) and extracted with dichloromethane (3 × 10 cm^3). The organic phase was washed with water (3 × 5 cm^3), dried ($MgSO_4$) and evaporated. The residue was subjected to column chromatography on silica gel using light petroleum–diethyl ether (3:1) as eluent, to give 2-(4-chlorooctafluorobutyl)-*N*,*N*-dimethylaniline **14h** (0.98 g, 55%) and 4-(4-chlorooctafluorobutyl)-*N*,*N*-dimethylaniline **14i** (0.57 g, 32%). **14h**: oil, ν_{max}/cm^{-1} 2930, 2810, 1600, 1580, 1450, 1310, 1290, 1075, 960, 830, 775 and 710; $\delta_H(CDCl_3)$ 2.19 (6 H, s, CH_3) and 7.00 (4 H, m); $\delta_F(CDCl_3)$ −8.6 (2 F, s), 28.0 (2 F, s), 43.4 (2 F, s) and 43.8 (2 F, s); *m/z* 357 (M^+, 30), 355 (M^+, 80), 320 (23), 171 [$M^+ - (CF_2)_3Cl + 1$, 100] and 170 (24). **14i**: oil, ν_{max}/cm^{-1} 2860, 1615, 1530, 1485, 1375, 1180, 1090, 1000, 945 and 775; δ_H([$^2H_6$]acetone) 2.46 (6 H, s, CH_3), 6.50 (2 H, d, *J* 9.0) and 6.96 (2 H, d, *J* 9.0); δ_F([$^2H_6$]acetone) −7.8 (2 F, s), 32.5 (2 F, s), 43.2 (2 F, s) and 44.6 (2 F, s); *m/z* 358 (M^+ + 1, 10), 357 (M^+, 27), 356 (M^+ + 1, 36), 355 (M^+, 93), 320 (32), 171 (10) and 170 [$M^+ - (CF_2)_3Cl$, 100].

2-(6-*Chlorododecafluorohexyl*)*aniline* **14a** *and* 4-(6-*chlorododecafluorohexyl*)*aniline* **14b**. **14a**: oil, ν_{max}/cm^{-1} 3355, 3300 (NH_2), 1635, 1590, 1465, 1330, 1200, 1045, 980 and 765; $\delta_H(CDCl_3)$ 4.10 (2 H, s, NH_2) and 6.35–7.40 (4 H, m); $\delta_F(CDCl_3)$ −7.8 (2 F, s), 30.1 (2 F, s), 44.0 (2 F, s) and 44.8 (2 F, s); *m/z* 430 (M^+ + 1, 21), 429 (M^+, 13), 428 (M^+ + 1, 54), 427 (M^+, 30), 308 (14), 142 [$M^+ - (CF_2)_5Cl$, 100]. **14b**: oil,

ν_{max}/cm^{-1} 3350, 3255 (NH_2), 1625, 1520, 1205, 1065, 960 and 760; δ_H($CDCl_3$) 3.75 (2 H, s, NH_2), 6.50 (2 H, d, *J* 8.5) and 7.25 (2 H, d, *J* 8.5); δ_F($CDCl_3$) −9.8 (2 F, s), 31.2 (2 F, s), 43.9 (2 F, s) and 44.9 (2 F, s); *m*/*z* 430 (M^+ + 1, 23), 429 (M^+, 16), 428 (M^+ + 1, 65), 427 (M^+, 44), 308 (21), 142 (66) and 93 ($C_6H_4NH_2^+$ + 1, 100).

4-Chloro-2-(6-chlorododecafluorohexyl)chloroaniline **14c**. Oil, ν_{max}/cm^{-1} 3450, 3400 (NH_2), 1650, 1505, 1200 and 980; δ_H($CDCl_3$) 4.02 (2 H, s, NH_2) and 6.30–7.50 (3 H, m); δ_F($CDCl_3$) −9.8 (2 F, s), 30.9 (2 F, s), 41.08 (2 F, s) and 43.1 (2 F, s); *m*/*z* 465 (M^+ + 1, 12), 464 (M^+, 4), 463 (M^+ + 1, 34), 462 (M^+, 10), 443 (11), 178 [M^+ − $(CF_2)_5Cl$, 46] and 176 [M^+ − $(CF_2)_5Cl$, 100].

2-(4-Chlorooctafluorobutyl)-N-*methylaniline* **14d** *and* 4-(4-*chlorooctafluorobutyl)*-N-*methylaniline* **14e**. **14d**: oil (Found: C, 38.7; H, 2.4; N, 4.0; F, 44.1. Calc. for $C_{11}H_8ClF_8N$: C, 38.67; H, 2.36; N, 4.10; F, 44.49%); ν_{max}/cm^{-1} 3340 (NH), 2955, 1505, 1195, 1040 and 940; δ_H($CDCl_3$) 2.50 (3 H, s, CH_3), 4.52 (1 H, s, NH) and 6.80–7.62 (4 H, m); δ_F($CDCl_3$) −7.4 (2 F, s), 30.1 (2 F, s), 42.0 (2 F, s) and 43.2 (2 F, s); *m*/*z* 344 (M^+ + 1, 40), 343 (M^+, 10), 342 (M^+ + 1, 100), 341 (M^+, 28), 306 (19), 286 (9), 156 (44) and 136 (70). **14e**: oil (Found: C, 38.5; H, 2.1; N, 4.2; F, 44.6. Calc. for $C_{11}H_8ClF_8N$: C, 38.67; H, 2.36; N, 4.10; F, 44.49%); ν_{max}/cm^{-1} 3320 (NH), 2940, 1500, 1205 and 945; δ_H($CDCl_3$) 2.45 (3 H, s, CH_3), 3.87 (1 H, s, NH), 6.80 (2 H, d, *J* 9.0) and 7.12 (2 H, d, *J* 9.0); δ_F($CDCl_3$) −8.6 (2 F, s,), 32.7 (2 F, s), 43.0 (2 F, s) and 44.6 (2 F, s); *m*/*z* 343 (M^+, 7), 341 (M^+, 17), 306 (M^+ − Cl, 11), 157 (11) and 156 [M^+ − $(CF_2)_3Cl$, 100].

2-(6-Chlorododecafluorohexyl)-N-*methylaniline* **14f** *and* 4-(6-*chlorododecafluorohexyl)*-N-*methylaniline* **14g**. **14f**: oil (Found: C, 35.2; H, 1.6; N, 3.3; F, 51.7. Calc. for $C_{13}H_8ClF_{12}N$: C, 35.35; H, 1.83; N, 3.17; F, 51.63%); ν_{max}/cm^{-1} 3400 (NH), 1500, 1435, 1285, 1210 and 980; δ_H($CDCl_3$) 2.72 (3 H, s, CH_3), 4.02 (1 H, s, NH) and 6.85–7.61 (4 H, m); δ_F($CDCl_3$) −8.6 (2 F, s), 39.6 (2 F, s), 44.0 (2 F, s) and 45.0 (2 F, s); *m*/*z* 443 (M^+, 14), 441 (M^+, 49), 406 (M^+ − Cl, 7), 157 (32) and 156 [M^+ − $(CF_2)_5Cl$, 100]. **14g**: oil (Found: C, 35.4; H, 1.9; N, 3.1; F, 51.2. Calc. for $C_{13}H_8ClF_{12}N$: C, 35.35; H, 1.83; N, 3.17; F, 51.63%); ν_{max}/cm^{-1} 3380 (NH), 1505, 1460, 1265, 1195 and 885; δ_H($CDCl_3$) 2.62 (3 H, s, CH_3), 3.25 (1 H, s, NH), 6.69 (2 H, d, *J* 9.0) and 7.24 (2 H, d, *J* 9.0); δ_F($CDCl_3$) 8.1 (2 F, s), 31.6 (2 F, s), 44.2 (2 F, s) and 45.2 (2 F, s); *m*/*z* 444 (M^+ + 1, 10), 442 (M^+ + 1, 32), 406 (M^+ − Cl, 7), 157 (32) and 91 (100).

2-(6-Chlorododecafluorohexyl)-N,N-*dimethylaniline* **14j** *and* 4-(6-*chlorododecafluorohexyl)*-N,N-*dimethylaniline* **14k**. **14j**: oil, ν_{max}/cm^{-1} 2940, 2830, 2760, 1600, 1495, 1285, 1160, 1070, 970 and 770; δ_H([$^2H_6$]acetone) 2.15 (6 H, s, CH_3) and 6.95–7.10 (4 H, m); δ_F([$^2H_6$]acetone) −8.1 (2 F, s), 27.9 (2 F, s) and 43.8 (8 F, s); *m*/*z* 458 (M^+ + 1, 10), 457 (M^+, 28), 456 (M^+ + 1, 30), 455 (M^+, 80), 436 (12), 420 (19), 171 (27), 170 (M^+ − C_5F_{11}, 100) and 120 (16). **14k**: oil, ν_{max}/cm^{-1} 1615, 1585, 1425, 1320, 1200, 1140, 1080 and 970; δ_H([$^2H_6$]acetone) 2.15 (6 H, s, CH_3), 6.90 (2 H, d, *J* 8.5) and 7.21 (2 H, d, *J* 8.5); δ_F([$^2H_6$]acetone) −8.1 (2 F, s), 31.4 (2 F, s) and 44.0 (8 F, s); *m*/*z* 457 (M^+, 3), 455 (M^+, 6), 441 (100), 406 (13), 156 (82) 136 (86) and 85 (10).

2-Perfluorohexyl-N,N-*dimethylaniline* **14i** *and* 4-*perfluorohexyl*-N,N-*dimethylaniline* **14m**. **14i**: oil (Found: C, 38.2; H, 2.3; N, 3.2; F, 56.4. Calc. for $C_{14}H_{10}F_{13}N$: C, 38.27; H, 2.28; N, 3.17; F, 56.26%); ν_{max}/cm^{-1} 2940, 1615, 1505, 1400, 1365, 1205, 1090, 965 and 780; δ_H($CDCl_3$) 2.65 (6 H, s, CH_3) and 6.52–7.13 (4 H, m); δ_F($CDCl_3$) 5.2 (3 F, s), 27.6 (2 F, s), 43.5 (2 F, s), 45.4 (2 F, s), 46.0 (2 F, s) and 49.8 (2 F, s); *m*/*z* 439 (M^+, 100), 438 (M^+ − H, 17), 420 (22), 170 (M^+ − C_5H_{11}, 21) and 120 (76). **14m**: oil (Found: C, 37.9; H, 2.3; N, 3.3; F, 55.8. Calc. for $C_{14}H_{18}F_{13}N$: C, 38.27; H, 2.28; N, 3.17; F, 56.26%); ν_{max}/cm^{-1} 2950, 1500, 1455, 1385, 1205, 945 and 895; δ_H($CDCl_3$) 2.47 (6 H, s, CH_3), 6.42 (2 H, d, *J* 9.0) and 6.95 (2 H, d, *J* 9.0); δ_F($CDCl_3$) 4.9 (3 F, s), 29.9 (2 F, s), 45.0 (6 F, s) and 46.0 (2 F, s); *m*/*z* 440 (M^+ + 1, 7), 439 (M^+, 46), 420 (M^+ − F, 11), 170 (M^+ − C_5F_{11}, 100) and 69 (13).

2-Perfluorooctyl-N,N-*dimethylaniline* **14n** *and* 4-*perfluorooctyl*-N,N-*dimethylaniline* **14o**. **14n**: oil (Found: C, 35.6; H, 1.7; N, 2.6; F, 60.4. Calc. for $C_{16}H_{10}F_{17}N$: C. 35.62; H, 1.86; N, 2.59; F, 59.93%); ν_{max}/cm^{-1} 2945, 1605, 1500, 1195, 935 and 785; δ_H($CDCl_3$) 2.42 (6 H, s, CH_3) and 7.13–7.42 (4 H, m); δ_F($CDCl_3$) 5.8 (3 F, s), 28.4 (2 F, s), 44.2 (2 F, s), 45.8 (8 F, s) and 50.6 (2 F, s); *m*/*z* 540 (M^+ + 1, 25), 538 (M^+ − H, 28), 525 (14), 170 (M^+ − C_7F_{15}, 100) and 69 (24). **14o**: oil (Found: C, 35.5; H, 1.5; N, 2.8; F, 59.95. Calc. for $C_{16}H_{10}F_{17}N$: C, 35.62; H, 1.86; N, 2.59; F, 59.93%); ν_{max}/cm^{-1} 2950, 1615, 1545, 1205 and 935; δ_H($CDCl_3$) 2.47 (4 H, s, CH_3), 6.62 (2 H, d, *J* 8.5) and 7.00 (2 H, d, *J* 8.5); δ_F($CDCl_3$) 6.0 (3 F, s), 31.0 (2 F, s), 44.4 (2 F, s), 46.0 (8 F, s) and 50.6 (2 F, s); *m*/*z* 540 (M^+ + 1, 28), 539 (M^+, 100), 520 (8), 470 (13), 170 (46), 156 (17) and 69 (21).

3-(4-Chlorooctafluorobutyl)-4-amino-4′-chlorobiphenyl **14p**. M.p. 58–60 °C (Found: C, 43.2; H, 2.0; N, 3.2; Cl, 16.2; F, 34.7. Calc. for $C_{16}H_9Cl_2F_8N$: C, 43.10; H, 1.69; N, 3.01; Cl, 16.18; F, 34.69%); ν_{max}/cm^{-1} 3350, 3320 (NH), 1580, 1390, 1230, 950 and 785; δ_H($CDCl_3$), 4.15 (2 H, s, NH_2), 6.78 (1 H, m) and 7.42–7.48 (6 H, m); δ_F($CDCl_3$) −8.9 (2 F, s), 32.2 (2 F, s), 43.1 (2 F, s) and 44.3 (2 F, s); *m*/*z* 439 (M^+, 45), 437 (M^+, 100), 418 (12), 254 (35), 252 (98), 202 (36) and 126 (13).

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References

1 N. F. Cheetham and A. D. E. Pullin, *J. Chem. Soc., Chem. Commun.*, 1965, 418.

2 (*a*) I. J. McNaught and A. D. E. Pullin, *Aust. J. Chem.*, 1974, **27**, 1009; (*b*) N. F. Cheetham, I. J. McNaught and A. D. E. Pullin, *Aust. J. Chem.*, 1974, **27**, 987; (*c*) A. Misher and A. D. E. Pullin, *Aust. J. Chem.*, 1971, **24**, 2493.

3 V. Gutman, in *The Donor–Acceptor Approach to Molecular Interaction*, Plenum Press, New York, 1978, p. 41.

4 Q.-Y. Chen, Y.-B. He and Z.-Y. Yang, *Jouji Huacue*, 1988, 451.

5 Q.-Y. Chen and Z.-M. Qiu, *J. Fluorine Chem.*, 1987, **35**, 79.

6 (*a*) R. Filler and Y. Kobayashi, *Biomedical Aspects of Fluorine Chemistry*, Kodonsha and Elsevier, New York, 1982; (*b*) R. E. Banks, *Organofluorine Compounds and Their Applications*, Ellis Horwood, Chichester, 1979; (*c*) J. T. Welch, *Tetrahedron*, 1987, **43**, 3123; (*d*) P. Calas, P. Moreau and A. Commeyras, *J. Chem. Soc., Chem. Commun.*, 1982, 433; (*e*) S. Sibille, E. d'Incan, L. Leport and J. Perichon, *Tetrahedron Lett.*, 1986, **27**, 3129; (*f*) W.-Y. Huang and B.-N. Huang, *Acta Chim. Sinica*, 1985, **43**, 663; (*g*) W.-Y. Huang and W.-P. Ma, *Chinese J. Chem.*, 1990, 175; (*h*) C.-M. Hu and F.-L. Qing, *J. Fluorine Chem.*, 1990, **49**, 275; (*i*) C.-M. Hu and Y.-L. Qiu, *J. Org. Chem.*, 1992, **57**, 3339; (*j*) Q.-Y. Chen and Z.-M. Qiu, *J. Fluorine Chem.*, 1986, **31**, 301; 1987, **35**, 343; (*k*) Q.-Y. Chen and Z.-M. Qiu, *J. Chem. Soc., Chem. Commun.*, 1987, 1240.

7 Q.-Y. Chen and Z.-T. Li, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1443.

8 For a review, see (*a*) S. G. Cohen, A. Parola and G. H. Parsons, Jr., *Chem. Rev.*, 1973, 73; (*b*) Y. N. Malkin and V. A. Kuzmin, *Russ. Chem. Rev. (Engl. Transl)*, 1985, 1041; (*c*) N. J. Pienta, in *Photoinduced Electron Transfer*, eds. A. M. Fox and M. Chanon, Elsevier, Amsterdam, 1988, part C, p. 42.

9 For examples, see (*a*) P. Maslak and J. Kula, *Tetrahedron Lett.*, 1990, **31**, 4969; (*b*) V. Guichard, A. Bourkba, M.-F. Lautie and O. Poizat, *Spectrochim. Acta, Part A*, 1989, **45A**, 187; (*c*) N. J. Turro, C.-H. Tung, I. R. Gould, G. W. Griffin, R. L. Smith and A. Manmade,

J. Photochem., 1984, **24**, 265; (*d*) S. A. Alkaitis and M. Gratzel, *J. Am. Chem. Soc.*, 1976, **98**, 3549.

10 (*a*) W.-Y. Huang, L. Lu and Y.-F. Zhang, *Chinese J. Chem.*, 1990, 348; (*b*) C. P. Audrieux, L. L. Gelis, M. Medebielle, J. Pinson and J.-M. Saveant, *J. Am. Chem. Soc.*, 1990, **112**, 35.

11 Y.-C. Liu, Z.-L. Liu, L.-M. Wu and P. Chen, *Tetrahedron Lett.*, 1985, **26**, 4201.

12 (*a*) Q.-Y. Chen and Z.-M. Qiu, *J. Fluorine Chem.*, 1986, **31**, 301; (*b*) Q.-Y. Chen and Z.-M. Qiu, *Acta Chim. Sinica*, 1987, **45**, 354.

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