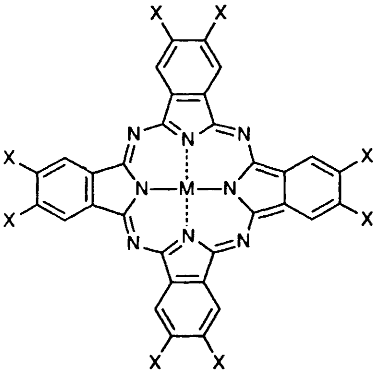
Synthesis and Characterisation of some 1,4,8,11,15,18,22,25-Octa(alkoxymethyl)phthalocyanines; a New Series of Discotic Liquid Crystals

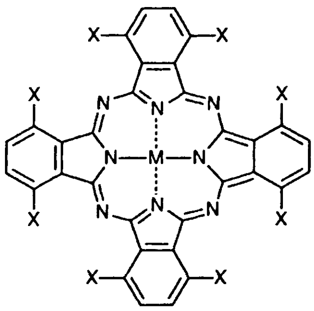
Andrew N. Cammidge,[a] **Michael J. Cook,***[,a] **Kenneth J. Harrison**[b] **and, in part, Neil B. McKeown**[a]
[a] *School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK*
[b] *Defence Research Agency, Electronics Division, RSRE, St Andrews Rd, Malvern WR14 3PS, UK*

A series of 3,6-bis(alkoxymethyl)phthalonitriles, prepared *via* Diels–Alder reactions of 2,5-bis(alkoxymethyl)furans with fumaronitrile, have been converted into the corresponding phthalocyanines. Zn(II) and Cu(II) derivatives of 1,4,8,11,15,18,22,25-octa(heptyloxymethyl)phthalocyanine were also prepared. Examples of the macrocycles were characterised using ^{1}H NMR spectrometry and optical spectroscopy. Those bearing straight chains aggregate in solutions of chloroform and toluene. The octa(butoxymethyl)phthalocyanine and its longer chain homologues exhibit a discotic liquid crystalline phase. Compounds containing branched sidechains are liquid crystals at room temperature.

Phthalocyanines, well known as commercial pigments, possess interesting conductivity and optoelectronic properties which further enhance their importance.[1] The discovery that certain derivatives exhibit liquid crystalline behaviour, in particular the formation of the so-called columnar discotic mesophases,[2] adds a new dimension to their potential applications in devices. The first of such phthalocyanines were described by Simon and coworkers[3] and by Hanack's group[4] and were octasubstituted at the peripheral (2,3,9,10,16,17,23,24) positions with long chained alkoxymethyl substituents, series **1**. Subsequently, mesophase behaviour has been reported for other metal-free and metallated phthalocyanines peripherally substituted with long chained alkyl[5,6] and alkoxy groups,[5,7–10] series **2** and **3**.

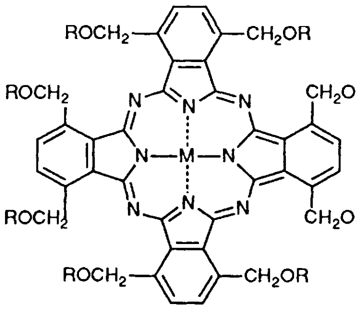


1 X = $CH_2OAlkyl$, M = H,H or metal
2 X = Alkyl, M = H,H or metal
3 X = OAlkyl, M = H,H or metal



4 X = Alkyl, M = H,H or metal
5 X = OAlkyl, M = H,H or metal

Research in our own laboratories has been concerned with parallel series of phthalocyanines in which eight substituents are located at the non-peripheral (1,4,8,11,15,18,22,25) sites.[11,12] To date we have observed a contrast in the behaviour exhibited by the octaalkyl **4** and octaalkoxy **5** series. Examples of the former, which include a compound with chains as short as pentyl,[13] exhibit one, two or three distinct liquid crystal phases depending upon chain length and the central ion.[14] However, the alkoxy phthalocyanines melt directly into the isotropic liquid state.[12] To develop the comparison with the peripherally substituted compounds, we have now turned our attention to the octaalkoxymethyl analogues **6** and the two metallated derivatives **7** and **8**. In the present paper, we describe their preparation, characterisation, and a preliminary examination of their melting behaviour.



6 M = H,H
a; R = C_3H_7
b; R = C_4H_9
c; R = C_5H_{11}
d; R = C_6H_{13}
e; R = C_7H_{15}
f; R = C_8H_{17}
g; R = C_9H_{19}
h; R = $C_{10}H_{21}$
i; R = 2-octyl
j; R = 2-ethylhexyl

7 M = Zn, R = C_7H_{15}
8 M = Cu, R = C_7H_{15}

Results and Discussion

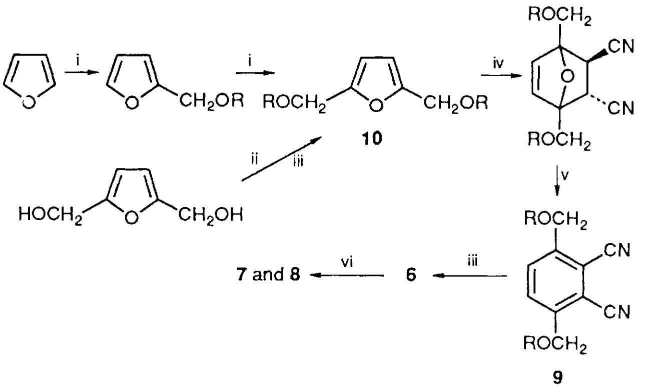
Preparation of Compounds.—In our previous work, we prepared the octasubstituted phthalocyanines by base catalysed cyclisation of the corresponding 3,6-disubstituted phthalonitriles.[11,12] In the light of this experience, we commenced the

Table 1 Preparation and characterisation of some 2,5-bis(alkoxymethyl)furans **10**

			Found (requires)[a]			
Compound[b]	Yield (%)	B.p./°C (p/mmHg)	Formula	C	H	δ(¹H)[c]
10a	36	150 (3)	$C_{12}H_{20}O_3$	—	—	0.92 (t, 6 H), 1.5 (m, 4 H), 3.40 (t, 4 H), 4.39 (s, 4 H), 6.20 (s, 2 H)
10b	64	168 (2.5)	$C_{14}H_{24}O_3$	70.4 (70.0)	10.2 (10.1)	0.90 (t, 6 H), 1.5 (m, 8 H), 3.44 (t, 4 H), 4.36 (s, 4 H), 6.19 (s, 2 H)
10c	49	230 (0.4)	$C_{16}H_{28}O_3$	71.2 (71.6)	10.3 (10.5)	0.88 (t, 6 H), 1.3 (m, 12 H), 3.40 (t, 4 H), 4.34 (s, 4 H), 6.19 (s, 2 H)
10d	78	185 (1)	$C_{18}H_{32}O_3$	73.05 (72.9)	11.0 (10.9)	0.88 (t, 6 H), 1.32 (m, 16 H), 3.40 (t, 4 H), 4.40 (s, 4 H), 6.21 (s, 2 H)
10e	57	240 (0.1)	$C_{20}H_{36}O_3$	74.4 (74.0)	11.6 (11.2)	0.88 (t, 6 H), 1.3 (m, 20 H), 3.42 (t, 4 H), 4.38 (s, 4 H), 6.21 (s, 2 H)
10f	81, 25[d]	—	$C_{22}H_{40}O_3$	—	—	0.90 (t, 6 H), 1.3 (m, 24 H), 3.40 (t, 4 H), 4.38 (s, 4 H), 6.15 (s, 2 H)
10g	47	>250 (0.1)	$C_{24}H_{44}O_3$	75.9 (75.7)	11.3 (11.65)	0.88 (t, 6 H), 1.3 (m, 28 H), 3.40 (t, 4 H), 4.39 (s, 4 H), 6.20 (s, 2 H)
10h	73	>250 (0.1)	$C_{26}H_{48}O_3$	76.5 (76.4)	11.45 (11.8)	0.88 (t, 6 H), 1.35 (m, 32 H), 3.44 (t, 4 H), 4.39 (s, 4 H), 6.20 (s, 2 H)
10i	44	190 (2)	$C_{22}H_{40}O_3$	74.65 (74.95)	11.6 (11.4)	0.88 (t, 6 H), 1.05 (d, 6 H), 1.30 (m, 20 H), 3.20 (m, 2 H), 4.38 (s, 4 H), 6.22 (s, 2 H)
10j	45	130 (0.1)	$C_{22}H_{40}O_3$	74.55 (74.95)	11.7 (11.4)	0.90 (t, 12 H), 1.3 (m, 18 H), 3.42 (br d, 4 H), 4.40 (s, 4 H), 6.25 (s 2 H)

[a] Compounds **10a** and **10f** were not obtained analytically pure and were used in the next step without further purification. [b] Prepared from 2,5-bis(chloromethyl)furan except **10f** which was prepared by a two step alkylation of furan, see text. [c] 60 MHz; $CDCl_3$. [d] See *b*: 81% for monoalkylation, 25% for the second alkylation. Product used in the next step without prior distillation.

present study seeking a convenient route to the 3,6-bis(alkoxymethyl)phthalonitriles **9**. However, our initial approach to obtain these by a Williamson's ether synthesis on 3,6-bis(bromomethyl)phthalonitrile faltered when we were unable to generate the latter cleanly from 3,6-dimethylphthalonitrile. Accordingly, we adapted our earlier route for preparing 3,6-dialkylphthalonitriles which exploited the Diels–Alder reaction of the appropriate 2,5-disubstituted furan with fumaronitrile.[15] This adaption is depicted in Scheme 1.



Scheme 1 *Reagents and conditions:* i, BuLi/$ROCH_2Br$; ii, $SOCl_2$; iii, RO^-; iv, fumaronitrile; v, $LiN(SiMe_3)_2$, THF, −78 °C; vi, Zn acetate or Cu acetate

The preparation of 2,5-bis(alkoxymethyl)furans **10** was achieved in two ways. The first, which was prompted by the commercial availability of bromomethyl octyl ether, involved functionalisation of furan. This was achieved by deprotonating the furan ring and quenching the anion with bromomethyl octyl ether. Direct disubstitution proved difficult and a two-step procedure to give first the 2- and then 2,5-bis(octyloxymethyl)furan was preferred. Even so, the second substitution proceeded in only 25% yield. This result, and the requirement to prepare the higher and lower homologues of bromomethyl octyl ether to obtain further furan derivatives, led to the evaluation of alternative procedures involving Williamson's ether synthesis on 2,5-bis(hydroxymethyl)furan and 2,5-bis(chloromethyl)furan. Of these, the route using the latter precursor proved more convenient,[16] Scheme 1. Yields after distillation are given in Table 1.

Conversion of the furans into the corresponding phthalonitriles, Scheme 1, was undertaken without isolation of the intermediate Diels–Alder adduct. The reversibility of the Diels–Alder reaction of the furans with fumaronitrile presented a dilemma. Adduct formation is encouraged at low temperature but the time required to reach the equilibrium ratio of adduct to starting materials is excessive (*ca.* 8–10 weeks at −8 °C). Attempts to enhance the rate at which the equilibrium mixture was formed by sonication, the addition of silica gel and the presence of a Lewis acid were unsuccessful.[16] Furthermore, the use of excess of fumaronitrile to drive the equilibrium towards adduct formation caused problems because the base required in the subsequent aromatisation step reacts with it.

The procedure which was eventually established to obtain the desired phthalonitriles involved reaction of the substituted furan and fumaronitrile at room temperature or at 0–5 °C, typically in a minimum quantity of dry THF. The reactions were monitored by NMR spectroscpy of aliquots over periods up to eight weeks during which times the conversions to adduct were 15–55%, Table 2. Conversions of the adducts to phthalonitriles were performed by adding lithium bis(trimethylsilyl)amide to the mixtures at −78 °C. The phthalonitriles proved difficult to purify and in most cases were used as isolated for conversion into the corresponding phthalocyanine.

The solubility of the straight chain phthalocyanines was surprisingly low in comparison with the octaalkyl and octalkoxy analogues of series **4** and **5**. However, with the exception of **6a** and **6b** there was sufficient solubility in warm toluene, acetone or THF to effect satisfactory recrystallisation. The branched-chain derivatives **6i** and **6j** are much more soluble and could be purified by column chromatography over silica gel. These materials are formed as mixtures of diastereoisomers by virtue of the eight chiral centres in each molecule but separation was not attempted. The zinc and copper derivatives of octa(heptyloxymethyl)phthalocyanine, *i.e.*, compounds **7** and **8**, were prepared by standard metal insertion reactions. Table 3 summarises the phthalocyanines prepared.

Table 2 The conversion of 2,5-bis(alkoxymethyl)furans **10** into the corresponding 3,6-bis(alkoxymethyl)phthalonitriles **9** *via* the cycloadduct with fumaronitrile, see Scheme 1

Furan	Solvent	Time (temp., T/°C)	Conversion[b] (%)	Product	% Yield[c]	B.p. (or m.p.)/°C(p/mmHg)	δ_H[d]
10a	$CHCl_2$	3 h (reflux) + 18 h (rt)[a]	30	**9a**	12	210 (0.7)	0.92 (t, 6 H), 1.52 (m, 4 H), 3.52 (t, 4 H), 4.97 (s, 4 H), 7.82 (s, 2 H)
10b	THF	5 weeks (0–5)	45	**9b**	8	250 (0.4)	0.90 (t, 6 H), 1.2–1.7 (m, 8 H), 3.44 (t, 4 H), 4.96 (s, 4 H), 7.84 (s, 2 H)
10c	THF	2 weeks (rt)	30	**9c**	12	> 250 (0.3)	0.88 (t, 6 H), 1.1–1.6 (m, 12 H), 3.55 (t, 4 H), 4.61 (s, 4 H), 7.80 (s, 2 H)
10d	THF	1 week (0–5)	35	**9d**	10	oil[f]	0.88 (t, 6 H), 1.3 (m, 16 H), 3.58 (t, 4 H), 4.68 (s, 4 H), 7.83 (s, 2 H)
10e	THF	3 weeks (rt)	28	**9e**	13	oil[e]	0.88 (t, 6 H), 1.3 (m, 20 H), 3.58 (t, 4 H), 4.65 (s, 4 H), 7.84 (s, 2 H)
10f	Me_2CO	1 week (0–5)	40	**9f**	23	(23)	0.90 (t, 6 H), 1.4 (m, 24 H), 3.58 (t, 4 H), 4.64 (s, 4 H), 7.82 (s, 2 H)
10g	THF	4 weeks (rt)	30	**9g**	10	oil[e]	0.88 (t, 6 H), 1.3 (m, 28 H), 3.56 (t, 4 H), 4.68 (s, 4 H), 7.82 (s, 2 H)
10h	THF	3 weeks (rt)	20	**9h**	4	(37)	0.88 (t, 6 H), 1.4 (m, 32 H), 3.57 (t, 4 H), 4.68 (s, 4 H), 7.84 (s, 2 H)
10i	CH_2Cl_2	4 weeks (0–5)	55	**9i**	19	> 250 (0.1)[e]	0.88 (t, 6 H), 1.05 (d, 6 H), 1.3 (m, 20 H), 3.6 (m, 2 H), 4.62 (s, 4 H), 7.80 (s, 2 H)
10j	THF	4 weeks (rt)	15	**9j**	5	oil[e]	0.90 (t, 12 H), 1.3 (m, 18 H), 3.4 (br d, 4 H), 4.64 (s, 4 H), 7.78 (s, 2 H)

[a] rt = room temperature. [b] Not isolated, conversion estimated by NMR. [c] With respect to starting furan. [d] 60 MHz; $CDCl_3$. [e] Oil could not be distilled. The material was used in the next step without further purification. [f] Purified by low temperature recrystallisation. Oil at room temperature.

Table 3 Preparation and characterisation of some 1,4,8,11,15,18,22,25-octa(alkoxymethyl)phthalocyanines **6**, **7** and **8**

Compd.	Purification[a]	Yield (%)	M.p./°C[b]	Formula	% Found (requires)			Q-band (toluene)	
					C	H	N	Conc./10^{-6} mol dm^{-3}	λ_{max}(log ε)/nm
6a	U	28	> 300	$C_{64}H_{82}N_8O_8$	70.1 (70.4)	7.5 (7.6)	10.2 (10.3)	*c*	712, 679, 646, 618
6b	V	26	185 (K–D)	$C_{72}H_{98}N_8O_8$	71.6 (71.85)	8.2 (8.2)	9.3 (9.3)	2.54	713 (4.33), 680 (4.34), 647 (4.04), 619 (3.90)
6c	W	34	123 (K–D)	$C_{80}H_{114}N_8O_8$	72.7 (73.0)	8.6 (8.7)	8.2 (8.5)	2.95	714 (4.39), 681 (4.39), 647 (4.19), 619 (3.90)
6d	V	13	85 (K–D)	$C_{88}H_{130}N_8O_8$	73.7 (74.0)	9.1 (9.2)	7.85 (7.85)	0.95	713 (4.65), 681 (4.66), 648 (4.42), 621 (4.30)
6e	X	28	79 (K–D)	$C_{96}H_{146}N_8O_8$	74.8 (74.9)	9.5 (9.6)	7.2 (7.3)	3.17	714 (4.27), 681 (4.34), 649 (4.18), 622 (4.00)
6f	Y	15	67 (K–D)	$C_{104}H_{162}N_8O_8$	75.6 (75.6)	10.0 (9.9)	6.8 (6.8)	2.97	714 (4.61), 681 (4.66), 648 (4.44), 620 (4.27)
6g	V	10	75 (K–D)	$C_{112}H_{178}N_8O_8$	76.1 (76.2)	10.4 (10.2)	6.1 (6.35)	1.71	712 (4.42), 680 (4.41), 646 (4.19), 620 (4.08)
6h	V	14	64 (K–D)	$C_{120}H_{194}N_8O_8$	76.6 (76.8)	10.5 (10.4)	6.0 (6.0)	2.54	714 (4.58), 682 (4.57), 649 (4.36), 618 (4.24)
6i	Z	27	< rt 108 (D–I)	$C_{104}H_{162}N_8O_8$	75.1 (75.6)	9.8 (9.9)	7.2 (6.8)	5.53	713 (4.23), 682 (4.20), 651 (3.84), 618 (3.70)
6j	Z	7	< rt 236 (D–I)	$C_{104}H_{162}N_8O_8$	75.2 (75.6)	9.9 (9.9)	6.9 (6.8)	4.45	713 (4.07), 681 (4.06), 649 (3.80), 618 (3.67)
7	W	87[d]	67 (K–D)	$C_{96}H_{144}N_8O_8Zn$	71.6 (71.9)	9.2 (9.05)	6.8 (7.0)	0.57	693 (5.12), 660 (4.65), 627 (4.63)
8	W	72[d]	80 (K–D)	$C_{96}H_{144}N_8O_8Cu$	71.7 (72.0)	9.0 (9.1)	6.9 (7.0)	0.235	694 (5.31), 655 (4.86), 628 (4.83)

[a] Procedure for purification: U, washed with water and toluene; V, recrystallisation from toluene; W, recrystallisation from THF; X, recrystallisation from dichloromethane; Y, recrystallisation fron THF–acetone; Z, chromatographic separation (silica gel, ethyl acetate as eluent. [b] M.p. or transition temperature for change from the crystal state to a discotic mesophase (K–D) or from the mesophase to the isotropic liquid (D–I). [c] Material shows low solubility, qualitative spectrum run. [d] Yield for conversion from the metal free derivative **6e**.

Characterisation of 1,4,8,11,15,18,22,25-*Octa(alkoxymethyl)-phthalocyanines*.—Each derivative gave a satisfactory elemental analysis, Table 3. Signals within the 60 MHz NMR spectra of the branched chain derivatives **6i** and **6j** in $CDCl_3$ were consistent with their structures. The signals are broadened, which can be attributed to the presence of stereoisomers. Difficulties were experienced in obtaining the ^1H NMR spectra of the straight chain analogues. Thus the 60 MHz spectrum of the octaheptyloxymethyl derivative **6e** as a solution in $CDCl_3$, at the limit of solubility, showed no discernible signals. Unusual effects similar to these, though less extreme, have been observed in the NMR spectra of cofacial dimeric phthalocyanines[17] and of compounds related to series **1**;[18] they can be attributed to molecular aggregation. Further experiments on **6e** demonstrated that this compound is indeed highly aggregated in solution. The 400 MHz spectrum of a dilute solution of **6e** in deuteriotoluene

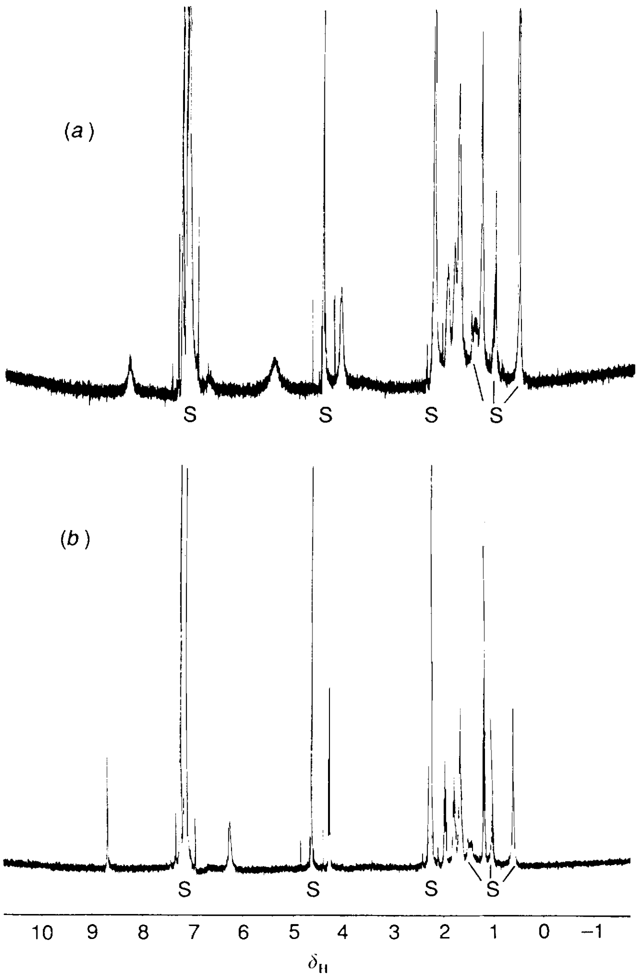


Fig. 1 ^{1}H NMR spectra of a 5.44 × 10^{-4} mol dm^{-3} solution of **6e** in [$^2H_8$]toluene: (*a*), at 25 °C; and (*b*), at 90 °C. S Denotes peaks arising from impurities in the solvent or residual protons in the deuteriated solvent.

(5.44 × 10^{-4} mol dm^{-3}) at 25 °C is shown in Fig. 1. At this dilution, signals from impurities in the solvent and residual solvent protons are apparent but, despite this, the signals from protons of the solute molecules are clearly identifiable. However, the aromatic protons at δ 8.3, and the benzylic protons at δ 5.4 give particularly broadened signals. The spectrum was re-run at 50, 70 and 90 °C (see Fig. 1). As the temperature is raised, there is increased resolution for all the signals. At 70 °C, the splitting pattern for all the protons in the aliphatic chains has become resolved and there is a marked downfield shift of the aromatic and benzylic protons to δ 8.6 and 6.05, respectively. At 90 °C, there is a further sharpening of the signals which now resonate at δ 8.7 and 6.25, Fig. 1(*b*). Finally, the spectrum of a 5.44 × 10^{-5} mol dm^{-3} solution of **6e** was obtained at 70 °C. This shows the signals at δ 8.8 and 6.4. The shielding of the benzylic and aromatic protons under conditions leading to enhanced aggregation is consistent with a co-facial association of molecules wherein the protons experience the shielding zone arising from the ring current of the nearest neighbour(s).

Visible-region absorption spectra provided further evidence for aggregation. Phthalocyanines in the monomeric state exhibit characteristic intense visible-region absorption (Q-band). Metallated derivatives give a single absorption from two degenerate transitions, but the degeneracy is lifted in the lower symmetry metal-free derivatives and a two-component Q-band is observed. Low-intensity bands, vibronic in origin, are also observed to shorter wavelength of the Q-band. However, aggregation of the solute molecules significantly affects the intensity/band-shape of the peaks; the sharp Q-band absorption of the monomer species diminishing while a new broad-band absorption becomes apparent.[19] The visible region spectrum of **6e** as a 5.44 × 10^{-4} mol dm^{-3} solution in toluene (the same concentration used to obtain the NMR spectrum shown in Fig. 1) is depicted in Fig. 2, line (*a*). It confirms that the solute is highly aggregated at this level of concentration. Spectra were also recorded of solutions diluted to 5.44 × 10^{-8} mol dm^{-3}, Fig. 2 lines (*b*)–(*e*). At the lowest concentration, the spectrum resembles that expected for the monomeric species. The spectrum was also recorded of 1,4,8,11,15,18,22,25-octanonylphthalocyanine **4** (X = C_9H_{19}, M = H,H) a compound having the same number of backbone atoms in the substituent chains as **6e**. This is much less aggregated; the spectrum of a 5.44 × 10^{-4} mol dm^{-3} solution is shown in Fig. 2 as line (*f*) and its bandshape is comparable to the spectrum of **6e** obtained at 5.44 × 10^{-7} mol dm^{-3}.

Other members of series **6**, and the metallated analogues **7** and **8**, are also associated in the solution phase and their visible region spectra were routinely recorded at concentrations lower than 3 × 10^{-6} mol dm^{-3}. Under these conditions, the Q-band absorption at λ_{max} was higher than the broad-band absorption to shorter wavelength, Table 3.

The split Q-band absorption of the metal-free compounds appears at *ca.* 680 and 713 nm, some 15 nm to the blue of the octaalkylphthalocyanines of series **4**. The copper and zinc phthalocyanines in the present work show the Q-band absorption at *ca.* 694 nm.

Thermotropic Behaviour.—The melting behaviour of the phthalocyanines was investigated by microscopy, with and without cross polarisers, and by differential scanning calorimetry (DSC). Investigation of the octapropyloxymethyl derivative **6a** by microscopy indicated that it remained crystalline up to 250 °C, at which temperature decomposition began. The absence of a phase transition was confirmed by the DSC trace which showed no peaks up to 300 °C. However, all but **6e** of the other straight chain analogues gave a single peak in their DSC thermograms on heating to 300 °C. Inspection by polarised microscopy showed that this corresponded to transition from the crystal to a discotic mesophase. Compound **6e** showed a total of three closely spaced peaks in the DSC thermogram in the region 65–79 °C. Microscopy showed that the highest temperature peak corresponded to transition into a mesophase. In all cases, decomposition of the phthalocyanines occurred between 250 and 290 °C without formation of an isotropic liquid phase; separate samples heated below the decomposition temperatures showed reversible transition from the mesophase into the crystalline state but this was accompanied by supercooling. Transition temperatures reported in Table 3 for these compounds correspond to the crystal-to-mesophase transition observed by microscopy on the second heating cycle.

The behaviour of the branched chain derivatives **6i** and **6j** is markedly different. Both compounds are viscous liquid crystals at room temperature and show a single peak in their DSC thermograms which was shown by polarised microscopy to correspond to a reversible transition into the isotropic liquid. The contrasting behaviour of the straight chain and branch chained derivatives is presumably a function of both the branching and a depression of transition temperatures through the presence of diastereoisomers in these derivatives.

The optical textures of liquid crystals observed under the polarising microscope, which normally provide evidence for the type of molecular ordering, are best observed by cooling from the isotropic liquid. Under these conditions, the branched chain

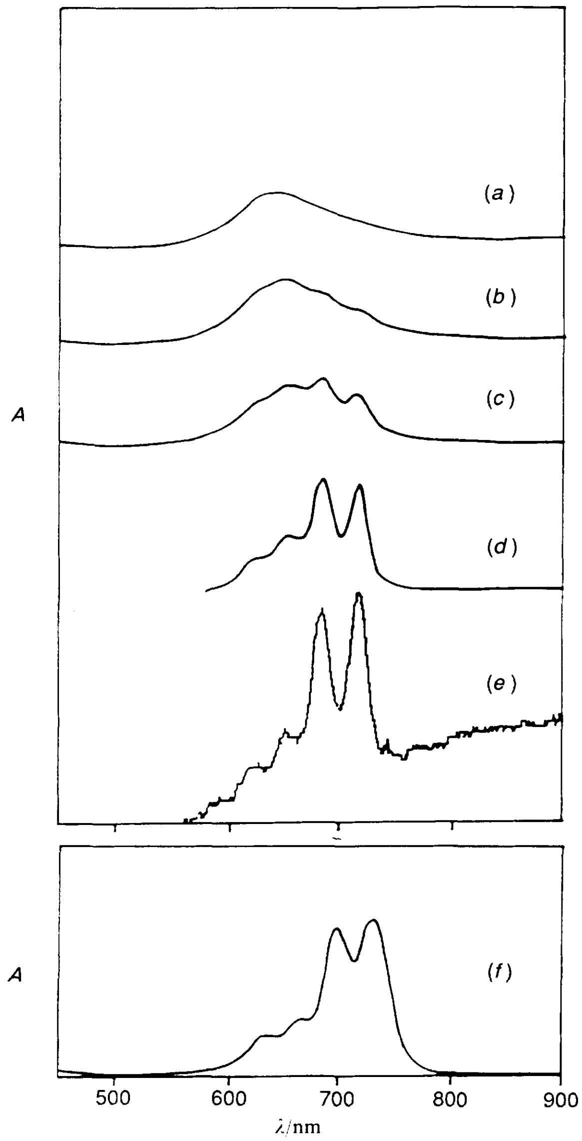


Fig. 2 (*a*), The visible region spectrum of **6e** in toluene at a concentration of 5.44×10^{-4} mol dm^{-3}; (*b*), as above but at 5.44×10^{-5} mol dm^{-3}; (*c*), as above but at 5.44×10^{-6} mol dm^{-3}; (*d*), as above but at 5.44×10^{-7} mol dm^{-3}; (*e*), as above but at 5.44×10^{-8} mol dm^{-3}; (*f*), the visible region spectrum of **4** ($X = C_9H_{19}$, M = H,H in toluene at a concentration of 5.44×10^{-4} mol dm^{-3}). Spectra have been offset and normalised to a common absorption scale.

compounds **6i** and **6j** show a fan-like texture. This is characteristic of hexagonal symmetry of the columnar arrangement with the columns themselves containing some disorder in terms of differential spacing between neighbouring molecules;[14] columnar disordered hexagonal mesophases are exhibited by a number of discotic liquid crystals including members of series **4**.[13,14] The textures exhibited by the straight chain derivatives are less distinct because they are only observed forming from the crystal state rather than the isotropic liquid. However, a preliminary X-ray diffraction analysis of the mesophases of **6e** and **6g** has revealed that they are also of hexagonal symmetry.[20] A full account of mesophase behaviour and characterisation will be given in a future publication.

In conclusion, 1,4,8,11,15,18,22,25-octa(alkoxymethyl)-phthalocyanines clearly constitute a novel series of thermotropic liquid crystals and as such their behaviour resembles, at least in kind, that exhibited by series **4** rather than that of series **5**. Indeed, the results demonstrate unambiguously that among the octasubstituted phthalocyanines represented by structures **1**–**6** the behaviour of series **5** is anomalous. Results from a separate study may shed some light on this point. Recently we attempted to perform a single-crystal X-ray diffraction analysis of **5** ($X = OC_7H_{15}$, M = H,H). The crystals proved to be brittle and gave only a weak diffraction pattern.[21] These results suggest that the supposed crystals have an almost glass-like structure with only short-range molecular order. We suppose that this lack of ordering in the crystal is most unlikely to be conducive to the formation of a columnar liquid crystal phase when the material is heated.

Experimental

Equipment and Measurements.—Bulb-to-bulb distillation was performed using a Kugelrohr apparatus. Routine ^1H NMR spectra were measured at 60 MHz using a JEOL JNM-PMX60SI spectrometer. Spectra measured at 400 MHz were recorded on a JEOL JNM GX-400 spectrometer. Visible spectra were recorded on either a Pye-Unicam PU8800, Hitachi U-2000 or a Cary 17D spectrophotometer. Measurement of transition temperatures for the changes from crystal to mesophase and mesophase to isotropic liquid (Table 3) were obtained by optical microscopy following dsc using a Mettler TA3000 thermal analyser with a Mettler DSC 30 cell. Optical microscopy was undertaken using a Vickers polarising microscope in conjunction with a Mettler FP82 hot-stage and carried out under a nitrogen atmosphere.

2-*Octyloxymethylfuran.*—Following the general procedure described in ref. 15, furan (20.5 g, 0.3 mol) was added dropwise to a stirred solution of butyllithium (0.3 mol, 200 cm^3 of a 1.6 mol dm^{-3} solution in hexane) and dry THF (100 cm^3) under a nitrogen atmosphere at −15 °C. The mixture was stirred for 16 h at room temperature. Bromomethyl octyl ether (66.9 g, 0.3 mol) was added dropwise, and the mixture stirred for a further 24 h at room temperature. The brown reaction mixture was worked up according to ref. 15 to afford 2-*octyloxymethylfuran* (51 g, 81%), as a pale yellow oil which was used in the next step without further purification; δ_H(60 MHz; CDCl$_3$) 0.9 (t, 3 H), 1.3 (m, 12 H), 3.42 (t, 2 H), 4.41 (s, 2 H), 6.23 (m, 2 H) and 7.32 (d, 1 H).

2,5-*Bis(octyloxymethyl)furan.*—Following ref. 15, 2-octyloxymethylfuran (42 g, 0.2 mol) was deprotonated using butyllithium (0.2 mol, 135 cm^3 of a 1.6 mol dm^{-3} solution in hexane) in dry THF (100 cm^3) and the anion quenched with bromomethyl octyl ether (44.6 h, 0.2 mol). The usual work-up[15] afforded 2,5-*bis(octyloxymethyl)furan* (17.6 g, 25%) as an oil which was used in the next step without further purification; δ_H(60 MHz; CDCl$_3$) 0.90 (t, 6 H), 1.3 (br m, 24 H), 3.40 (t, 4 H), 4.38 (s, 4 H) and 6.15 (s, 2 H).

2,5-*Bis(alkyloxymethyl)furans from Furan-2,5-diyldimethanol, Table 1.*—In a typical procedure, thionyl chloride (80 g, 0.6 mol) was added to a solution of furan-2,5-diyldimethanol (20 g, 0.15 mol) in ethyl acetate at 0 °C over 30 min, and the mixture stirred for a further 30 min. The resulting black solution was poured carefully onto solid sodium hydrogen carbonate (100 g). When all effervescence had subsided, the solid was filtered and the solvent removed under reduced pressure to give a viscous black oil. The crude product was extracted with petroleum ether (3 × 100 cm^3) and the solvent removed to afford 2,5-bis(chloromethyl)furan as a pale brown oil, which was added immediately to a solution of sodium metal (6.5 g, 0.28 mol) in heptanol (300 cm^3). The mixture was stirred for 18 h and water (150 cm^3) added. The resulting dark solution was extracted with dichloromethane (2 × 100 cm^3) and the solvents were removed under reduced pressure to give a dark oil. Bulb-bo-bulb distillation at an oven temperature of 240 °C under reduced pressure, 0.1 mmHg, afforded 2,5-*bis(heptyloxymethyl)furan* (27.5 g, 57%) as a colourless oil (Found: C, 74.4; H, 11.6. $C_{20}H_{36}O_3$ requires C, 74.0; H, 11.2%); δ_H(60 MHz; $CDCl_3$) 0.88 (t, 6 H), 1.30 (m, 20 H), 3.42 (t, 4 H), 4.38 (s, 4 H) and 6.21 (s, 2 H).

3,6-*Bis(alkyloxymethyl) phthalonitriles, Table 2.*—In a typical reaction procedure, 2,5-bis(heptyloxymethyl)furan (27.5 g, 0.085 mol) and fumaronitrile (7 g, 0.089 mol) were dissolved in THF (100 cm^3) and allowed to stand at room temperature for 3 weeks. The NMR spectrum of an aliquot indicated 28% conversion to the Diels–Alder adduct. The solution was stirred at −78 °C under nitrogen, lithium bis(trimethylsilyl)amide (100 cm^3; 1 mol dm^{-3} in THF, 0.1 mol) was added over 45 min, and the mixture stirred for a further 1 h. The black solution was poured onto dil. hydrochloric acid (100 cm^3) and the aqueous mixture extracted with hexane (2 × 150 cm^3). The extracts were dried, evaporated, and the volatile components separated from the residue by bulb-to-bulb distillation under reduced pressure. The black residue was extracted with hexane (3 × 40 cm^3) and the solvent removed to afford 3,6-*bis(heptyloxymethyl)-phthalonitrile* (4.1 g, 13%) as a pale yellow oil; δ_H(60 MHz; $CDCl_3$) 0.88 (t, 6 H), 1.30 (m, 20 H), 3.58 (t, 4 H), 4.65 (s, 4 H) and 7.84 (s, 2 H); ν_{max}(neat)/cm^{-1} 2233 (CN).

The product was used in the next step without further purification.

Metal-free Phthalocyanines, Table 3.—In a typical experiment, 3,6-bis(heptyloxymethyl)phthalonitrile (1 g, 2.6 mmol) was stirred in refluxing butyl alcohol (20 cm^3). A small piece of lithium was added and the mixture was refluxed for 2 h, allowed to cool and poured onto glacial acetic acid (30 cm^3). The mixture was stirred for a further 30 min and the solid was filtered, washed with ethanol (50 cm^3) and recrystallised from dichloromethane to afford *metal-free* 1,4,8,11,15,18,22,25-*octa-(heptyloxymethyl)phthalocyanine* (0.28 g, 28%) (Found: C, 74.77; H, 9.54; N, 7.22. $C_{96}H_{146}N_8O_8$ requires C, 74.86; H, 9.56; N, 7.28%); λ_{max}/nm (log ε) (3.17 × 10^{-6} mol dm^{-3} in toluene) 714 (4.27), 681 (4.34), 649 (4.18) and 622 (400); ν_{max}(Nujol)/cm^{-1} 3300 (NH), 1612 and 1577 (C–C, aromatic).

Metal Phthalocyanines, Table 3.—In a typical procedure, metal-free 1,4,8,11,15,18,22,25-octa(heptyloxymethyl)phthalocyanine (50 mg) and zinc acetate (0.5 g) in a mixture of toluene (30 cm^3) and ethanol (5 cm^3) were heated under reflux for 12 h. The solvent was removed and the residue purified by column chromatography (silica gel, THF eluent). Recrystallisation from THF afforded 1,4,8,11,15,18,22,25-*octa(heptyloxymethyl)-phthalocyaninatozinc* (45 mg, 87%) (Found: C, 71.6; H, 9.2; N, 6.8. $C_{96}H_{144}N_8O_8Zn$ requires C, 71.9; H, 9.05; N, 7.0%); λ_{max}/nm (log ε) (5.69 × 10^{-7} mol dm^{-3} in toluene) 693 (5.12), 660 (4.65) and 627 (4.63); ν_{max}(Nujol)/cm^{-1} 1602 and 1580 (C–C, aromatic).

Acknowledgements

We thank the SERC and RSRE-Malvern for a CASE studentship for A. N. C. and Professor A. J. Thomson for helpful discussions.

References

1 See C. C. Leznoff and A. B. P. Lever, *Phthalocyanines—Properties and Applications*, VCH, NY, 1989.
2 S. Chandrasekhar and G. S. Ranganath, *Rep. Prog. Phys.*, 1990, **53**, 57.
3 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, *Mol. Cryst. Liq. Cryst.*, 1985, **130**, 223; P. Weber, D. Guillon and A. Skoulios, *J. Phys. Chem.*, 1987, **91**, 2242.
4 M. Hanack, A. Beck and H. Lehmann, *Synthesis*, 1987, 703.
5 K. Ohta, L. Jacquemin, C. Sirlin, L. Bosio and J. Simon, *New J. Chem.*, 1988, **12**, 751.
6 D. Masurel, C. Sirlin and J. Simon, *New J. Chem.*, 1987, **11**, 455.
7 J. F. van der Pol, W. Drenth, J. H. Sluyters and A. Baas, *J. Electroanal. Chem.*, 1989, **271**, 41.
8 J. F. van der Pol, W. Drenth, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, J. Aerts, R. Visser and S. J. Picken, *Liq. Cryst.*, 1989, **6**, 577.
9 J. F. van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 615.
10 D. Lelievre, M. A. Petit and J. Simon, *Liq. Cryst.*, 1989, **4**, 707.
11 M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1987, 1086.
12 M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson and K. J. Harrison, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2453.
13 M. J. Cook, S. J. Cracknell and K. J. Harrison, *J. Mater. Chem.*, 1991, **1**, 703.
14 A. S. Cherodian, A. N. Davies, R. M. Richardson, M. J. Cook, N. B. McKeown, A. J. Thomson, J. Feijoo, G. Ungar and K. J. Harrison, *Mol. Cryst. Liq. Cryst.*, 1991, **196**, 103.
15 N. B. McKeown, I. Chambrier and M. J. Cook, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1169.
16 For details see A. N. Cammidge, PhD Thesis, University of East Anglia, 1990.
17 S. M. Marcuccio, P. I. Svirskaya, S. Greenberg, A. B. P. Lever and C. C. Leznoff, *Can. J. Chem.*, 1985, **63**, 3057.
18 C. Piechocki and J. Simon, *J. Chem. Soc., Chem. Commun.*, 1985, 259.
19 See ref. 1, M. J. Stillman and T. Nyokong, p. 133–289.
20 R. M. Richardson and S. Haslam, personal communication.
21 A. K. Powell, personal communication.

Paper 1/03825G
Received 25*th July* 1991
Accepted 9*th August* 1991