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Perfluoroalkylation of Quinolinones and Phenoxazones with Bis(perfluoroalkanoyl) Peroxides

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ABSTRACT

Bis(perfluoroalkanoyl) peroxides reacted with quinolinones and phenoxazones to give the perfluoroalkyl derivatives. Their absorption and emission bands and photostability were examined.

1 INTRODUCTION

Introduction of the perfluoroalkyl group into organic molecules changes the physical properties of the compounds.[1] For example, 3-perfluoroalkylcoumarins have excellent photostability[2] and disazo dyes containing a perfluorobutylsulfonyl group have good second-order optical nonlinearities. Bis(perfluoroalkanoyl) peroxides are useful perfluoroalkylation reagents for electron-rich compounds such as aromatics, olefins and polymers.[3–10] In our continuing study on the synthesis and properties of dyes containing a perfluoroalkyl group,[2,11–13] we have now examined the perfluoroalkylation of 2-quinolinones and phenoxazones, which contain the basic skeletons of the carbostyril and oxazine dyes used as raw materials in lasers, electron luminescence technology and fluorescence analysis.

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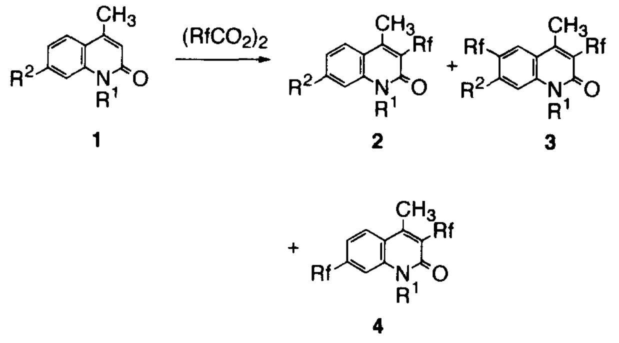


Scheme 1

TABLE 1
Perfluoroalkylation of Quinolinones

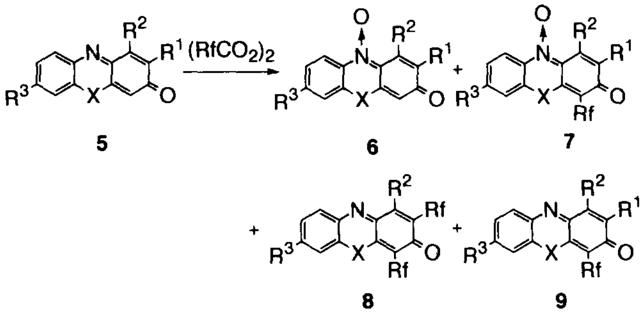
Run	*Compound*	*R^1*	*R^2*	*IP[a] (V)*	*R_f*	*Conversion (%)*	*Yield (%)*		
							2	*3*	*4*
1	**a**	H	H	1·24	C_3F_7	68	0	0	0
2	**b**	CH_3	H	1·04	C_3F_7	80	33	0	0
3	**c**	C_2H_5	H	1·09	C_3F_7	52	35	0	0
4	**c**	C_2H_5	H	1·09	C_3F_7	100[b]	29	31	18
5	**d**	C_2H_5	CH_3	1·10	C_3F_7	82	42	0	—
6	**e**	C_4H_9	H	1·25	C_3F_7	70	38	0	0
7	**f**	H	$N(CH_3)_2$	0·53	CF_3	70	0	0	—
8	**f**	H	$N(CH_3)_2$	0·53	C_3F_7	64	5	0	0
9	**f**	H	$N(CH_3)_2$	0·53	C_6F_{13}	67	6	0	—

[a] Versus Ag/Ag^+ in MeCN.
[b] Molar ratio: substrate/peroxide = 1/2.

2 RESULTS AND DISCUSSION

2.1 Perfluoroalkylation

The perfluoroalkylation of quinolinones is outlined in Scheme 1 and Table 1. The reaction of **1a** with an equimolar amount of bis(perfluorobutyryl) peroxide gave unidentified products which were not separated by column chromatography (SiO_2, $CHCl_3$: Me_2CO = 8:1) (run 1). However, the reactions of **1b–f** (**1f**: carbostyril 165) preferentially afforded the corresponding 3-perfluoroalkyl derivatives **2** (runs 2, 3, 5, 6, 8). The reaction of **1c** with excess peroxide gave both the mono- and bis(perfluoroalkyl) derivatives **2c**, **3c** and **4c** (run 4). The trifluoromethylation of **1f** was complicated and gave only polymeric products (run 7); however, the



Scheme 2

TABLE 2

Perfluoroalkylation of Phenoxazones and Phenothiazone

Run	*Compound*	*X*	*R¹*	*R²*	*R³*	*IP*[a] *(V)*	*R*$_f$	*Conversion (%)*	*Yield (%)*			
									6	*7*	*8*	*9*
1	**g**	O	H	H	H	1·21	C_3F_7	62	23	6	9	0
2	**h**	O	$-(CH{=}CH)_2-$		$N(C_2H_5)_2$	0·30	CF_3	61	0	0	—	11
3	**h**	O	$-(CH{=}CH)_2-$		$N(C_2H_5)_2$	0·30	C_3F_7	55	0	0	—	17
4	**h**	O	$-(CH{=}CH)_2-$		$N(C_2H_5)_2$	0·30	C_6F_{13}	55	0	0	—	15
5	**i**	S	H	H	$N(CH_3)_2$	0·87	C_3F_7	52	0	0	3	0

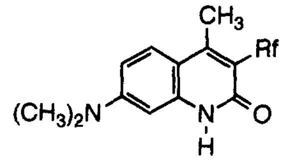
[a] Versus Ag/Ag^+ in MeCN.

perfluorohexylation of **1f** gave the corresponding 3-substituted derivative **2f″** in low yield (run 9).

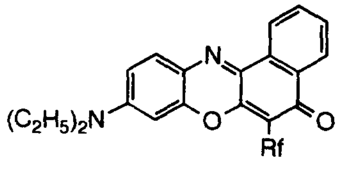
A single electron transfer (SET) mechanism from substrate to the peroxides has been proposed for the reaction.[3] It was found in this study that both the ionization potential (IP) and solubility of the substrate in a solvent affected the reaction. Though the IP of **1f** is low enough to proceed through SET, the solubility of **1f** was very low, giving the perfluoroalkylated products in low yields. However, 1-alkyl derivatives **1b–e**, which have higher IP values than **1f**, were more soluble than **1f** and gave the products in moderate yields.

Perfluoroalkylation reactions of phenoxazones and phenothiazone are shown in Scheme 2 and Table 2. The reaction of **5g** gave both oxidation and perfluoroalkylation products **6g**, **7g** and **8g** (run 1). This result indicates that the SET process competes with the oxidation reaction, as in the perfluoroalkylation of azobenzenes.[12] The oxazine dye **5h** (Nile Red) reacted with bis(perfluoroalkanoyl) peroxides to give the corresponding 6-perfluoroalkyl derivatives **9** (runs 2–4). Perfluoropropylation of the thiazine dye **5i** (Methylene Violet) was complicated, and afforded only the bis(perfluoroalkyl) derivative **8i** in low yield (run 5).

TABLE 3
Absorption and Fluorescence Spectra



1, 2



5, 9

Run	*Compound*	R_f	λ_{max} *(nm)*[a]	ε[a]	λ_{em} *(nm)*[b]	*RFI*[b]
1	**1f**	H	361	19000	420	1·00
2	**2f**	C_3F_7	381	19200	440	0·79
3	**2f"**	C_6F_{13}	381	22700	440	0·81
4	**5h**	H	549	31000	625	0·09
5	**9h'**	CF_3	560	20000	625	0·08
6	**9h**	C_3F_7	561	24000	620	0·11
7	**9h"**	C_6F_{13}	561	21000	620	0·12

[a] Measured in EtOH.

[b] Measured in EtOH (1×10^{-6} mol dm^{-3}, 7-dimethylamino-4-methylcoumarin: λ_{max} = 371 nm, ε = 21500, λ_{em} = 449 nm, RFI = 0·90).

2.2 Absorption and emission bands and photostability

The absorption and emission spectra of the carbostyril and oxazine dyes are summarized in Table 3. The absorption and emission maxima of **2f** and **2f"** showed a bathochromic shift (ca. 20 nm) compared with **1f** (runs 1–3). No significant difference in the absorption and emission maxima of the 3-perfluoropropyl and 3-perfluorohexyl derivatives was observed (runs

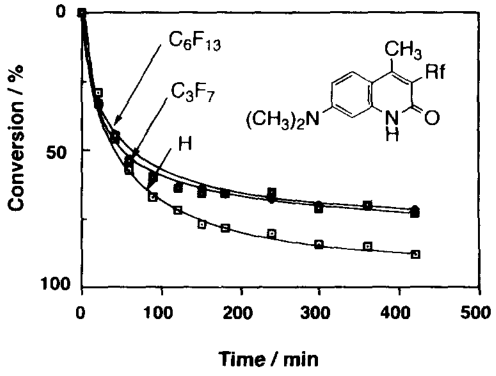


Fig. 1. Photostability of carbostyril dyes.

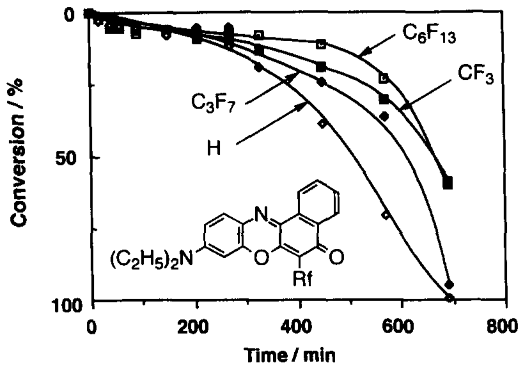


Fig. 2. Photostability of oxazine dyes.

2, 3). In the case of the oxazine dyes **5h**, **9h**, **9h'** and **9h"**, introduction of the perfluoroalkyl group did not result in any marked shifts in the absorption and emission maxima (runs 4–7).

The photostabilities of the carbostyril and oxazine dyes are shown in Figs 1 and 2, respectively. The stability was calculated on the basis of the change in absorption maximum. In each case, the perfluoroalkyl derivatives showed better photostability than the unsubstituted analogues.

3 EXPERIMENTAL

3.1 Instruments

Melting points were measured on a Yanagimoto micro-melting point apparatus and are uncorrected. ^{1}H NMR, mass and UV spectra were taken on Jeol JNM 270, Shimadzu QP-1000 and Shimadzu UV-160 spectrometers, respectively.

3.2 Materials

Bis(perfluoroalkanoyl) peroxides,[14] 2-quinolinones **1**[15] and 3H-phenoxazin-3-one (**5g**)[16] were synthesized as described in the literature. Dyes **1f**, **5h** and **5i** were purchased from Eastman Kodak Co. and used without further purification.

3.3 Perfluoroalkylation with bis(perfluoroalkanoyl) peroxides

In a general procedure, a Freon 113 solution of bis(perfluoroalkanoyl) peroxide was added to a dichloromethane solution (20–160 ml) of substrate

(1·0 mmol). The mixture was refluxed for 4 h under a nitrogen atmosphere. After the reaction, the mixture was washed with brine (20–160 ml), 10% aqueous sodium hydrogen carbonate solution (20–160 ml) and brine (20–160 ml). The organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvent, the product was isolated by column chromatography (SiO_2, $CHCl_3$: Me_2CO = 8:1). Physical and spectral data of the products are given below.

*1,4-Dimethyl-3-(perfluoropropyl)-2-quinolinone (**2b**)*
M.p. 142–143°C; ^{1}H NMR ($CDCl_3$) δ 2·69 (t, J = 2·9 Hz, 3H), 3·72 (s, 3H), 7·32 (t, J = 8·4 Hz, 1H), 7·39 (d, J = 8·4 Hz, 1H), 7·67 (t, J = 8·4 Hz, 1H), 7·96 (d, J = 8·4 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 341 (39) [M$^+$], 222 (100). $C_{14}H_{10}F_7NO$ (341·2): calculated C 49·28, H 2·95, N 4·10; found C 49·27, H 2·97, N 4·15.

*1-Ethyl-4-methyl-3-(perfluoropropyl)-2-quinolinone (**2c**)*
M.p. 115–117°C; ^{1}H NMR ($CDCl_3$) δ 1·36 (t, J = 7·1 Hz, 3H), 2·68 (t, J = 2·9 Hz, 3H), 4·36 (q, J = 7·1 Hz, 2H), 7·30 (t, J = 8·2 Hz, 1H), 7·40 (d, J = 8·2 Hz, 1H), 7·67 (t, J = 8·2 Hz, 1H), 7·96 (d, J = 8·2 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 355 (36) [M$^+$], 354 (40), 208 (100), 160 (22). $C_{15}H_{12}F_7NO$ (355·3): calculated C 50·71, H 3·40, N 3·94; found C 51·03, H 3·48, N 4·08.

*4,7-Dimethyl-1-ethyl-3-(perfluoropropyl)-2-quinolinone (**2d**)*
M.p. 115–117°C; ^{1}H NMR ($CDCl_3$) δ 1·36 (t, J = 7·3 Hz, 3H), 2·53 (s, 3H), 2·65 (t, J = 2·9 Hz, 3H), 4·34 (q, J = 7·3 Hz, 2H), 7·12 (d, J = 8·4 Hz, 1H), 7·18 (s, 1H), 7·83 (d, J = 8·4 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 369 (53) [M$^+$], 368 (61), 354 (24), 348 (27), 250 (29), 222 (100), 208 (33). $C_{16}H_{14}F_7NO$ (369·3): calculated C 52·04, H 3·82, N 3·79; found C 52·20, H 3·82, N 4·00.

*1-Butyl-4-methyl-3-(perfluoropropyl)-2-quinolinone (**2e**)*
M.p. 90–92°C; ^{1}H NMR ($CDCl_3$) δ 1·00 (t, J = 7·3 Hz, 3H), 1·49 (sextet, J = 7·3 Hz, 2H), 1·72 (quintet, J = 7·3 Hz, 2H), 2·67 (t, J = 3·0 Hz, 3H), 4·26 (dd, J = 7·3, 7·3 Hz, 2H), 7·29 (t, J = 7·5 Hz, 1H), 7·37 (d, J = 7·5 Hz, 1H), 7·65 (t, J = 7·5 Hz, 1H), 7·95 (d, J = 7·5 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 383 (100) [M$^+$], 382 (73), 208 (27). $C_{17}H_{16}F_7NO$ (383·3): calculated C 53·27, H 4·21, N 3·65; found C 53·49, H 4·18, N 3·90.

*2(1$\underline{H}$)-7-(Dimethylamino)-4-methyl-3-(perfluoropropyl)-2-quinolinone (**2f**)*
M.p. 267–269°C; ^{1}H NMR ($CDCl_3$) δ 2·59 (s, 3H), 3·08 (s, 6H), 6·42 (d, J = 2·4 Hz, 1H), 6·67 (dd, J = 9·4, 2·4 Hz, 1H), 7·66 (d, J = 9·4 Hz, 1H),

12·01 (br s, 1H); MS (EI, 70 eV) *m/z* (%) 370 (44) [M$^+$], 251 (100). $C_{15}H_{13}F_7N_2O$ (370·3): calculated C 48·66, H 3·54, N 7·57; found C 48·59, H 3·44, N 7·44.

*2(1H)-7-(Dimethylamino)-4-methyl-3-(perfluorohexyl)quinolinone (**2f"**)*
M.p. 294–295°C; ^{1}H NMR ($CDCl_3$) δ 2·60 (s, 3H), 3·07 (s, 6H), 6·42 (d, *J* = 1·9 Hz, 1H), 6·67 (dd, *J* = 9·2, 1·9 Hz, 1H), 7·67 (d, *J* = 9·2 Hz, 1H), 11·98 (br s, 1H); MS (EI, 70 eV) *m/z* (%) 520 (14) [M$^+$], 251 (100). $C_{18}H_{13}F_{13}N_2O$ (520·3): calculated C 41·55, H 2·52, N 5·38; found C 41·31, H 2·64, N 5·61.

*3,6-Bis(perfluoropropyl)-1-ethyl-4-methyl-2-quinolinone (**3c**)*
M.p. 109–111°C; ^{1}H NMR ($CDCl_3$) δ 1·38 (t, *J* = 7·2 Hz, 3H), 2·72 (t, *J* = 2·8 Hz, 3H), 4·37 (q, *J* = 7·2 Hz, 2H), 7·51 (d, *J* = 9·2 Hz, 1H), 7·83 (d, *J* = 9·2 Hz, 1H), 8·14 (s, 1H); MS (EI, 70 eV) *m/z* (%) 523 (56) [M$^+$], 522 (45), 376 (100). $C_{18}H_{11}F_{14}NO$ (523·3): calculated C 41·32, H 2·12, N 2·68; found C 41·46, H 2·09, N 2·73.

*3,7-Bis(perfluoropropyl)-1-ethyl-4-methyl-2-quinolinone (**4c**)*
M.p. 108–110°C; ^{1}H NMR ($CDCl_3$) δ 1·37 (t, *J* = 7·2 Hz, 3H), 2·71 (t, *J* = 2·8 Hz, 3H), 4·38 (q, *J* = 7·2 Hz, 2H), 7·49 (d, *J* = 8·4 Hz, 1H), 7·55 (S, 1H), 8·10 (d, *J* = 8·4 Hz, 1H); MS (EI, 70 eV): *m/z* (%) 523 (31) [M$^+$], 522 (37), 376 (100). $C_{18}H_{11}F_{14}NO$ (523·3): calculated C 41·32, H 2·12, N 2·68; found C 41·61, H 2·23, N 2·56.

*3H-Phenoxazin-3-one N-oxide (**6g**)*
M.p. 169–170°C (lit.[17] 162–165°C).

*3H-4-(Perfluoropropyl)phenoxazin-3-one N-oxide (**7g**)*
M.p. 126–128°C; ^{1}H NMR ($CDCl_3$) δ 6·91 (d, *J* = 9·9 Hz, 1H), 7·50 (dd, *J* = 7·7, 1·5 Hz, 1H), 7·51 (td, *J* = 7·7, 1·5 Hz, 1H), 7·54 (d, *J* = 9·9 Hz, 1H), 7·91 (dd, *J* = 7·7, 1·5 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 381 (18) [M$^+$], 365 (49), 246 (100). $C_{15}H_6F_7NO_3$ (381·2): calculated C 47·26, H 1·59, N 3·67; found C 47·05, H 1·73, N 3·98.

*3H-2,4-Bis(perfluoropropyl)phenoxazin-3-one (**8g**)*
M.p. 128–129°C; ^{1}H NMR ($CDCl_3$) δ 7·52 (dd, *J* = 8·4, 1·3 Hz, 1H), 7·58 (dd, *J* = 8·4, 1·3 Hz, 1H), 7·76 (td, *J* = 8·4, 1·3 Hz, 1H), 7·96 (s, 1H), 7·97 (dd, *J* = 8·4, 1·3 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 533 (18) [M$^+$], 414 (100), 299 (34), 69 (23). $C_{18}H_5F_{14}NO_2$ (533·2): calculated C 40·55, H 0·95, N 2·63; found C 40·77, H 0·97, N 3·36.

3H-2,4-Bis(perfluoropropyl)-7-(dimethylamino)phenothiazin-3-one (**8i**)
M.p. 220–221°C; ^{1}H NMR ($CDCl_3$) δ 3·27 (s, 6H), 6·78 (d, J = 2·5 Hz, 1H), 7·03 (dd, J = 9·5, 2·5 Hz, 1H), 7·81 (d, J = 9·5 Hz, 1H), 8·01 (s, 1H); MS (EI, 70 eV) *m/z* (%) 592 (16) [M^+], 473 (100), 69 (19), 57 (23). $C_{20}H_{10}F_{14}N_2OS$ (592·4): calculated C 40·55, H 1·70, N 4·73; found C 40·46, H 1·58, N 4·55.

5H-9-(Diethylamino)-6-(trifluoromethyl)benzo[a]phenoxazin-5-one (**9h'**)
M.p. 222–223°C; ^{1}H NMR ($CDCl_3$) δ 1·28 (t, J = 7·1 Hz, 6H), 3·49 (q, J = 7·1 Hz, 4H), 6·52 (d, J = 2·6 Hz, 1H), 6·77 (dd, J = 8·4, 2·6 Hz, 1H), 7·61–7·71 (m, 3H), 8·32 (dd, J = 7·9, 1·4 Hz, 1H), 8·63 (dd, J = 7·9, 1·4 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 386 (53) [M^+], 371 (100), 343 (23). $C_{21}H_{17}F_3N_2O_2$ (386·4): calculated C 65·28, H 4·44, N 7·25; found C 65·00, H 4·21, N 6·99.

5H-9-(Diethylamino)-6-(perfluoropropyl)benzo[a]phenoxazin-5-one (**9h**)
M.p. 192–194°C; ^{1}H NMR ($CDCl_3$) δ 1·29 (t, J = 7·2 Hz, 6H), 3·50 (q, J = 7·2 Hz, 4H), 6·48 (d, J = 2·8 Hz, 1H), 6·79 (dd, J = 9·2, 2·8 Hz, 1H), 7·61–7·71 (m, 3H), 8·32 (dd, J = 7·9, 1·1 Hz, 1H), 8·62 (dd, J = 7·9, 1·1 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 486 (68) [M^+], 471 (100), 323 (35). $C_{23}H_{17}F_7N_2O_2$ (486·4): calculated C 56·80, H 3·52, N 5·76; found C 57·05, H 3·40, N 5·76.

5H-9-(Diethylamino)-6-(perfluorohexyl)benzo[a]phenoxazin-5-one (**9h''**)
M.p. 162–163°C; ^{1}H NMR ($CDCl_3$) δ 1·22 (t, J = 7·1 Hz, 6H), 3·54 (q, J = 7·1 Hz, 4H), 6·45 (d, J = 2·7 Hz, 1H), 6·76 (dd, J = 8·7, 2·7 Hz, 1H), 7·75–7·60 (m, 3H), 8·31 (dd, J = 8·2, 1·1 Hz, 1H), 8·62 (dd, J = 8·2, 1·1 Hz, 1H); MS (EI, 70 eV) *m/z* (%) 636 (68) [M^+], 621 (30), 367 (100), 323 (35), 145 (31). $C_{26}H_{17}F_{13}N_2O_2$ (636·4): calculated C 49·07, H 2·69, N 4·40; found C 49·14, H 2·65, N 4·72.

3.4 Photostability

An ethanol solution (30 ml) of dye (5×10^{-5} mol dm^{-3}) in a borosilicate glass tube was irradiated with a 200 W high pressure mercury lamp using a 'merry-go-round' apparatus at room temperature under an air atmosphere. The conversion was calculated on the basis of the change of absorbance at absorption maximum of the solution using equation (1):

$$\text{Conversion (\%)} = [(A_0 - A_t)/A_0] \times 100 \qquad (1)$$

where A_0 and A_t are the absorbance at 0 and t hours, respectively.

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