

Synthesis and Characterisation of some 1,4,8,11,15,18,22,25-Octa-alkyl- and 1,4,8,11,15,18-Hexa-alkyl-22,25-bis(carboxypropyl)phthalocyanines

Neil B. McKeown, Isabelle Chambrier, and Michael J. Cook*
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

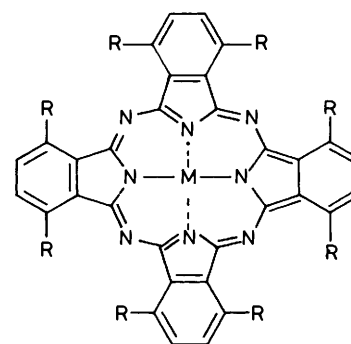
A series of 3,6-dialkylphthalonitriles and 3,6-bis(4,4,4-trimethoxybutyl)phthalonitrile have been prepared *via* Diels–Alder reactions of 2,5-disubstituted furans or thiophene 1,1-dioxides with fumaronitrile. The phthalonitriles were converted into the title phthalocyanines as metal-free and copper(II) derivatives. The macrocycles were characterised using ^1H NMR and optical spectroscopy, and fast-atom bombardment mass spectrometry. Certain examples exhibit discotic liquid crystal behaviour.

Interest in exploiting the attractive optical and electrical properties of the phthalocyanine (Pc) ring system continues to grow rapidly. Roberts and co-workers demonstrated that certain derivatives could be deposited as thin films using the Langmuir–Blodgett (L–B) technique¹ and described a number of potential applications in chemical sensors and electronic devices.² These and other results have stimulated research into examining new Pc compounds whose structures promote their deposition as films having a very high degree of molecular order.³ Recently we described the deposition of multilayer L–B films of 1,4,8,11,15,18,22,25-octa-alkoxy phthalocyanines,⁴ materials prepared initially as far-red/near infra-red absorbing dyes.⁵ The degree of ordering within the films was found to depend upon the length of the alkoxy chain and the central metal ion. The best films were obtained from copper and zinc octapentylphthalocyanines and gave X-ray diffraction patterns consistent with domains of layer structuring. These encouraging results have led us to examine other derivatives substituted in the 1,4,8,11,15,18,22,25 positions, *viz* two series of octa-alkyl phthalocyanines, (1) and (2), and some 1,4,8,11,15,18-hexa-alkyl-22,25-bis(carboxypropyl)phthalocyanines (3) and (4). Members of the first two series do not behave well as Langmuir monolayers and fail to deposit by the L–B technique. Compounds of series (3) and (4), having a combination of hydrophilic and hydrophobic groups, behave very differently and give highly ordered films.^{6,7}

In this paper we report the synthesis and characterisation of the compounds. Papers to follow will identify the molecular assemblies present in the columnar liquid crystal phases exhibited by certain members of series (1) and (2) and their relationship to the molecular architecture in the L–B films of series (3) and (4).

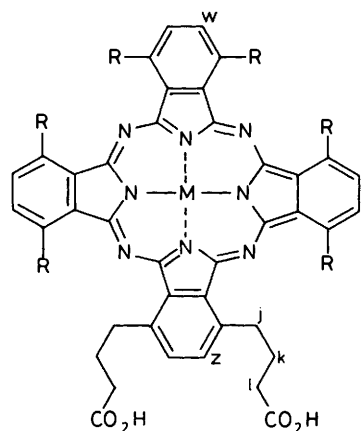
Results and Discussion

Preparation of Compounds.—Phthalocyanines can be prepared from derivatives of phthalic acid, the reaction of a phthalonitrile with an alkoxide base being especially convenient. We therefore sought routes to 3,6-disubstituted phthalonitriles (5) which are sufficiently versatile to enable us to introduce chains of any length and which would also allow incorporation, at some stage, of hydrophilic functionality. The Diels–Alder reaction, well suited for synthesising multiply substituted six-membered rings, has been used previously as a step in preparations of 3,6-disubstituted phthalonitriles. In particular, fumaronitrile has been used as dienophile in reactions with various conjugated dienes,⁸ the products being subsequently dehydrogenated over sulphur. Alternatively, dicyanoacetylene has been added across both furans⁹ and thiophenes.¹⁰ The



(1) M = H, H

(2) M = Cu



(3) M = H, H

(4) M = Cu

a; R = Me	h; R = Me[CH ₂] ₇
b; R = Et	i; R = Me[CH ₂] ₈
c; R = Pr ⁿ	j; R = Me[CH ₂] ₉
d; R = Bu ⁿ	k; R = Pr ⁱ [CH ₂] ₂
e; R = Me[CH ₂] ₄	l; R = CH ₂ –CH[CH ₂] ₃
f; R = Me[CH ₂] ₅	m; R = Ph[CH ₂] ₃
g; R = Me[CH ₂] ₆	n; R = (MeO) ₃ C[CH ₂] ₃

attractions inherent in the greater accessibility of fumaronitrile over dicyanoacetylene and the potential ease of preparing 2,5-dialkylfurans (7) and 2,5-dialkylthiophenes (8), *via* lithiation of

Table 1. Preparation from furan and ¹H NMR spectral characterisation of some 2-alkylfurans (6).

Compound	% Yield	δ(¹ H) ^a	Lit., ^b b.p., t/°C (p/mmHg)
(6c)	56	0.92 (t, 3 H), 1.30–1.92 (m, 2 H), 2.61 (t, 2 H), 5.90 (m, 1 H), 6.23 (m, 1 H), 7.24 (s, 1 H)	115(760) ^c
(6d)	50	0.91 (t, 3 H), 1.20–1.93 (m, 4 H), 2.60 (t, 2 H), 5.90 (m, 1 H), 6.22 (m, 1 H), 7.22 (s, 1 H)	138(760) ^c
(6e)	80	0.90 (t, 3 H), 1.15–1.93 (m, 6 H), 2.62 (t, 2 H), 5.91 (m, 1 H), 6.21 (m, 1 H), 7.21 (s, 1 H)	165(760) ^d
(6f)	73	0.90 (t, 3 H), 1.10–2.02 (br s, 8 H), 2.61 (t, 2 H), 5.92 (m, 1 H), 6.21 (m, 1 H), 7.22 (s, 1 H)	68(11) ^e
(6g)	75	0.90 (t, 3 H), 1.10–2.00 (br s, 10 H), 2.60 (t, 2 H), 5.90 (m, 1 H), 6.22 (m, 1 H), 7.23 (s, 1 H)	83(11) ^e
(6h)	81	0.90 (t, 3 H), 1.10–1.95 (br s, 12 H), 2.61 (t, 2 H), 5.90 (m, 1 H), 6.23 (m, 1 H), 7.22 (s, 1 H)	103(11) ^e
(6i)	85	0.90 (t, 3 H), 1.10–1.98 (br s, 14 H), 2.62 (t, 2 H), 5.90 (m, 1 H), 6.23 (m, 1 H), 7.22 (s, 1 H)	40(0.01) ^f
(6j)	80	0.90 (t, 3 H), 1.10–1.95 (br s, 16 H), 2.60 (t, 2 H), 5.90 (m, 1 H), 6.22 (m, 1 H), 7.22 (s, 1 H)	g
(6k)	70	0.95 (d, 6 H), 1.20–1.91 (m, 3 H), 2.60 (t, 2 H), 5.92 (m, 1 H), 6.22 (m, 1 H), 7.23 (s, 1 H)	152(760) ^c
(6l)	82	1.50–2.42 (m, 4 H), 2.62 (t, 2 H), 4.82–5.20 (m, 2 H), 5.40–6.02 (m, 1 H), 5.90 (m, 1 H), 6.20 (m, 1 H), 7.22 (s, 1 H)	—
(6m)	75	1.60–2.07 (m, 2 H), 2.62 (t, 4 H), 5.92 (m, 1 H), 6.21 (m, 1 H), 7.21 (s, 6 H)	134(10) ^h
(6n)	78	1.60–2.07 (m, 4 H), 2.62 (t, 2 H), 3.23 (s, 9 H), 5.90 (m, 1 H), 6.23 (m, 1 H), 7.23 (s, 1 H)	—

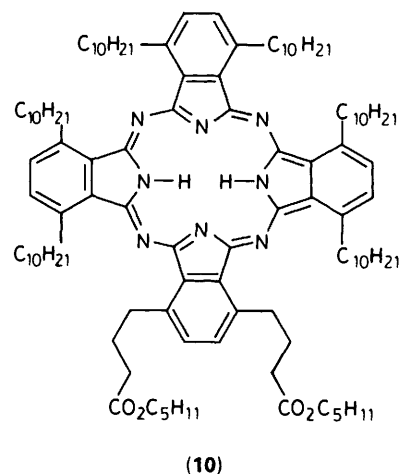
^a 60 MHz; CDCl₃. ^b Previous characterisation in the literature. ^c Ref. 13. ^d Ref. 14. ^e Ref. 15. ^f Ref. 16. ^g Ref. 17; ¹H NMR data only. ^h Ref. 18.

Table 2. Preparation from the corresponding 2-alkylfuran and ¹H NMR spectral characterisation of 2,5-dialkylfurans (7).

Compound	% Yield	δ(¹ H) ^a	Lit. b.p. ^b (t/°C)
(7b) ^c	45	1.00 (t, 6 H), 2.52 (q, 4 H), 5.85 (s, 2 H)	138 ^d
(7c)	62	0.95 (t, 6 H), 1.20–1.98 (m, 4 H), 2.50 (t, 4 H), 5.80 (s, 2 H)	173 ^d
(7d)	75	0.93 (t, 6 H), 1.10–1.90 (m, 8 H), 2.50 (t, 4 H), 5.81 (s, 2 H)	196 ^e
(7e)	83	0.90 (t, 6 H), 1.10–1.90 (m, 12 H), 2.50 (t, 4 H), 5.82 (s, 2 H)	—
(7f)	60	0.95 (t, 6 H), 1.00–2.00 (br s, 16 H), 2.50 (t, 4 H), 5.80 (s, 2 H)	—
(7g)	75	0.90 (t, 6 H), 1.00–2.02 (br s, 20 H), 2.50 (t, 4 H), 5.82 (s, 2 H)	—
(7h)	75	0.90 (t, 6 H), 1.02–2.02 (br s, 24 H), 2.50 (t, 4 H), 5.80 (s, 2 H)	—
(7i)	80	0.90 (t, 6 H), 1.00–2.00 (br s, 28 H), 2.51 (t, 4 H), 5.82 (s, 2 H)	—
(7j)	70	0.90 (t, 6 H), 1.00–2.02 (br s, 32 H), 2.50 (t, 4 H), 5.80 (s, 2 H)	—
(7k)	50	1.00 (d, 12 H), 1.23–1.91 (m, 6 H), 2.50 (t, 4 H), 5.82 (s, 2 H)	210 ^e
(7l)	85	1.51–2.40 (m, 8 H), 2.60 (t, 4 H), 4.40–5.22 (m, 4 H), 5.40–5.98 (m, 2 H), 5.80 (s, 2 H)	—
(7m)	75	1.72–2.24 (m, 4 H), 2.42–2.81 (m, 8 H), 5.82 (s, 2 H), 7.20 (s, 10 H)	—
(7n)	0–70	1.60–2.09 (m, 8 H), 2.58 (t, 4 H), 3.23 (s, 18 H), 5.82 (s, 2 H)	—

^a 60 MHz, CDCl₃. ^b At 760 mmHg; previous characterisation in the literature. ^c 2-Ethylfuran (6b) was obtained from a commercial source. ^d Ref. 19. ^e Ref. 13.

ratio of 1:9. Statistical considerations (Experimental section) indicate that such a mixture should lead to a product mixture containing just two major components, (1) and esterified derivatives of (3); little of the difficult to prepare bis-orthoester precursor becomes wasted in the formation of Pcs resulting from other combinations of the two starting materials. In the event, TLC analysis (toluene–ethyl acetate, 9:1) of the product mixture following work-up of each of the three reactions showed several green components. The octa-alkylphthalocyanine, the major product, travelled with the solvent front. In the middle of the plate there appeared three closely grouped spots. Column chromatography afforded a separation of the octa-alkyl derivative from the slower moving mixture. The IR spectrum of the latter showed a strong carbonyl absorption, confirming expectations that the acetic acid work-up had converted the ortho-ester functions into carboxylic acid ester groups. Interestingly, the ¹H NMR spectrum showed signals for both methyl and pentyl ester functions. We deduced therefore that the three components of the mixture are the dimethyl, dipentyl, and the mixed methyl pentyl ester. We attribute the presence of the pentyl groups to either a trans-orthoesterification during the original dissolution of the precursor in pentanol, or a trans-esterification during the work-up. In one experiment, an example of a dipentyl ester, (10), was isolated from the product mixture and characterised by ¹H NMR and FAB-MS, see Experimental section. The ester derivatives of (3) were saponified in a two-phase medium using phase-transfer



catalysis, procedure C in Experimental section. Data characterising series (3) are collected in Table 7.

A number of the metal-free Pcs of series (1) and (3) were converted into the corresponding copper derivatives, (2) and (4), by addition of copper(II) acetate to a refluxing solution of the Pc in THF (Table 8).

Characterisation of Compounds.—The octamethylphthalo-

Table 3. The conversion of 2,5-dialkylfurans (7) into the corresponding 3,6-dialkylphthalonitriles (5), via the cycloadduct with fumaronitrile. See Scheme 1.

Furan	Cycloadduct		3,6-Dialkylphthalonitrile; yield and characterisation							
	Solvent ^c	% Yield ^a	% Yield ^b	M.p. (t/°C)	Formula	% Found (requires)			δ(¹ H) ^e	
						C	H	N		
(7a)	X	85	(5a)	72	160 ^d	C ₁₀ H ₈ N ₂	76.7 (76.9)	5.2 (5.2)	18.0 (17.9)	2.57 (s, 6 H), 7.48 (s, 2 H)
(7b)	X	55	(5b)	40	121	C ₁₂ H ₁₂ N ₂	78.2 (78.2)	6.7 (6.6)	15.3 (15.5)	1.32 (t, 6 H), 2.88 (q, 4 H), 7.48 (s, 2 H)
(7c)	X	50	(5c)	33	70	C ₁₄ H ₁₆ N ₂	79.2 (79.2)	7.7 (7.6)	13.2 (13.2)	1.00 (t, 6 H), 1.3–2.04 (m, 4 H), 2.90 (t, 4 H), 7.50 (s, 2 H)
(7d)	X	55	(5d)	35	26	C ₁₆ H ₂₀ N ₂	79.6 (79.9)	8.4 (8.4)	11.5 (11.7)	0.98 (t, 6 H), 1.1–1.9 (m, 8 H), 2.85 (t, 4 H), 7.50 (s, 2 H)
(7e)	Y	45	(5e)	30	15	C ₁₈ H ₂₄ N ₂	80.6 (80.5)	9.2 (9.0)	10.3 (10.4)	0.93 (t, 6 H), 1.0–1.9 (m, 12 H), 2.90 (t, 4 H), 7.50 (s, 2 H)
(7f)	Y	40	(5f)	27	38	C ₂₀ H ₂₈ N ₂	81.0 (81.0)	9.6 (9.5)	9.35 (9.45)	0.92 (t, 6 H), 1.0–1.9 (m, 16 H), 2.85 (t, 4 H), 7.50 (s, 2 H)
(7g)	Y	40	(5g)	25	46	C ₂₂ H ₃₂ N ₂	81.3 (81.4)	10.1 (10.0)	8.5 (8.6)	0.90 (t, 6 H), 1.0–1.9 (m, 20 H), 2.85 (t, 4 H), 7.52 (s, 2 H)
(7h)	Z	45	(5h)	28	59	C ₂₄ H ₃₆ N ₂	81.6 (81.7)	10.6 (10.3)	7.85 (7.95)	0.90 (t, 6 H), 1.0–1.9 (m, 24 H), 2.85 (t, 4 H), 7.50 (s, 2 H)
(7i)	Z	45	(5i)	29	64	C ₂₆ H ₄₀ N ₂	82.2 (82.0)	10.7 (10.6)	7.3 (7.4)	0.90 (t, 6 H), 1.0–1.9 (m, 28 H), 2.85 (t, 4 H), 7.50 (s, 2 H)
(7j)	Z	40	(5j)	25	70	C ₂₈ H ₄₄ N ₂	82.1 (82.3)	11.2 (10.9)	6.8 (6.9)	0.90 (t, 6 H), 1.0–1.9 (m, 32 H), 2.85 (t, 4 H), 7.50 (s, 2 H)
(7k)	X	50	(5k)	36	60	C ₁₈ H ₂₄ N ₂	80.35 (80.35)	9.3 (9.0)	10.4 (10.4)	0.95 (d, 12 H), 1.28–1.82 (m, 6 H), 2.85 (t, 4 H), 7.44 (s, 2 H)
(7l)	Y	45	(5l)	29	Oil	C ₁₈ H ₂₀ N ₂	<i>f</i>			1.4–2.4 (m, 8 H), 2.90 (t, 4 H), 4.80–5.25 (m, 4 H), 5.5–6.2 (m, 2 H), 7.55 (s, 2 H)
(7m)	X	50	(5m)	32	104	C ₂₆ H ₂₄ N ₂	85.6 (85.6)	6.6 (6.65)	7.7 (7.7)	1.8–2.3 (m, 4 H), 2.45–3.05 (m, 8 H), 7.2 (s, 10 H), 7.45 (s, 2 H)
(7n)	X	55	(5n)	35	Oil	C ₂₂ H ₃₂ N ₂ O ₆	<i>f</i>			1.6–2.0 (m, 8 H), 2.90 (t, 4 H), 3.23 (s, 18 H), 7.50 (s, 2 H)

^a Not isolated; conversion estimated by NMR (see Experimental section). ^b With respect to starting furan. ^c X = Acetone; Y = acetone-THF (1:1); Z = acetone-THF (1:2). ^d Lit.¹⁰ m.p. 163 °C. ^e 60 MHz; CDCl₃. ^f Oil could not be distilled. The material was used in the next step without further purification.

Table 4. Preparation and characterisation of some 2,5-dialkylthiophenes (8).

Compound	% Yield	B.p. (t/°C) at 0.1 mmHg	Formula	% Found (requires)			δ(¹ H) ^c
				C	H	S	
(8f)	65	106	C ₁₆ H ₂₈ S	76.3 (76.1)	11.3 (11.2)	12.65 (12.7)	0.90 (t, 6 H), 1.25 (m, 16 H), 2.70 (t, 4 H), 6.52 (s, 2 H)
(8g)	76	127	C ₁₈ H ₃₂ S	77.3 (77.1)	11.8 (11.5)	11.2 (11.4)	0.88 (t, 6 H), 1.3 (m, 20 H), 2.72 (t, 4 H), 6.50 (s, 2 H)
(8h)	72	136	C ₂₀ H ₃₆ S	78.1 (77.85)	11.8 (11.8)	10.3 (10.4)	0.90 (t, 6 H), 1.3 (m, 24 H), 2.75 (t, 4 H), 6.50 (s, 2 H)
(8i)	70	149	C ₂₂ H ₄₀ S	78.7 (78.5)	12.3 (12.0)	9.6 (9.5)	0.90 (t, 6 H), 1.3 (m, 28 H), 2.71 (t, 4 H), 6.48 (s, 2 H)
(8j)	70	166	C ₂₄ H ₄₄ S	79.2 (79.0)	12.3 (12.2)	8.7 (8.8)	0.90 (t, 6 H), 1.3 (m, 32 H), 2.72 (t, 4 H), 6.50 (s, 2 H)
(8n)	61 ^a	<i>b</i>					1.6–1.9 (m, 8 H), 2.78 (t, 4 H), 3.2 (s, 18 H), 6.58 (s, 2 H)

^a Yield estimated using ¹H NMR data. ^b Distillation was not attempted. ^c 60 MHz; CDCl₃.

cyanine (1a) is insoluble in organic solvents and was purified by recrystallisation from aqueous sulphuric acid. Other derivatives of series (1) and those of series (2) show some solubility in aprotic organic solvents such as benzene and toluene. Those of series (1) are also soluble in dichloromethane. In each solvent, solubility is greater for the longer-chain compounds. Compounds of series (3) and (4) are much less soluble in these solvents but soluble in THF. With the exception of (1a), which was recovered as dark blue crystals, the metal-free Pcs are turquoise green and the copper Pcs bright

blue in the crystalline state. All gave satisfactory elemental analyses.

Routine 60 MHz ¹H NMR spectra were obtained of the more soluble metal-free derivatives for solutions in [²H₆]benzene (Table 6), the spectral data confirming their structures. Example of a compound from series (1) and from series (3) were also investigated by ¹H NMR spectroscopy at 400 MHz. Data and assignments for the nonyl substituted derivatives (1i) and (3i) are summarised in Figure 1. The lower symmetry of (3i) gives rise to the more complex spectrum. In particular, the signals for

Table 5. Preparation and characterisation of some 2,5-dialkylthiophene 1,1-dioxides (9), and their conversion into 3,6-dialkylphthalonitriles (5). See Scheme 2.

Compound	% Yield	M.p. (t/°C)	Formula	% Found (requires)			$\delta(^1\text{H})^e$	% Conversion (5)
				C	H	S		
(9f)	51	43–44	C ₁₆ H ₂₈ SO ₂	67.2 (67.6)	9.9 (9.9)	11.1 (11.3)	0.90 (t, 6 H), 1.4 (m, 16 H), 2.50 (t, 4 H), 6.21 (s, 2 H)	(5f) 42
(9g)	30	47	C ₁₈ H ₃₂ SO ₂	69.5 (69.2)	10.55 (10.3)	9.85 (10.3)	0.90 (t, 6 H), 1.3 (m, 20 H), 2.44 (t, 4 H), 6.24 (s, 2 H)	(5g) 47
(9h)	35	52–53	C ₂₀ H ₃₆ SO ₂	70.5 (70.5)	10.8 (10.7)	9.3 (9.4)	0.90 (t, 6 H), 1.3 (m, 24 H), 2.50 (t, 4 H), 6.28 (s, 2 H)	(5h) 40
(9i)	40	49–50	C ₂₂ H ₄₀ SO ₂	71.3 (71.7)	11.05 (10.9)	8.95 (8.7)	0.90 (t, 6 H), 1.3 (m, 28 H), 2.50 (t, 4 H), 6.20 (s, 2 H)	(5i) 48
(9j)	46	61–62	C ₂₄ H ₄₄ SO ₂	72.6 (72.7)	10.9 (11.2)	7.8 (8.1)	0.90 (t, 6 H), 1.3 (m, 32 H), 2.50 (t, 4 H), 6.22 (s, 2 H)	(5j) 44

^e 60 MHz; CDCl₃.**Table 6.** Preparation and characterisation of some 1,4,8,11,15,18,22,25-octa-alkylphthalocyanines (I).

Compd.	Preparation			M.p. (t/°C) ^c	Formula	% Found (requires)				$\lambda_{\text{max}}(\text{toluene})/\text{nm}$ ($\epsilon \times 10^{-5}$) (Q-band)
	Procedure ^e	Recryst. solvent ^b	% Yield			C	H	N	$\delta(^1\text{H})^d$	
(1a)	A	V	35	> 300	C ₄₀ H ₃₄ N ₈ ·H ₂ O	74.55 (74.5)	5.3 (5.6)	17.0 (17.3)	—	—
(1b)	A	W	27	> 300	C ₄₈ H ₅₀ N ₈	77.7 (78.0)	6.8 (6.8)	14.9 (15.2)	—	—
(1c)	A	X	30	292	C ₅₆ H ₆₆ N ₈	79.1 (79.0)	7.8 (7.8)	13.1 (13.2)	—	726, 694, 662, 629
(1d)	A	X	20	230	C ₆₄ H ₈₂ N ₈	79.4 (79.8)	8.5 (8.6)	11.5 (11.6)	1.00 (t, 24 H), 1.30–2.48 (m, 32 H), 4.48 (t, 16 H), 7.78 (s, 8 H)	727 (1.26), 695 (1.06), 665 (0.38), 633 (0.26)
(1e)	A	X	25	218	C ₇₂ H ₉₈ N ₈	80.35 (80.4)	9.45 (9.2)	10.4 (10.4)	0.90 (t, 24 H), 1.15–2.24 (m, 48 H), 4.40 (t, 16 H), 7.76 (s, 8 H)	728, 697, 662, 632
(1f)	A	Y	10	161 (K→D) 171 (D→I)	C ₈₀ H ₁₁₄ N ₈	80.7 (80.9)	9.7 (9.7)	9.4 (9.4)	0.90 (t, 24 H), 1.10–2.43 (m, 64 H), 4.45 (t, 16 H), 7.78 (s, 8 H)	728, 697, 666, 630
(1g)	A	Y	21	113 (K→D) 163 (D→I)	C ₈₈ H ₁₃₀ N ₈	81.05 (81.3)	10.2 (10.1)	8.5 (8.6)	0.90 (t, 24 H), 1.05–2.45 (m, 80 H), 4.46 (t, 16 H), 7.76 (s, 8 H)	728, 696, 667, 633
(1h)	B	Z	10	84.5 (K→D) 152 (D→I)	C ₉₆ H ₁₄₆ N ₈	81.7 (81.6)	10.8 (10.4)	7.9 (7.9)	0.90 (t, 24 H), 1.05–2.50 (m, 96 H), 4.43 (t, 16 H), 7.79 (s, 8 H)	728, 697, 666, 633
(1i)	B	Y	15	103 (K→D) 142 (D→I)	C ₁₀₄ H ₁₆₂ N ₈	82.0 (81.9)	10.9 (10.7)	7.3 (7.35)	0.90 (t, 24 H), 1.05–2.50 (m, 112 H), 4.42 (t, 16 H), 7.78 (s, 8 H)	728 (1.25), 697 (1.06), 665 (0.37), 635 (0.26)
(1j)	B	Y	5	77.5 (K→D) 133 (D→I)	C ₁₁₂ H ₁₇₈ N ₈	82.2 (82.2)	11.2 (11.0)	6.9 (6.85)	0.90 (t, 24 H), 1.05–2.48 (m, 128 H), 4.43 (t, 16 H), 7.79 (s, 8 H)	728, 697, 666, 628
(1k)	A	Y	21	254	C ₇₂ H ₉₈ N ₈	80.3 (80.4)	9.4 (9.2)	10.4 (10.4)	0.96 (d, 48 H), 1.60–2.22 (m, 24 H), 4.48 (t, 16 H), 7.82 (s, 8 H)	733, 701, 666, 635
(1l)	B	Y	15	179	C ₇₂ H ₈₂ N ₈	81.7 (81.6)	7.8 (7.8)	10.5 (10.6)	3.00 (m, 32 H), 4.42 (t, 16 H), 5.04 (t, 16 H), 5.58–6.24 (m, 8 H), 7.64 (s, 8 H)	727, 695, 663, 632
(1m)	A	Y	23	196	C ₁₀₄ H ₉₈ N ₈	85.3 (85.5)	6.7 (6.8)	7.7 (7.7)	2.30–3.30 (m, 32 H), 4.62 (t, 16 H), 7.08 (s, 40 H), 7.74 (s, 8 H)	735 (1.22), 703 (1.04), 668 (0.37), 636 (0.26)

^e Procedure, see Experimental section. ^b V = aq. H₂SO₄; W = 1,2,4-Cl₃C₆H₃; X = toluene; Y = THF–acetone; Z = toluene–acetone. ^c M.p. or transition temperature for change from the crystal state to a discotic mesophase (K→D) and from the mesophase to the isotropic liquid (D→I). ^d 60 MHz; C₆D₆.

the aromatic protons in the four non-equivalent environments are well resolved and the non-equivalence of the nonyl chains is manifested especially well by the signals for protons at site (i). The latter appear as a triplet for four protons and two

overlapping triplets (eight protons) in the region δ 4.2–4.3 (Figure 1).

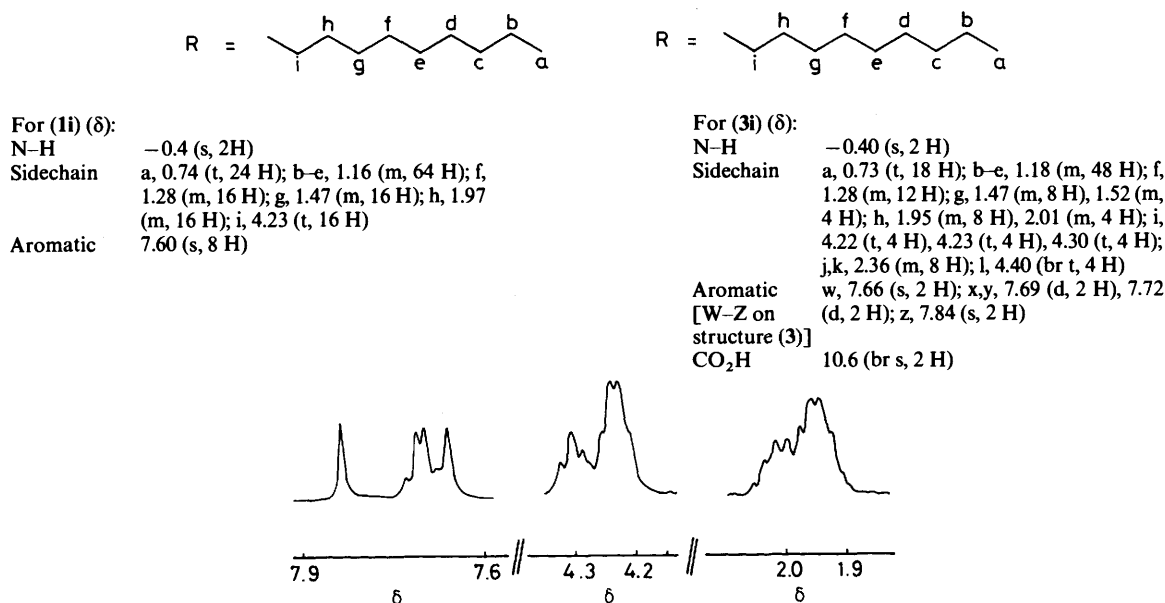
The characteristic UV (Soret band) and intense visible region (Q band) absorptions of the Pc nucleus are well documented.

Table 7. Preparation and characterisation of some 1,4,8,11,15,18-hexa-alkyl-22,25-bis(carboxypropyl)phthalocyanines (3).

Compound	% Yield ^a	M.p. (t/°C)	Formula	% Found (requires)			λ_{\max} (toluene)/nm ($\epsilon \times 10^{-5}$) (Q-band)
				C	H	N	
(3h)	2	185	C ₈₈ H ₁₂₆ N ₈ O ₄	77.7 (77.7)	9.5 (9.4)	8.1 (8.2)	727, 695, 665, 633
(3i)	2	—	C ₉₄ H ₁₃₈ N ₈ O ₄	78.1 (78.2)	10.0 (9.65)	7.6 (7.8)	727, 695, 665, 633
(3j)	1	166	C ₁₀₀ H ₁₅₀ N ₈ O ₄	78.7 (78.6)	9.95 (9.9)	7.2 (7.2)	727, 695, 665, 633
(3l)	1	—	C ₇₀ H ₇₈ N ₈ O ₄	76.9 (76.7)	7.4 (7.2)	9.9 (10.2)	728 (1.17), 696 (1.02), 666 (0.42), 633 (0.28)

^a Overall yield recovered from procedures B and C combined.**Table 8.** Preparation and characterisation of some copper-1,4,8,11,15,18,22,25-octa-substituted phthalocyanines, (2) and (4).

Compound	% Yield	M.p. (t/°C) ^a	Formula	% Found (requires)			λ_{\max} (toluene)/nm ($\epsilon \times 10^{-5}$) (Q-band) ^b
				C	H	N	
(2d)	78	265	C ₆₄ H ₈₀ CuN ₈	75.1 (75.0)	7.9 (7.9)	10.8 (10.9)	705, 675sh, 635
(2e)	80	261	C ₇₂ H ₉₆ CuN ₈	76.0 (76.0)	8.5 (8.5)	9.8 (9.85)	706, 675sh, 634
(2f)	85	184 (K→D) 242 (D→I)	C ₈₀ H ₁₁₂ CuN ₈	76.8 (76.9)	9.0 (9.05)	8.9 (9.0)	706, 674sh, 635
(2g)	85	144.5 (K→D) 235.5 (D→I)	C ₈₈ H ₁₂₈ CuN ₈	77.5 (77.6)	9.5 (9.5)	8.15 (8.2)	706, 674sh, 635
(2h)	80	95.5 (K→D) 220 (D→I)	C ₉₆ H ₁₄₄ CuN ₈	78.3 (78.2)	10.0 (9.9)	7.5 (7.6)	706, 675sh, 635
(2i)	82	108 (K→D) 208 (D→I)	C ₁₀₄ H ₁₆₀ CuN ₈	78.55 (78.7)	10.4 (10.2)	7.0 (7.1)	706 (1.97), 675sh, 635 (0.35)
(2j)	72	88 (K→D) 198 (D→I)	C ₁₁₂ H ₁₇₆ CuN ₈	78.9 (79.2)	10.6 (10.5)	6.5 (6.6)	706, 675sh, 635
(2k)	85	289	C ₇₂ H ₉₆ CuN ₈	75.7 (76.05)	8.6 (8.5)	9.6 (9.9)	710, 678sh, 638
(2l)	83	211	C ₇₂ H ₈₀ CuN ₈	76.9 (77.1)	7.0 (7.2)	10.0 (10.0)	704, 674sh, 634
(4i)	72	161	C ₉₄ H ₁₃₆ CuN ₈ O ₄	74.7 (75.0)	9.3 (9.1)	7.2 (7.4)	704, 672sh, 634

^a See footnote ^c, Table 6. ^b sh = shoulder.**Figure 1.** ¹H NMR chemical shift data in ppm for compounds (1i) and (3i) and parts of the spectrum of (3i) showing signals for the aromatic protons and for the protons at sites i and h of the nonyl chains. Spectra recorded at 400 MHz.

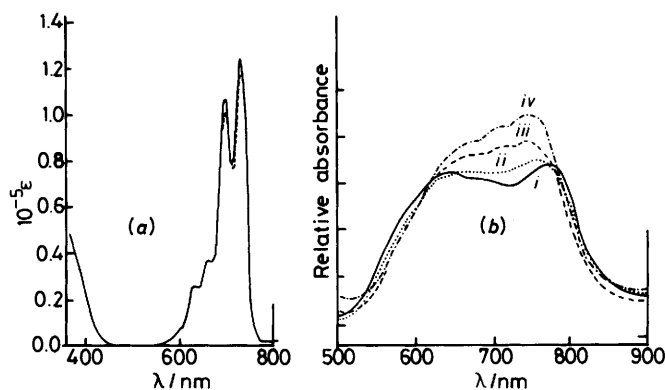


Figure 2. (a) The UV-visible spectrum of (1i) in toluene at concentrations of $1\mu\text{M}$ (—) and 0.1 mM (---). (b) Visible region spectrum of a film of the same compound on a silica slide at various temperatures: *i*, $30\text{ }^\circ\text{C}$ (Crystalline); *ii*, $100\text{ }^\circ\text{C}$ (mesophase); *iii*, $120\text{ }^\circ\text{C}$ (mesophase); *iv*, $150\text{ }^\circ\text{C}$ (isotropic liquid).

Metal and metal-free Pcs differ in having D_{4h} and D_{2h} symmetry respectively and this is manifested in differences especially in the Q-band region. The degeneracy of the lowest energy singlet state in the former is lifted in the latter giving rise to splitting of the Q-band into the Q_x and Q_y components. (Low intensity bands to shorter wavelength of the Q band are vibronic in origin). A further feature of the Pc absorption spectrum is its sensitivity to aggregation which affects significantly the intensity-band shape of the peaks in the Q-band region; typically, the Q-band absorption diminishes while a new broad band absorption appears at shorter wavelength.²⁸ Spectra for toluene solutions of each of the compounds in the present study are largely characteristic of the monomer species (Table 6–8. For series (1) the Q_x and Q_y bands appear at *ca.* 697 and 728 nm respectively [Figure 2(a)], some 30 nm to the red of phthalocyanine itself²⁹ and to the red of 'peripherally' alkyl substituted derivatives. Thus 2,3,9,10,16,17,23,24-octabutylphthalocyanine shows λ_{max} at 673 and 708 nm.³⁰ The copper Pcs in the present work show the single Q band absorption at *ca.* 705 nm.

Three compounds of series (1), *viz* (1d), (1i), and (1m), and one of the copper Pcs, (2i), were examined in greater detail as 1×10^{-4} , 1×10^{-5} , and $1 \times 10^{-6}\text{ M}$ solutions. The metal-free derivatives were measured in both toluene and dichloromethane. Small increases (between 0 and 6%) in extinction coefficient of the Q bands are observed in both solvents during the 100-fold dilution [Figure 2(a)] implying that aggregation is not completely absent at these concentrations. Extinction coefficient data quoted in Tables 6 and 8 refer to measurements on the $1 \times 10^{-6}\text{ M}$ solutions.

For some compounds, gentle heating of the crystalline sample caused unexpected changes in colour shade. These changes were reversible. Investigation using a polarising microscope revealed that these compounds underwent a reversible transition from the crystal state to a liquid crystal phase. Several classes of hexa- or octa-substituted polybenzoannulated aromatic compounds including a number of 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines³¹ exhibit discotic columnar mesophase behaviour, in which the essentially flat disc-like molecules stack in columns. We found this behaviour is exhibited by those members of series (1) and (2) which have straight alkyl chains containing six or more carbon atoms; compound (10) is the only example of the asymmetrically substituted Pcs which gives a mesophase. The temperatures for the crystal to mesophase and mesophase to isotropic liquid transitions are listed in Tables 6 and 8. A detailed investigation, results of which will be given in a subsequent paper,³² revealed

that some compounds exhibit more than one mesophase. Here we show in Figure 2(b) the visible region spectrum of a melted film of (1i) and how the spectrum changes as the film is cooled through the mesophase to the crystalline state. The variations account for the observed changes in colour shade with temperature which we noted above.

Investigations of structural features which encourage mesophase behaviour are in progress.

Experimental

Equipment and measurements.—IR spectra were recorded on a Perkin-Elmer 297 or 298 spectrophotometer. Routine ^1H NMR spectra were measured at 60 MHz using a Jeol JNM-PMX60SI spectrometer. Spectra measured at 400 MHz were obtained on a Bruker WH400 spectrometer through the SERC service at Warwick University. FAB-MS spectra were obtained using phosphoric acid as the viscous matrix and measured using the VG ZAB-E high-resolution SERC service equipment at Swansea University. UV-visible spectra of solutions in spectroscopic grade toluene or dichloromethane were measured using a Pye-Unicam SP8-200 spectrometer. The variable-temperature study of the visible region absorptions of material as a thin film on a silica slide (Figure 2) was performed on a Cary 17D UV-visible spectrometer fitted with a Mettler FP 82 hot stage. Measurements of transition temperatures for the changes from crystal to mesophase and mesophase to isotropic liquid (Tables 7 and 8) were obtained by differential scanning calorimetry using a Mettler TA3000 thermal analyser with a Mettler DSC 30 cell.

Materials.—2-Ethylfuran (6b) and 2,5-dimethylfuran (7a) were obtained from the Aldrich Chemical Co. 4,4,4-Trimethoxybutyl bromide was prepared from 4-bromobutyronitrile according to the method in ref. 33.

Preparation of 2-Alkylfurans (6) (Table 1).—2-Heptylfuran (6g). In the typical procedure, furan (20.5 g, 0.3 mol) was added dropwise to a stirred solution of *n*-butyl-lithium (0.3 mol; 200 ml of a 1.6M solution in hexane) and dry THF (130 ml) under nitrogen at $-15\text{ }^\circ\text{C}$. The mixture was stirred for 24 h at room temperature. 1-Bromoheptane was added dropwise, and the mixture stirred for a further 24 h at room temperature. The brown mixture was then poured onto ice and the crude product extracted with diethyl ether ($4 \times 50\text{ ml}$). The organic layer was dried (MgSO_4) and the solvents removed under reduced pressure using a rotary evaporator. The resultant crude product was dissolved in dichloromethane and eluted through a silica column to remove residual polar impurities. The dichloromethane was removed to afford 2-heptylfuran (38 g, 75%), as a colourless oil which was used in the next step without further purification; δ_{H} (60 MHz; CDCl_3) 0.9 (t, 3 H), 1.10–2.00 (m, 10 H), 2.60 (t, 2 H), 5.90 (m, 1 H), 6.22 (m, 1 H), and 7.23 (s, 1 H).

Preparation of 2,5-Dialkylfurans (7) (Table 2).—2,5-Diheptylfuran (7g). In the typical procedure, 2-heptylfuran (6g) (38 g, 0.23 mol) was added dropwise to a stirred solution of *n*-butyl-lithium (0.23 mol; 156 ml of a 1.6M solution in hexane) in dry THF (100 ml). After stirring for 24 h at room temperature, 1-bromoheptane (41 g, 0.23 mol) was added and stirring was continued for a further 24 h. The resultant mixture was poured onto ice and the product extracted with diethyl ether ($3 \times 50\text{ ml}$). The dried (MgSO_4) organic layer was evaporated to dryness under reduced pressure and the crude product heated ($150\text{ }^\circ\text{C}$ at 18 mmHg) to remove excess of 1-bromoheptane. The remaining liquid was dissolved in dichloromethane and eluted through a silica column to remove polar impurities. After removal of the dichloromethane 2,5-diheptylfuran (7g) (48 g,

75%) was obtained as an oil; δ_{H} (60 MHz; CDCl_3) 0.90 (t, 6 H), 1.10–2.02 (m, 20 H), 2.5 (t, 4 H), and 5.80 (s, 2 H). The material was used in the next step without further purification.

Preparation of 3,6-Dialkylphthalonitriles (5) from 2,5-Dialkylfurans (7) (Table 3).—3,6-Diheptylphthalonitrile (**5g**). 2,5-Diheptylfuran (**7g**) (20 g, 0.075 mol) and fumaronitrile (5.9 g, 0.075 mol) were dissolved in the minimum amount of a THF–acetone mixture (1:1) and left for one week at -5°C . The solvent was removed at room temperature using a rotary evaporator. The ^1H NMR spectrum showed a 40:60 ratio of the Diels–Alder adduct to starting material. The rest of the slurry was dissolved in freshly distilled dry THF. The reaction vessel was flushed with nitrogen and the temperature of the solution lowered to -78°C . Lithium bis(trimethylsilyl)amide (75 ml of a 1M solution in THF) was added dropwise during 1 h, with vigorous stirring. The solution was neutralised with an excess of saturated aqueous ammonium chloride (150 ml) and the temperature allowed to rise to room temperature. The crude product was extracted with diethyl ether (2×100 ml), the extract dried (MgSO_4), and the solvents removed under reduced pressure on a rotary evaporator. The resultant black oil was eluted through a silica column with toluene. A yellowish fraction was obtained which, on recrystallisation from ethanol, afforded 3,6-diheptylphthalonitrile (**5g**) (5.1 g, 25%), m.p. 46°C (Found: C, 81.3; H, 10.1; N, 8.5. $\text{C}_{22}\text{H}_{32}\text{N}_2$ requires C, 81.4; H, 10.0; N, 8.6%); ν_{max} (Nujol) $2\,230\text{ cm}^{-1}$ ($\text{C}\equiv\text{N}$); δ_{H} (60 MHz; CDCl_3) 0.95 (t, 6 H), 1.00–1.90 (m, 20 H), 2.85 (t, 4 H), and 7.52 (s, 2 H).

Preparation of 2,5-Dialkylthiophenes (8) (Table 4).—2,5-Diheptylthiophene (**8g**). In a typical experiment, thiophene (8.4 g, 0.1 mol) in THF (dried over sodium; 50 ml) was treated with 3.5M n-butyl-lithium in hexane (2.5 equiv., 0.25 mol, 71 ml) at 0°C . When addition was completed the mixture was stirred at room temperature for 24 h. The solution was cooled to 0°C , the dianion quenched with 1-bromoheptane (44.5 g, 0.25 mol), and the mixture stirred at room temperature for 24 h. The mixture was poured onto ice, extracted with ether (3×75 ml), the extract dried (MgSO_4), the solvent evaporated, and the residue distilled to afford 2,5-diheptylthiophene (**8g**) (21.3 g, 76%) as a colourless oil, b.p. 127°C at 0.1 mmHg (Found: C, 77.3; H, 11.8; S, 11.2. $\text{C}_{18}\text{H}_{32}\text{S}$ requires C, 77.1; H, 11.5; S, 11.4%); δ_{H} (60 MHz; CDCl_3) 6.5 (s, 2 H); 2.7 (t, 4 H), 1.3 (m, 20 H), and 0.88 (t, 6 H).

Preparation of 2,5-Dialkylthiophene 1,1-Dioxides (9) (Table 5).—2,5-Diheptylthiophene 1,1-dioxide (**9g**). In a typical experiment 2,5-diheptylthiophene (**8g**) (5 g, 0.018 mol) was treated with MCPBA (50–60% tech. grade; 12.5 g) in CH_2Cl_2 (100 ml) at 0°C for 3 h with stirring in the presence of excess of NaHCO_3 . The mixture was then left overnight in a refrigerator. The precipitate (MCBA) was filtered off and the solution washed with 20% aqueous NaOH (2×50 ml) and water and dried (MgSO_4), and the solvent removed. The crude sulphone (**9g**) was recrystallised from light petroleum (1.7 g, 30%), m.p. 47°C (Found: C, 69.5; H, 10.55; S, 9.85. $\text{C}_{18}\text{H}_{32}\text{O}_2\text{S}$ requires C, 69.2; H, 10.3; S, 10.3%); δ_{H} (60 MHz; CDCl_3) 6.24 (s, 2 H), 2.44 (t, 4 H), 1.3 (m, 20 H), and 0.9 (t, 6 H).

Preparation of 3,6-Dialkylphthalonitriles (5) from 2,5-Dialkylthiophene 1,1-Dioxides (9) (Table 5).—3,6-Diheptylphthalonitrile (**5g**). In a typical experiment 2,5-diheptylthiophene 1,1-dioxide (**9g**) (2 g, 6.4 mmol) and fumaronitrile (0.5 g, 6.4 mmol) in chloroform (5 ml) were heated in a sealed tube at 150°C for 18 h. The contents of the tube were evaporated to dryness and chromatographed over silica (toluene as eluant) to afford 3,6-diheptylphthalonitrile (**5g**) (0.98 g, 47%) as a yellow

solid. The material was recrystallised from ethanol to afford a colourless solid, m.p. $44\text{--}46^\circ\text{C}$.

Preparation of Metal-free Phthalocyanines (Tables 6 and 7).—**Procedure A:** 1,4,8,11,15,18,22,25-octaheptylphthalocyanine (**1g**). In a typical experiment, 3,6-diheptylphthalonitrile (0.7 g, 2.2 mmol) was dissolved in pentanol (7 ml). Lithium (0.3 g) was added in small portions and the mixture heated for 1 h during which time a deep green colour developed. On cooling, the reaction mixture was dissolved in acetone (30 ml), the solution filtered, and acetic acid added. The precipitate was collected and recrystallised from THF–acetone (ca. 1:1) to afford 1,4,8,11,15,18,22,25-octaheptylphthalocyanine (**1g**) (155 mg, 22%) (Found: C, 81.05; H, 10.2; N, 8.5. $\text{C}_{88}\text{H}_{130}\text{N}_8$ requires: C, 81.3; H, 10.1; N, 8.6%); λ_{max} (toluene) 728, 696, 667, 633, and 359 nm; ν_{max} (Nujol) $3\,300\text{ cm}^{-1}$ (N–H), 1 605, and $1\,577\text{ cm}^{-1}$ (C–C, aromatic); δ_{H} (60 MHz; C_6D_6) 0.90 (t, 24 H), 1.05–2.45 (m, 80 H), 4.46 (t, 16 H), and 7.76 (s, 8 H).

Procedure B: 1,4,8,11,15,22,25-octadecylphthalocyanine (**1j**) and 1,4,8,11,15,18-hexadecyl-22,25-bis(3-alkoxycarbonylpropyl)phthalocyanines. In a typical procedure, a 9:1 mixture of 3,6-didecylphthalonitrile (**5j**) (3.2 g, 7.8 mmol) and 3,6-di(4,4,4-trimethoxybutyl)phthalonitrile (**5n**) (0.35 g, 0.9 mmol) was dissolved in pentanol (30 ml) and lithium (0.6g) was added in small portions. On heating under reflux for 1 h the solution turned dark green. After cooling, acetic acid (30 ml) was added and the mixture stirred for 10 min, after which the solvents were removed by rotary evaporation. The residue was chromatographed through a silica column using toluene–ethyl acetate (9:1) as eluant. The first fraction was recrystallised from THF–acetone (ca. 1:2) to yield 1,4,8,11,15,18,22,25-octadecylphthalocyanine (**1j**) (150 mg, 5%) (Found: C, 82.2; H, 11.2; N, 6.9. $\text{C}_{112}\text{H}_{178}\text{N}_8$ requires C, 82.2; H, 11.0; N, 6.85%); FAB-MS ($M + H$) $^+$ 1 637.4280. ^{13}C $_{111}\text{H}_{179}\text{N}_8$ requires 1 637.4286; λ_{max} (toluene) 728, 697, 666, 628, and 359 nm; ν_{max} (Nujol) $3\,300\text{ cm}^{-1}$ (N–H), 1 605, and $1\,577\text{ cm}^{-1}$ (C–C, aromatic); δ_{H} (60 MHz; C_6D_6) 0.90 (t, 24 H), 1.05–2.48 (br s, 128 H), 4.43 (t, 16 H), and 7.79 (s, 8 H).

Recrystallisation of the second fraction afforded 1,4,8,11,15,18-hexadecyl-22,25-bis(3-pentoxycarbonylpropyl)phthalocyanine (**10**), K \rightarrow D 70.5°C , D \rightarrow I $119.5\text{--}120.5^\circ\text{C}$ (18 mg, 0.5%) (Found: C, 79.5; H, 10.5; N, 6.7. $\text{C}_{110}\text{H}_{170}\text{N}_8\text{O}_4$ requires: C, 79.2; H, 10.3; N, 6.7%); FAB-MS ($M + H$) $^+$ 1 669.3457. ^{13}C $_{109}\text{H}_{171}\text{N}_8\text{O}_4$ requires 1 669.3457; λ_{max} (toluene) 729, 698, 666, 633, and 342 nm; ν_{max} (Nujol) $3\,300\text{ cm}^{-1}$ (N–H), 1 735 (C–O), 1 605, and $1\,577\text{ cm}^{-1}$ (C–C, aromatic); δ_{H} (60 MHz; C_6D_6) 0.89 (t, 24 H), 1.05–1.08 (br s, 96 H), 2.48 (br s, 8 H), 3.92 (t, 4 H), 4.44 (t, 16 H), and 7.85 (s, 8 H).

The third fraction was identified as a mixture of 1,4,8,11,15,18-hexadecyl-22,25-bis(3-alkoxycarbonylpropyl)phthalocyanines (25 mg) in which the alkoxy groups were methoxy and pentoxy.

Statistical Analysis of the Molar Ratio of Substrates used in Procedure B.—The choice of a 9:1 ratio of substrates in the above procedure followed from a statistical analysis of the Pc products expected to be formed from various combinations of two phthalonitrile precursors, A and B, assuming that the two are equally susceptible to reaction. Thus if the ratio of A to B is X:1 then the chance of picking at random a molecule of A is given by equation (1), where N is the total number of molecules

$$XN/[(X + 1)N] \quad (1)$$

of B. The probability of the first molecule of A reacting with a second molecule of A is as in equation (2). Similarly the

$$[X(N - 1)]/[(X + 1)N - 1] \quad (2)$$

Table 9. Variation of the statistical yield of (1) and (3) with molar ratio of phthalonitriles.

X	Pc(1) (via AAAA)	Pc(3) (via AAAB)	Other Pcs (via AABB, ABAB, ABBB, BBBB)
1	6	25	69
3	33	44	23
9	66	29	5
25	85	14	1

probability of four molecules of A reacting together to form the octa-alkyl phthalocyanine of type (1) is given by equation (3), or approximately $X^4/(X+1)^4$ because N is *ca.* 10^{20} for a

$$\frac{XN[X(N-1)][X(N-2)][X(N-3)]}{[(X+1)N-1][(X+1)N-2][(X+1)N-3]} \quad (3)$$

millimolar reaction. Similarly, the probability of the reaction of three molecules of A with one of B to give an asymmetrically substituted Pc of type (3) is as in equation (4), or

$$\frac{4N(XN)[X(N-1)][X(N-2)]}{[(X+1)N-1][(X+1)N-2][(X+1)N-3]} \quad (4)$$

approximately $4X^3/(X+1)^4$. Examples of the statistical yields of Pcs (1) and (3) [or, more precisely, the ester derivative of (3)] for various values of X are in Table 9.

Procedure C: 1,4,8,11,15,18-hexadecyl-22,25-bis(3-carboxypropyl)phthalocyanine (**3j**). In a typical experiment, a solution of the mixture of 1,4,8,11,15,18-hexadecyl-22,25-bis(3-alkoxycarbonylpropyl)phthalocyanine obtained in the foregoing reaction (25 mg, 0.02 mmol) in THF (20 ml) was added to 4M aqueous NaOH (20 ml). Tetra-*t*-butylammonium bromide (2 mg) was added and the two-phase system heated under reflux for 6 h. On cooling, diethyl ether (30 ml) was added to the organic layer which was then washed with 2M HCl and, thoroughly, with water. The ether layer was dried ($MgSO_4$) and the solvent removed using a rotary evaporator. The crude product was recrystallised (from THF-acetone) to afford 1,4,8,11,15,18-hexadecyl-22,25-bis(3-carboxypropyl)phthalocyanine (**3j**) (18 mg, 79%) (Found: C, 78.7; H, 9.95; N, 7.2, $C_{100}H_{150}N_8O_4$ requires C, 78.6; H, 9.9; N, 7.2%; λ_{max} (toluene) 727, 695, 665, 633, and 340 nm; ν_{max} (thin film) 3 500–2 500 (O–H), 3 300 (N–H), 1 720 (C=O), 1 605, and 1 577 cm^{-1} (C–C, aromatic).

Preparation of Metal Phthalocyanines (2) (Table 8).—1,4,8,11,15,18,22,25-Octaheptylphthalocyaninatocopper (**2g**). In a typical procedure, metal-free 1,4,8,11,15,18,22,25-octaheptylphthalocyanine (70 mg, 0.05 mmol) and copper(II) acetate (500 mg, 2.5 mmol) were heated in refluxing pentanol (7 ml) for 1 h. On cooling, the resultant slurry was dissolved in toluene (20 ml) and filtered to remove excess of copper(II) acetate. The crude product was purified by elution through a silica column with toluene to yield 1,4,8,11,15,18,22,25-octaheptylphthalocyaninatocopper (**2g**) (62 mg, 85%) (Found: C, 77.5; H, 9.5; N, 8.15. $C_{88}H_{128}CuN_8$ requires C, 77.6; H, 9.5; N, 8.2%; λ_{max} (toluene) 706, 674, 635, and 348 nm; ν_{max} (Nujol) 1 602 and 1 572 cm^{-1} (C–C, aromatic).

Acknowledgements

We thank the University for a research studentship (to I. C.) and the SERC and RSRE-Malvern for a CASE studentship (to N.B.M.). 400 MHz spectra and FAB mass spectra were obtained through SERC facilities at the Universities of Warwick and Swansea respectively. We thank Dr K. J. Harrison and Dr M. F. Daniel of RSRE-Malvern and Professor A. J.

Thomson for invaluable support and discussions. Help from Dr Harrison with DSC measurements on the liquid-crystal phases is also gratefully acknowledged.

References

- S. Baker, M. C. Petty, G. G. Roberts, and M. V. Twigg, *Thin Solid Films*, 1983, **99**, 53.
- For examples, see: S. Baker, G. G. Roberts, and M. C. Petty, *Proc. Inst. Electr. Eng.*, 1983, **130**, 260; M. C. Petty, G. G. Roberts, and D. R. Wight, *Electron. Lett.*, 1984, **20**, 489; J. Batey, M. C. Petty, G. G. Roberts, and D. R. Wight, *ibid.*, 1984, **20**, 489.
- For examples, see: Y. L. Hua, G. G. Roberts, M. M. Ahmad, M. C. Petty, M. Hanack, and M. Rein, *Philos. Mag. B*, 1986, **53**, 105; H. Wohltjen, W. R. Barger, A. W. Snow, and N. L. Jarvis, *IEEE Trans. ED*, 1985, **32**, 1170; D. W. Kalina and S. W. Crane, *Thin Solid Films*, 1985, **134**, 109; K. Ogawa, S. Kinoshita, H. Yonehara, H. Nakahara, and K. Fukuda, *J. Chem. Soc., Chem. Commun.*, 1989, 477.
- M. J. Cook, A. J. Dunn, M. F. Daniel, R. C. O. Hart, R. M. Richardson, and S. J. Roser, *Thin Solid Films*, 1988, **159**, 395.
- M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson, and K. J. Harrison, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2453.
- M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown, and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1987, 1148.
- N. B. McKeown, M. J. Cook, A. J. Thomson, K. J. Harrison, M. F. Daniel, R. M. Richardson, and S. J. Roser, *Thin Solid Films*, 1988, **159**, 469.
- A. Mukoh, T. Kitamura, M. Kaneko, and T. Ozawa, *Eur. Pat. Appl.* 1983, E.P. 87 963 (*Chem. Abstr.*, 1984, **100**, 15417y).
- H. Hogeveen and T. B. Middelkoop, *Tetrahedron Lett.*, 1973, 3671.
- R. Helder and H. Wynberg, *Tetrahedron Lett.*, 1972, 605.
- V. Ramanathan and R. Levine, *J. Org. Chem.*, 1962, **27**, 1216.
- D. J. Chadwick and C. Willbe, *J. Chem. Soc., Perkin Trans. 1*, 1977, 887.
- E. A. Lissi, M. V. Encinas, F. Castaneda, and F. A. Olea, *J. Phys. Chem.*, 1980, **84**, 251.
- H. Normant, *Ann. Chim. (Paris)*, 1942, **17**, 335.
- E. Buchta and C. Huhm, *Liebigs Ann. Chem.*, 1965, **686**, 77.
- L. F. Fieser and R. G. Kennely, *J. Am. Chem. Soc.*, 1935, **57**, 1611.
- M. D'Auria, A. DeMico, G. Piancatelli, and A. Scettri, *Tetrahedron*, 1982, **38**, 1661.
- A. St. Pfau, J. Pictet, P. Plattner, and B. Susz, *Helv. Chim. Acta*, 1935, **18**, 935.
- M. Fetizon and P. Baranger, *C.R. Acad. Sci. Paris*, 1953, **236**, 499.
- B. L. Feringa, R. Hulst, R. Rikers, and L. Brandsma, *Synthesis*, 1988, 316.
- D. T. Mowry, *J. Am. Chem. Soc.*, 1947, **69**, 573.
- H. Kotsuki and H. Nishizawa, *Heterocycles*, 1981, **16**, 1287.
- F. Kienzle, *Helv. Chim. Acta*, 1975, **58**, 1180.
- P. F. Schuda and J. M. Bennett, *Tetrahedron Lett.*, 1982, **23**, 5525.
- M. J. S. Dewar and A. B. Pierini, *J. Am. Chem. Soc.*, 1984, **106**, 203.
- F. Brion, *Tetrahedron Lett.*, 1982, **23**, 5299 (footnote 18).
- W. J. M. van Tilborg, *Synth. Commun.*, 1976, **6**, 583.
- M. Whalley, *J. Chem. Soc.*, 1961, 866.
- E. A. Cuellar and T. J. Marks, *Inorg. Chem.*, 1981, **20**, 3766.
- M. Abkowitz and A. R. Monahan, *J. Chem. Phys.*, 1973, **58**, 2281; A. Skorobogaty, T. D. Smith, G. Dougherty, and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 1985, 651; O. E. Sielcken, M. M. van Tilborg, M. F. M. Roks, R. Hendriks, W. Drenth, and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1987, **109**, 4261.
- C. Piechocki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, *J. Am. Chem. Soc.*, 1982, **104**, 5245; D. Guillon, A. Skoulios, C. Piechocki, J. Simon, and P. Weber, *Mol. Cryst. Liq. Cryst.*, 1983, **100**, 275; D. Guillon, P. Weber, A. Skoulios, C. Piechocki, and J. Simon, *ibid.*, 1985, **130**, 223; C. Piechocki and J. Simon, *J. Chem. Soc., Chem. Commun.*, 1985, 259; I. Cho and Y. Lim, *Mol. Cryst. Liq. Cryst.*, 1988, **154**, 9.
- In preparation. For a preliminary communication see M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown, and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1987, 1086.
- G. Casy, M. Furber, K. A. Richardson, G. R. Stephenson, and R. J. K. Taylor, *Tetrahedron*, 1986, **42**, 5849.