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3,4,9,10-Perylenetetracarboxdiimides Containing Perfluoroalkyl Substituents

Kazuhito Deyama,[a] Hideyuki Tomoda,[a] Hiroshige Muramatsu[b] & Masaki Matsui[b]*

[a] Central Research Laboratory, NEOS Co., Ltd,
Oike-machi 1-1, Kosei-cho, Koga-gun, Shiga 520-32, Japan
[b] Department of Chemistry, Faculty of Engineering, Gifu University,
Yanagido, Gifu 501-11, Japan

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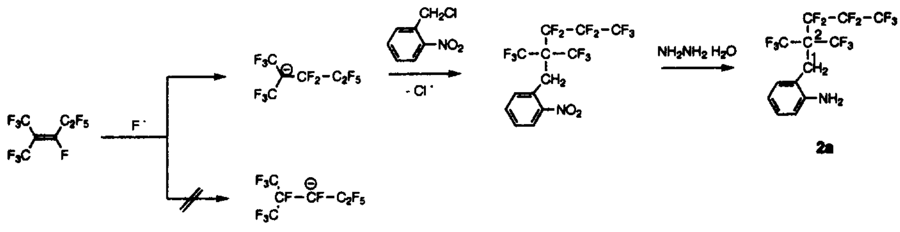
ABSTRACT

No significant difference in either the absorption or fluorescence spectra between N,N'-*di(perfluoroalkyl) and* N,N'-*dialkyl substituted 3,4,9,10-perylenetetracarboxdiimides was observed. The perfluoroalkyl-substituted derivatives were more soluble than the alkyl derivatives.*

1 INTRODUCTION

Much attention has been focused on the synthesis and properties of organic functional materials.[1–4] 3,4,9,10-Perylenetetracarboxdiimides have been described as dichroic dyes,[5] charge generation materials in dual type organic photoconductors,[6,7] and as fluorescent collectors.[8] However, the solubility of 3,4,9,10-perylenetetracarboxdiimides is very low. To improve this, Langhal *et al.* introduced bulky alkyl groups into the imido moieties and found that the 1-hexylheptylimino derivative was very soluble.[9] Seybold *et al.* have prepared *N*,*N*'-disubstituted 1,6,7,12-tetraphenoxy-3,4,9,10-perylenetetracarboxdiimides.[10] We have previously found that anthraquinone dyes substituted with perfluoroalkyl group(s) were much more soluble than those without the substituent[11] and in our continuing study on fluorine-containing dyes,[12-18] we report here the synthesis, absorption and fluorescence spectra and solubility of 3,4,9,10-perylenetetracarboxdiimides containing perfluoroalkyl groups.

* Corresponding author.

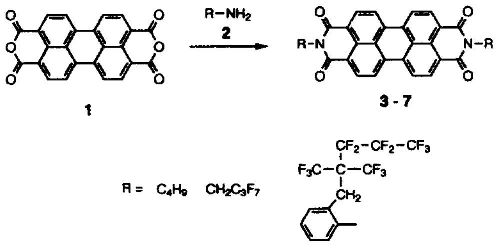


Scheme 1

2 RESULTS AND DISCUSSION

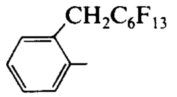
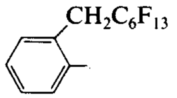
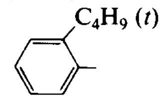
To obtain an aniline substituted with a bulky fluorine-containing group, 2-nitrobenzyl chloride was treated with the perfluoropropene dimer, (perfluoro-2-methyl-2-pentene) in the presence of potassium fluoride. The reaction sequence involves interaction of a fluoride anion with perfluoro-2-methyl-2-pentene to give the more stable tertiary perfluoroalkyl anion. Nucleophilic substitution reaction of the anion with 2-nitrobenzyl chloride then gives 2-(*1H,1H*-perfluoro-2,2-dimethylpentyl)nitrobenzene, reduction of which with hydrazine hydrate affords 2-(*1H,1H*-perfluoro-2,2-dimethylpentyl)aniline **2a** (Scheme 1). Electron impact (EI) mass spectrum of **2a** showed the molecular ion peak at *m*/*z* 425. The [^{1}H] NMR spectrum revealed a singlet proton peak based on the methylene group at 3·43, a broad amino peak at 3·57, and aromatic 4 proton peaks from 6·63 to 7·16 ppm. The [^{19}F] NMR spectrum of **2a** taken in deuterochloroform using trifluoroacetic acid as external standard showed a multiplet peak based on two trifluoromethyl peaks at 0 ~ −0·12, one trifluoromethyl peak at −18·15 ~ −18·23, and two perfluoromethylene peaks at −45·31 ~ −45·51 and −60·60 ~ −60·85 ppm. The derivative **2a** was identified as 2-(*1H,1H*-perfluoro-2,2-dimethylpentyl)aniline.

3,4,9,10-Perylenetetracarboxylic dianhydride **1** was heated with an amine **2** in the presence of zinc acetate to afford *N*,*N*′-disubstituted 3,4,9,10-perylenetetracarboxdiimides **3–6** (Scheme 2). *cis*-Isomers were separated from the *trans*-isomers by column chromatography (SiO_2—CH_2Cl_2). The



Scheme 2

TABLE 1
Physical Properties

Compd	*R*	*Solubility*[a]			λ_{max}[b] *(ε)* *(nm)*	λ_{em}[c] *(nm)*	*RFI*[d]
		Solvent	*mg/ 100 ml*	*(mmol* dm^{-3}*)*			
3	C_4H_9	$CHCl_3$	9·5	(0·19)	459 (16700)	533	390
					490 (45800)	572	126
					526 (75900)		
4	$C_3F_7CH_2$	$CHCl_3$	20	(0·27)	458 (14600)	532	344
					489 (41600)	572	113
					525 (70000)		
5		$CHCl_3$	$1{\cdot}4 \times 10^3$	(12)	459 (16300)	534	368
					490 (45300)	573	116
					527 (75400)		
	(*cis*)	C_6H_{14}	1·1	(0·0088)			
		C_6H_6	$1{\cdot}0 \times 10^2$	(0·85)			
		$1,3\text{-}(CF_3)_2C_6H_4$	$1{\cdot}1 \times 10^2$	(0·94)			
		CH_3OH	97	(0·080)			
6		$CHCl_3$	650	(5·3)	459 (22000)	534	409
					490 (57700)	573	131
					527 (93900)		
	(trans)						
7		$CHCl_3$	$8{\cdot}4 \times 10^2$	(13)	460 (14600)	534	100
					491 (41600)	574	30
					528 (70000)		
		C_6H_{14}	0·52	(0·0080)			
	(*trans*)	C_6H_6	22	(0·34)			
		$1,3\text{-}(CF_3)_2C_6H_4$	16	(0·24)			
		CH_3OH	3·0	(0·046)			

[a] Measured at 30°C.
[b] In $CHCl_3$.
[c] In $CHCl_3$ at 25°C.
[d] Relative fluorescence intensity in $CHCl_3$ at 25°C. **7** (λ_{em} at 534 nm): 100.

component having the larger retention on the silica gel column was identified as the *cis*-isomer, as in the case of *N*,*N*'-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenetetracarboximide.[19]

Absorption and fluorescence spectra, and the solubility of the *N*,*N*'-disubstituted 3,4,9,10-perylenetetracarboxdiimides **3**–**6**, together with di(2-*tert*-butylphenyl) derivative **7**, are summarized in Table 1.

No significant differences were apparent in the absorption and fluorescence spectra of the fluorine-containing derivatives **4**, **5**, **6** and the non-fluorinated **3** and **7**. Similarly, no marked difference between the alkyl derivatives **3** and

4 and the aryl derivatives **5–7** was observed. These results indicate that the imido moieties in the molecule do not affect either the absorption or fluorescence spectra.

Chloroform was the most suitable solvent to dissolve both the alkyl and aryl perylene dyes. The fluorine-containing derivative **4** was more soluble than the corresponding non-fluorinated derivative **3**. The aromatic derivatives **5–7** were much more soluble than the alkyl derivatives **3** and **4**. The perfluoroalkyl derivative **5** was more soluble than the *tert*-butyl derivative **7**. These results suggest that introduction of perfluoroalkyl and aryl substituents having a bulky fluorine-containing group at the *ortho* position lowers intermolecular interaction of the perylene rings, with resultant increase in their solubilities.

3 EXPERIMENTAL

3.1 Instruments

Melting points were measured with a Yanagimoto MP-S2 micro melting point apparatus. NMR spectra were recorded on Jeol α-400 and 270-GX spectrometers. Mass, UV, and fluorescence spectra were taken on Shimadzu 9020-DF, Shimadzu UV-160A, and Hitachi F-4500 spectrometers, respectively.

3.2 Synthesis of 2-(*1H,1H*-perfluoro-2,2-dimethylpentyl)nitrobenzene

The perfluoropropene dimer, perfluoro-2-methyl-2-pentene (67 g, 0·22 mol) was added to a DMF solution (500 ml) of 2-nitrobenzyl chloride (75 g, 0·44 mol), potassium fluoride (31·4 g, 0·54 mol), and tetrabutylammonium iodide (8·11 g) and the mixture refluxed for 15 h. Perfluoro-2-methyl-2-pentene (67 g, 0·22 mol) was then added and refluxing continued for a further 4 h. After the reaction was complete, the mixture was cooled and filtered. The product was extracted with chloroform. The extract was poured into an ice-water solution (1400 ml) of potassium carbonate (80 g). The organic layer was washed with water and dried over anhydrous magnesium sulfate. The product was purified by column chromatography (Al_2O_3, C_6H_{14}) and recrystallized from hexane.

Yield 60%; m.p. 45·5–46·0°C; [^{1}H] NMR ($CDCl_3$) δ 4·10 (s, 2H), 7·15–8·04 (m, 4H).

3.3 Synthesis of 2-(*1H,1H*-perfluoro-2,2-dimethylpentyl)aniline (2a)

To an ethanol solution (500 ml) of 2-(*1H,1H*-perfluoroheptyl)nitrobenzene (120 g, 0·26 mol) was added ferric chloride hexahydrate (5·3 g, 0·02 mol) and charcoal (12 g). The mixture was refluxed for 1 h and cooled to 60°C. Hydrazine monohydrate (22 g, 0·44 mol) was then added and the mixture refluxed for 14 h. After the reaction was complete, the resulting precipitate was filtered and washed with chloroform. The filtrate was concentrated and the product purified by column chromatography (SiO_2, CCl_4).

Yield 40%; m.p. 58–59°C; [^{1}H] NMR ($CDCl_3$) δ 3·43 (s, 2H), 3·57 (br s, 2H), 6·63 (dd, 1H), 6·72 (ddd, 1H), 7·10 (ddd, 1H), 7·16 (dd, 1H); [^{19}F] NMR (ext. CF_3COOH, $CDCl_3$) δ 0 ~ −0·12 (m, 6F), −18·15 ~ −18·23 (m, 3F), −45·31 ~ −45·51 (m, 2F), −60·60 ~ −60·85 (m, 2F); MS (EI, 70 eV) *m/z* (%) 425 (5) [M^+] and 106 (100).

3.4 Synthesis of *N,N'*-disubstituted 3,4,9,10-perylenetetracarboxdiimides 3–6

The appropriate amine (3·0 mmol) and zinc acetate (0·175 g) was added to a quinoline suspension (5 ml) of 3,4,9,10-perylenetetracarboxylic dianhydride (0·5 g, 1·25 mmol) and the mixture heated at 200°C for 4 h under a nitrogen atmosphere. The mixture was poured into an aqueous solution (100 ml) of sodium hydrogen carbonate (5 g) and the resulting precipitate filtered and purified by column chromatography (SiO_2, CH_2Cl_2).

N,N'-*Dibutyl-3,4,9,10-perylenetetracarboxdiimide (3)*
Yield 53%; m.p. > 300°C; MS (EI, 70 eV) *m/z* (%) 502 (100) [M^+], 485 (40), 429 (21), 404 (40), 391 (23), 390 (69), 56 (22). [^{1}H] NMR spectrum could not be measured due to its low solubility.

N,N'-*(*1H,1H-*perfluorobutyl)-3,4,9,10-perylenetetracarboxdiimide (4)*
Yield 20%; m.p. > 300°C; [^{1}H] NMR ($CDCl_3$) δ 5·06 (s, 4H), 8·72 (d, J = 8·2 Hz, 4H), 8·78 (d, J = 8·2 Hz, 4H); MS (EI, 70 eV) *m/z* (%) 754 (100) [M^+].

cis-N,N'-*Bis[2-(*1H,1H-*perfluoroheptyl)phenyl]-3,4,9,10-perylenetetracarboxdiimide (5)*
Yield 8·2%; m.p. > 300°C; [^{1}H] NMR ($CDCl_3$) δ 3·54 (s, 4H), 7·36 (dd, J = 7·8 and 1·5 Hz, 2H), 7·52 (td, J = 7·8 and 1·5 Hz, 4H), 7·63 (td, J = 7·8 and 1·5 Hz, 2H), 8·76 (d, J = 8·2 Hz, 4H), 8·79 (d, J = 8·2 Hz, 4H); MS (EI, 70 eV) *m/z* (%) 1206 (91) [M^+], 1038 (53), 1037 (100), 873 (22), 802 (41), 286 (22), 231 (26), 69 (12).

trans-N,N'-*Bis[2-(*1H,1H-*perfluoroheptyl)phenyl]-3,4,9,10-perylenetetracarboxdiimide (6)*
Yield 8·4%; m.p. > 300°C; [^{1}H] NMR ($CDCl_3$) δ 3·54 (s, 4H), 7·36 (dd, J = 7·8 and 1·5 Hz, 2H), 7·51 (td, J = 7·8 and 1·5 Hz, 4H), 7·62 (td, J = 7·8

and 1·5 Hz, 2H), 8·73 (d, J = 8·1 Hz, 4H), 8·78 (d, J = 8·1 Hz, 4H); MS (EI, 70 eV) m/z (%) 1206 (89) [M^+], 1038 (53), 1037 (100), 902 (35), 873 (22), 802 (38), 800 (35), 799 (84), 733 (22), 631 (40), 630 (100), 466 (51), 396 (24), 395 (91), 394 (29), 374 (47), 339 (21), 274 (25), 273 (25), 231 (36), 181 (30), 106 (27), 69 (35), 57 (25).

REFERENCES

1. Yoshida, Z. & Kitao, T., *Chemistry of Functional Dyes*. Mita Press, Tokyo, 1989.
2. Shirota, Y. & Yoshida, Z., *Chemistry of Functional Dyes, Vol. 2*. Mita Press, Tokyo, 1993.
3. Zollinger, H., *Dye Chemistry*. VCH, Weinheim, 1991.
4. Gregoly, P., *High-Technology Application of Organic Colorants*. Plenum Publication Co., Ltd, 1991.
5. Leslie, T. M., Goodbye, J. M. & Filas, R. W., *Liq. Cryst. Ordered Fluids*, **4** (1984) 43.
6. Nakazawa, T., Kawahara, A., Mizuta, Y., Miyamoto, E. & Mutoh, N., *Jpn J. Appl. Phys.*, **32** (1993) L1005.
7. Nakazawa, T., Mutoh, N., Mizuta, Y., Kawahara, A., Miyamoto, E., Tsutsumi, M., Ikeda, T. & Nagahashi, K., *Nippon Kagaku Kai Shi* (1992) 1007.
8. Stahl, W. & Zastrow, A., *Physik in unserer Zeit*, **16** (1985) 167.
9. Demmig, S. & Langhals, H., *Chem. Ber.*, **121** (1988) 225.
10. Seybold, G. & Wagenblast, G., *Dyes and Pigments*, **11** (1989) 303.
11. Matsui, M., Kondoh, S., Shibata, K. & Muramatsu, H., *Bull. Chem. Soc. Jpn*, **68** (1995) 1042.
12. Matsui, M., Ishikawa, H., Hiramatsu, K., Shibata, K. & Muramatsu, H., *Dyes and Pigments*, **27** (1995) 143.
13. Muramatsu, H., Okumura, A., Shibata, K. & Matsui, M., *Chem. Ber.*, **127** (1994) 1627.
14. Matsui, M., Joglekar, B., Ishigure, Y., Shibata, K., Muramatsu, H. & Murata, Y., *Bull. Chem. Soc. Jpn*, **66** (1993) 1790.
15. Nishida, M., Hayakawa, Y., Matsui, M., Shibata, K. & Muramatsu, H., *Bull. Chem. Soc. Jpn*, **65** (1992) 1999.
16. Hayakawa, Y., Nishida, M., Okumura, A., Matsui, M. & Muramatsu, H., *Polymer Bull.*, **28** (1992) 293.
17. Matsui, M., Kawamura, S., Shibata, K., Muramatsu, H., Mitani, M., Sawada, H. & Nakayama, M., *J. Fluorine Chem.*, **57** (1992) 209.
18. Matsui, M., Shibata, K., Muramatsu, H., Sawada, H. & Nakayama, M., *Synlett* (1991) 113.
19. Langhals, H., *Chem. Ber.*, **118** (1985) 4641.