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Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Discotic liquid crystals of transition metal complexes X. Phthalocyanine derivatives substituted with *n*-alkyloxyphenyl side chains

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To cite this Article Ohta, Kazuchika , Watanabe, Takuya , Tanak, Satoshi , Fujimoto, Testsuya , Yamamoto, Iwao , Bassoul, Pierre , Kucharczyk, Nathalie and Simon, Jacques(1991) 'Discotic liquid crystals of transition metal complexes X. Phthalocyanine derivatives substituted with *n*-alkyloxyphenyl side chains', Liquid Crystals, 10: 3, 357 — 368

To link to this Article: DOI: 10.1080/02678299108026282

URL: http://dx.doi.org/10.1080/02678299108026282

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LIQUID CRYSTALS, 1991, VOL. 10, NO. 3, 357–368

Discotic liquid crystals of transition metal complexes

X. Phthalocyanine derivatives substituted with *n*-alkyloxyphenyl side chains

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(Received 10 December 1990; accepted 13 March 1991)

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Octakis(alkyloxyphenyl)-phthalocyanine derivatives ($(C_nOph)_8PcH_2$ $n=8$, 10, 12 and 18), their corresponding copper (II) complexes ($(C_nOph)_8PcCu$, $n=10$, 12 and 18) and octakis(2-ethylhexyl)-PcH_2 have been synthesized and their mesomorphic properties characterized. $(C_nOph)_8PcH_2$, ($n=12$ and 18) exhibit hexagonal disordered columnar mesophases whereas $(C_nOph)_8PcCu$ ($n=12$ and 18) yields a rectangular disordered columnar liquid crystal. An alkylphenyl-oxymethyl derivative, $(C_{12}phOCH_2)_8PcH_2$, was synthesized to determine the influence of the connecting link between the side chains and the phthalocyanine macrocycle on the mesomorphic properties.

1. Introduction

Columnar mesophases are formed from discotic mesogens. They have been classified into hexagonal disordered (D_{hd}), hexagonal ordered (D_{ho}), rectangular disordered (D_{rd} ($P2_1/a$), $D_{rd}(P2/a)$, $D_{rd}(C2/m)$), and oblique ($D_{ob.d}$) columnar mesophases [1–3]. A nematic lenticular mesophase [3, 8] (D_L) can also be obtained. Columnar mesophases of substituted phthalocyanines (Pc) were observed for the first time in 1982 [4]. Since then, various alkyl side chains have been used to substitute the Pc macrocycle. In most cases, the mesophases are of D_{hd} or D_{ho} type [5]; as exceptions, tetragonal [6], nematic [7–8] or lamellar [9] phthalocyanine mesophases have been described.

In the present paper, *p*-alkyloxyphenyl substituted side chains have been used to substitute the phthalocyanine macrocycle (see figure 1). 4,5-Diphenyl substituted derivatives cannot adopt a planar conformation because of the steric hindrance between the phenyl rings. The effect of the presence of such bulky groups in the side chains of substituted phthalocyanines on the mesomorphic properties of the materials is studied here. An alkylphenyloxymethyl derivative, $(C_{12}phOCH_2)_8PcH_2$ (**10**) in which the phenyl rings can be coplanar with the phthalocyanine macrocycle has been synthesized for comparison.

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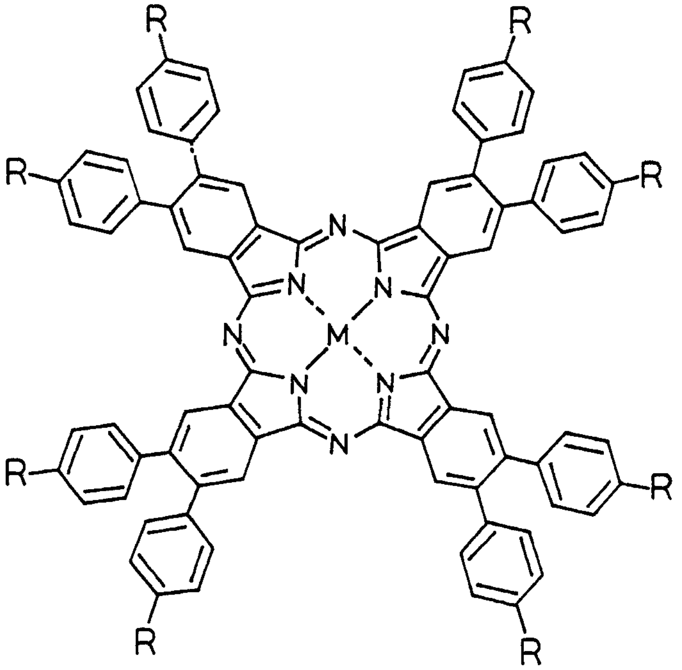

Figure 1. Chemical formula of the compounds synthesized $(Rph)_8PcM$. M = 2H **8**; M = Cu **9**. R = $OC_{18}H_{37}$(*a*); R = $OC_{12}H_{25}$(*b*); R = $OC_{10}H_{21}$(*c*); R = OC_8H_{17}(*d*); R = O-(2-Et)hexyl(*e*). In $(C_{12}phOCH_2)_8PcH_2$ **10** the phenyl ring is connected via a $-OCH_2-$ group to the phthalocyanine ring.

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2. Experimental

2.1. *Synthesis*

The synthetic route to the octa(4-alkyloxyphenyl)Pc*M* (*M* = 2H or Cu) derivatives, $(C_nOph)_8PcH_2$ (**8a–e**) and their copper(II) complexes, $(C_nOph)_8PcCu$ (**9a–c**), is shown in figure 2. The compounds **6a–e** were prepared in five steps by the method described by Wenz [10]. Dicyanoacetylene was prepared in two steps according to previously described procedures [11, 12].

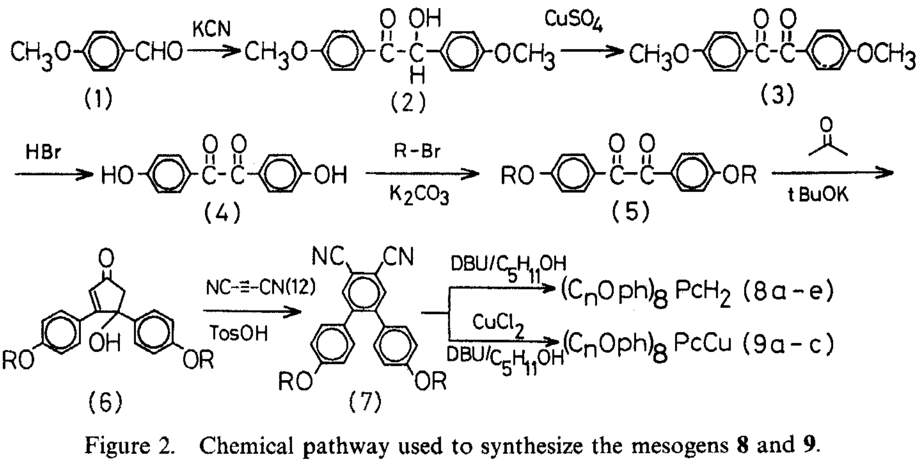
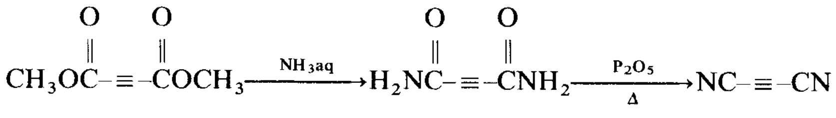


Figure 2. Chemical pathway used to synthesize the mesogens **8** and **9**.



$$CH_3O\overset{\overset{O}{\|}}{C}-\equiv-\overset{\overset{O}{\|}}{C}OCH_3 \xrightarrow{NH_{3aq}} H_2N\overset{\overset{O}{\|}}{C}-\equiv-\overset{\overset{O}{\|}}{C}NH_2 \xrightarrow[\Delta]{P_2O_5} NC-\equiv-CN$$

(10) **(11)** **(12)**

The substituted phthalocyanine derivatives (**8a–e**, **9a–c**) were synthesized by the method described by Tomoda *et al.* [13]. The results of elemental analyses of the previously unreported final products are listed in table 1. ^{1}H NMR spectra (250 MHz, $CDCl_3$) were in agreement with the proposed structures. **8a** (typical example); 8·88 (8 H, s, Pc), 7·40 (16 H, d, ph, $J=8·50$ Hz), 6·18 (16 H, d, ph, $J=8·50$ Hz), 4·05 (16 H, t, OCH_2), 1·90 (16 H, q, CH_2), 1·65 ~ 1·25 (240 H, m, CH_2), 0·88 (24 H, t, CH_3), −2·02 (2H, bs, NH). The UV VIS absorption spectra were slightly shifted ($\lambda_{max}=722$ nm for **8a**; $\lambda_{max}=703$ nm for **9a**) as compared to the alkyl substituted derivatives [14] ($\lambda_{max}=705$ nm)

λ_{max}/nm (log ε)

8a $(C_{18}O_{ph})_8PcH_2$ 301 (4·93) 365 (4·92) 421 (4·59) 574 (3·68) (sh) 594 (3·99) (sh) 625 (4·61) 658 (4·78) 691 (5·25) 722 (5·29). **9a** $(C_{18}Oph)_8PcCu$ 294 (4·96) 347 (4·90) 420 (4·52) 632 (4·75) 671 (4·78) (sh) 703 (5·45).

2.1.1. *3,4-Bis (4-octadecyloxyphenyl)-4-hydroxy-2-cyclopenten-1-one* (**6a**)

A mixture of 8·0 g (11 mmol) of 4,4′-dioctadecyloxybenzyl (**5a**), 0·60 g (5·5 mmol) of potassium *t*-butanolate, and 12·4 g (0·21 mol) of acetone in a mixture of 150 ml of dry ethanol and 30 ml of dry tetrahydrofuran was refluxed under nitrogen for 18 h. For the synthesis of (**6b–e**), no tetrahydrofuran was needed. After cooling to room temperature, the reaction mixture was poured into 400 ml of a two per cent aqueous acetic acid solution and extracted with dichloromethane. The organic layer was washed with water, dried over sodium sulphate and evaporated to dryness. The product was purified by chromatography (SiO_2; eluent: $CHCl_3$/ethyl acetate 5 : 1 v/v) and by recrystallization from ethanol. White powder; yield: 5·8 g (67 per cent); mp = 84–85°C.

^{1}H NMR ($CDCl_3$, TMS) $\delta=7·50–6·33$ (m, 8 H, ph) 6·50 (s, 1 H, olefin) 3·90 (t, 4 H, $O–CH_2$) 2·88 (s, 2H, CH_2CO) 2·57 (s, 1 H, OH) 1·33 (m, 64 H, CH_2) 0·72 (t, 6H, CH_3). IR (KBr, cm^{-1}) $\nu=3250$ (OH) 2900, 2850 (CH_2) 1660 (CO) 1590, 1500 (ph) 1240 (–Oph).

Table 1. Elemental analysis data of the octakis(alkyloxyphenyl)PcH_2 derivatives (**8a–e**) and their copper (II) complexes (**9a–c**). In parenthesis is indicated the theoretical value.

Compound	Molecular formula		Elemental analysis; Calc.% (Found.%) N	C	H
8a $(C_{18}Oph)_8PcH_2$	$C_{224}H_{338}N_8O_8$	(3271·22)	3·43 (3·48)	82·25 (82·31)	10·41 (10·78)
8b $(C_{12}Oph)_8PcH_2$	$C_{176}H_{242}N_8O_8$	(2597·93)	4·31 (4·26)	81·37 (81·20)	9·39 (9·59)
8c $(C_{10}Oph)_8PcH_2$	$C_{160}H_{210}N_8O_8$	(2373·50)	4·72 (4·69)	80·97 (80·88)	8·92 (9·05)
8d $(C_8Oph)_8PcH_2$	$C_{144}H_{178}N_8O_8$	(2149·06)	5·21 (4·44)	80·48 (79·33)	8·35 (8·75)
8e $(2Et\text{-}C_6Oph)_8PcH_2$	$C_{144}H_{178}N_8O_8$	(2149·06)	5·21 (5·13)	80·48 (80·18)	8·35 (8·63)
9a $(C_{18}Oph)_8PcCu$	$C_{224}H_{336}N_8O_8Cu$	(3332·75)	3·36 (3·29)	80·73 (80·70)	10·16 (10·49)
9b $(C_{12}Oph)_8PcCu$	$C_{176}H_{240}N_8O_8Cu$	(2659·46)	4·21 (4·19)	79·49 (79·50)	9·10 (9·24)
9c $(C_{10}Oph)_8PcCu$	$C_{160}H_{208}N_8O_8Cu$	(2435·03)	4·60 (4·64)	78·92 (78·65)	8·61 (8·95)

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(**6b**) Chromatography: SiO_2, chloroform/ethyl acetate, 5 : 1, $R_f = 0{\cdot}54$. Pale yellow crystals; yield: 61 per cent; mp = 65–68°C. (**6c**) Chromatography: SiO_2, chloroform/ethyl acetate, 5 : 1, $R_f = 0{\cdot}60$. Pale yellow crystals; yield: 58 per cent; mp = 54–57°C. (**6d**) Chromatography: SiO_2, chloroform/ethyl acetate, 4 : 1, $R_f = 0{\cdot}51$. Pale yellow crystals; yield: 60 per cent; mp ≈ 48°C, MS (*m*/*e*): 506 (M^+). (**6e**) Chromatography: SiO_2, chloroform/ethyl acetate, 5 : 1, $R_f = 0{\cdot}56$. Yellow crystals; yield: 62 per cent; mp = 96–98°C. ^{1}H NMR ($CDCl_3$, TMS) $\delta = 7{\cdot}67$–$6{\cdot}77$ (m, 8 H, ph) 6·33 (s, 1 H, olefin) 3·87 (d, 4 H, $OCH_2CH(CH_2)_2$) 2·97 (s, 2H, CH_2CO) 2·67 (s, 1 H, -OH) 1·33 (m, 18 H, CH_2) 0·93 (t, 12·H, CH_3). IR (KBr, cm^{-1}) $\nu = 3350$ (–OH) 2950, 2880(CH_2) 1680(CO) 1610 (olefin) 1600, 1500(ph) 1240(O–ph). MS (*m*/*e*): 508($M^+ + 2$).

2.1.2. *4,4′-Dioctadecyloxy-o-terphenyl-4′,5′-dicarbonitrile* (**7a**)

An excess of dicyanoacetylene (**12**) and 4·0 g (5·1 mmol) of the cyclopentenone derivative (**6a**) in 40 ml of chlorobenzene in a special flask [12] was stirred under nitrogen and maintained at 60–70°C. A solution of 9·7 mg (0·051 mmol) of *p*-toluenesulphonic acid in 0·4 ml of 1,4-dioxane was added dropwise. The mixture was stirred for 20 min and then heated under reflux for 10 min to complete the reaction. The solvent was evaporated to dryness and the residue was dried *in vacuo*. After chromatography (SiO_2; $CHCl_3$) the pure product was obtained ($R_f = 0{\cdot}72$). White powder; yield: 3·4 g (81 per cent); mp = 98°C.

^{1}H NMR ($CDCl_3$, TMS) $\delta = 7{\cdot}70$ (s, 2 H, ph) 6·98 (d, 4 H, ph) 6·70 (d, 4 H, ph) 3·90 (t, 4H, OCH_2) 1·22 (m, 64 H, CH_2) 0·87 (t, 6H, CH_3). IR (KBr, cm^{-1}) $\nu = 2900$, 2860 (CH_2) 2210 (CN) 1590, 1500 (pH) 1240 (–O–ph). (**7b**) Chromatography: SiO_2, benzene/carbon tetrachloride, 2 : 1, $R_f = 0{\cdot}42$. White plate-like crystals; yield: 69 per cent; mp = 88°C. (**7c**) Chromatography: SiO_2, benzene, $R_f = 0{\cdot}58$. White plate-like crystals; yield: 74 per cent; mp = 88°C. (**7d**) Chromatography: SiO_2, dichloromethane, $R_f = 0{\cdot}74$. White plate-like crystals; yield: 17 per cent; mp = 85–87°C; MS (*m*/*e*): 537 ($M^+ + 1$). The special flask [12] was not used in this case. (**7e**) Chromatography: SiO_2, chloroform, $R_f = 0{\cdot}80$. Pale yellow oily liquid; yield: 60 per cent. ^{1}H NMR ($CDCl_3$, TMS) $\delta = 7{\cdot}70$ (s, 2H, ph) 6·79 (d, 4 H, ph) 6·70 (d, 4 H, ph) 3·80 (d, 4 H, OCH_2) 1·35 (m, 18 H, CH_2) 0·92 (t, 12 H, CH_3). IR (neat, cm^{-1}) $\nu = 2950$, 2890 (CH_2) 2250 (CN) 1610, 1520 (ph) 1260 (O–ph). MS (*m*/*e*): 537 ($M^+ + 1$).

2.1.3. *2.3.9.10.16.17.23.24-Octakis (4-octadecyloxyphenyl)-29H, 31H-phthalocyanine* (**8a**)

A mixture of 1·50 g (1·8 mmol) of the dicarbonitrile **7a** and 0·42 g (2·7 mmol) of 1,8-diazabicylo[5, 4, 0]undec-7-ene (DBU) was refluxed for 18 h. After cooling to room temperature, the precipitate was collected by filtration, washed with ethanol and ethyl acetate, and then dried. The crude product was purified by chromatography (SiO_2, benzene $R_f = 1{\cdot}0$) and by recrystallization from a mixture of dichloromethane and a small amount of ethyl acetate. Green crystals; yield: 42 per cent.

(**8b**) Chromatography: SiO_2, dichloromethane, $R_f = 1{\cdot}0$. Solvent of recrystallization: dichloromethane with a small amount of ethyl acetate. Yield: 16 per cent. (**8c**) Chromatography: SiO_2, dichloromethane, $R_f = 1{\cdot}0$. Solvent of recrystallization: dichloromethane with a small amount of ethyl acetate. Yield: 21 per cent. (**8d**) Chromatography: SiO_2, carbon tetrachloride/benzene, 1 : 1, $R_f = 0{\cdot}80$. Solvent of recrystallization: 1,4-dioxane. Yield: 20 per cent. (**8e**) Chromatography: SiO_2, benzene/*n*-hexane, 3 : 2, $R_f = 0{\cdot}80$. Solvent of recrystallization: ethyl acetate. Yield: 15 per cent.

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2.1.4. *2,3,9,10,16,17,23,24-Octakis (4-octadecyloxyphenyl)-phthalocyanine copper (II) sample* (**9a**)

A mixture of 1·50 g (1·8 mmol) of the dinitrile **7a**, 0·41 g (2·8 mmol) of DBU and 0·072 g (0·51 mmol) of copper (II) chloride in 30 ml of *n*-pentanol was refluxed for 18 h. After cooling to room temperature, the precipitate was filtered, washed with ethanol and ethyl acetate, and dried. The crude product was purified by chromatography (SiO_2, benzene, $R_f = 1{\cdot}0$), and by recrystallization from a mixture of dichloromethane and ethyl acetate. Yield: 1·12 g (73 per cent).

(**9b**) Chromatography: SiO_2, chloroform, $R_f = 1{\cdot}0$. Solvent of recrystallization: dichloromethane with a small amount of ethyl acetate. Yield: 76 per cent. (**9c**) Chromatography: SiO_2, chloroform, $R_f = 1{\cdot}0$. Solvent of recrystallization: a mixture of dichloromethane and a small amount of ethyl acetate. Yield: 70 per cent.

2.1.5. *Acetylene diamide* (**11**) [11]

Dimethyl acetylenedicarboxylate (28 g, 0·20 mmol) was added dropwise to 130 ml of ammonium hydroxide stirred at room temperature for 2 h and then for 30 min at −5°C. The precipitate was collected by filtration, washed with water and ethanol, and dried. Light tan crystals; yield: 19 g (68 per cent); decomposition temperature = *c.* 200°C (lit. mp = 190–192°C); MS (*m*/*e*): 112 (M^+).

2.1.6. *Dicyanoacetylene* (**12**) [11]

Acetylenediamide (**11**: 6·0 g) and 100 g of sea sand were mixed together. The mixture and 50 g of P_2O_5 were put into a 300 ml flask and shaken until homogeneous. The mixture was divided into six test tubes and a small amount of glass wool was put on the top of the tubes. The system was evacuated under vacuum and refilled with dry nitrogen several times. The system was then evacuated (1 mmHg). After the special flask had been cooled to −78°C (dry ice/acetone bath), the test tubes were placed in a preheated silicone oil bath at 215°C whereupon distillation of C_4N_2 took place; the needle-like crystals were grown in the special flask. After *c.* 30 min, the oil bath was removed and the system was filled with dry nitrogen. Yield: 1·1 g (20 per cent).

2.1.7. *p-dodecylphenol*

The procedures given in [15–18] have been used to prepare p-dodecylphenol.

10 g (38·3 mmol) of 4-dodecylaniline (Janssen) were heated to 60°C in 50 ml of water. A solution of 10·8 ml of concentrated H_2SO_4 in 10 ml of water was added dropwise yielding a white precipitate. The mixture was cooled in ice ($T < 10$°C); a solution of 2·65 g of $NaNO_2$ (38·3 mmol) in water was then quickly added. The formation of yellowish vapours was noticed. The mixture was stirred for 10 min and then added to a solution of 21·6 ml of concentrated H_2SO_4 in 250 ml of water at 100°C. The mixture was heated under reflux. When the release of nitrogen gas was complete, an oily reddish liquid was obtained. The heating was continued for 30 min. At room temperature, the product was extracted with heptane. Recrystallization from heptane. Yield: 40 per cent; mp 66°C.

^{1}H NMR ($CDCl_3$, TMS) $\delta = 6{\cdot}77$ (m, 4 H, ph) 4·17 (s, 1 H, OH) 2·50 (t, 2 H, CH_2ph) 1·30 (bs, 20 H, CH_2) 0·95 (d, 3H, CH_2).

It is possible to add methylethylcetone at the beginning of the reaction to permit the dissolution of the amino derivative in the reaction medium.

2.1.8. *1,2-dibromo-4,5-bis(dodecylphenyloxymethyl-)benzene*

3 g (11·4 mmol) of *p*-dodecylphenol, 1·80 g (13·0 mmol) of anhydrous K_2CO_3, 2·42 g (5·72 mmol) of 1,2-dibromo-4,5-bis(bromethyl)benzene [19, 20] and 40 ml of acetone were heated under reflux for 24 h. At room temperature, the insoluble compounds were filtered off. The crude product was recrystallized from acetone. Yield: 60 per cent; mp 53°C.

^1H NMR ($CDCl_3$, TMS) $\delta = 7{\cdot}65$ (s, 2 H, ph) 6·85 (q, 8 H, ph) 4·9 (s, 4 H, CH_2O) 2·5 (t, 4 H, CH_2ph) 1·25 (s, 40 H, CH_2) 0·9 (d, 6 H, CH_3).

2.1.9. *1,2-dicyano-4,5-bis(dodecylphenyloxymethyl-)benzene*

1 g (1·27 mmol) of the corresponding dibromo derivative, 345 mg (3 eq.) of CuCN and 5 g of anhydrous DMF were heated under reflux, under nitrogen, for 6 h. The reaction medium was filtered hot and the filtrate was evaporated to dryness. The product was purified by chromatography (SiO_2, eluent: heptane/ethyl acetate 90/10). The product was recrystallized from acetone. Yield: 46 per cent; mp 90°C.

^1H NMR ($CDCl_3$, TMS) $\delta = 8{\cdot}0$ (s, 2 H, ph) 6·95 (q, 8 H, ph) 5·15 (s, 4 H, OCH_2) 2·5 (t, 4 H, $phCH_2$) 1·3 (s, 40 H, CH_2) 0·9 (d, 6 H, CH_3).

2.1.10. *Phthalocyanine* **10**

The dicyano derivative was converted into the corresponding diimino derivative following a previously described procedure [14].

620 mg of diiminoisoindole in 2 ml of dimethylaminoethanol were heated under reflux for 10 h. The solvent was evaporated to dryness and the precipitate was washed with 20 ml of hot ethanol. The product was purified by chromatography (SiO_2, eluent: pentane/$CHCl_3$ (60/40). Recrystallization from ethyl acetate/heptane 95/5. Yield: 20 per cent.

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2.2. *Measurements*

The final products were identified by elemental analysis using a Perkin–Elmer Elemental Analyser 240B. UV VIS spectra were recorded using an Hitachi 330 spectrophotometer. NMR spectra (250 MHz) were recorded on a Bruker AC-250. The phase transitions were observed with a heating plate controlled by a thermoregulator (Mettler FP80 and 82) and measured with a differential scanning calorimeter, Rigaku Thermoflex TG-DSC. Powder X-ray diffractions were measured with Cu–K_α radiation with a Rigaku Geigerflex diffractometer equipped with a controlled heating plate [21].

3. Results and discussion

3.1. *Mesomorphism of* $(C_nOph)_8PcH_2$ (**8a–e**) *and* $(C_nOph)_8PcCu$ (**9a–c**)

The transition temperatures and enthalpy changes of these compounds are summarized in table 2. The metal free derivatives with an alkyl chain length of $n = 18$–10 (**8a–c**) exhibit mesomorphism as well as the copper (II) complexes with an alkyl chain length of $n = 18$–12 (**9a–b**).

The identification of the mesophases was achieved by X-ray diffraction at small angles. In table 3 are summarized the types of mesophase, the lattice constants, the spacings, and the corresponding Miller indices. Representative X-ray diffraction patterns of the D_{hd} and D_{rd} mesophases are shown in figures 3 and 4, respectively.

The genuine crystals (C_1) of $(C_{18}Oph)_8PcH_2$ (**8a**) transform into a hexagonal disordered columnar mesophase (D_{hd}) at 78°C. The same behaviour is observed for $(C_{12}Oph)_8PcH_2$ (**8b**) and $(C_{10}Oph)_8PcH_2$ (**8c**). However, $(C_8Oph)_8PcH_2$ (**8d**) exhibits

Table 2. Transition temperatures (T_t) and enthalpy changes (ΔH_t) of the octakis(alkyloxyphenyl)PcH$_2$ derivatives (**8a–e**) and their copper (II) complexes (**9a–c**).

Compound	Phase $\xrightarrow[\Delta H_t/\text{kJ mol}^{-1}]{T_t/^\circ\text{C}}$ Phase†
8a	$C_1 \xrightarrow[86\cdot6]{78} D_{hd} \xrightarrow{253} \text{1st decomp.}\ddagger \xrightarrow{349} \text{2nd decomp.}\ddagger$
8b	$C_1 \xrightarrow[29\cdot3]{120} C_2 \xrightarrow[3\cdot52]{192} D_{hd} \xrightarrow{261} \text{1st decomp.}\ddagger \xrightarrow{382} \text{2nd decomp.}\ddagger$
8c	$C_1 \xrightarrow[20\cdot9]{165} C_2 \xrightarrow[5\cdot86]{229} M\S \xrightarrow{267} \text{1st decomp.}\ddagger \xrightarrow{401} \text{2nd decomp.}\ddagger$
8d	$C_1 \xrightarrow[28\cdot7]{243} C_2 \xrightarrow{285} \text{1st decomp.}\ddagger \xrightarrow{391} \text{2nd decomp.}\ddagger$
8e	$C_1 \xrightarrow{168} C_2 \xrightarrow{275} \text{1st decomp.}\ddagger \xrightarrow{372} \text{2nd decomp.}\ddagger$
9a	$C \xrightarrow[91\cdot2]{82} D_{rd}(C2/m) \xrightarrow{220} \text{1st decomp.} \xrightarrow{393} \text{2nd decomp.}\ddagger$
9b	$C_1 \xrightarrow[\P]{67} C_2 \xrightarrow[27\cdot6]{120} D_{rd}(C2/m) \xrightarrow{227} \text{1st decomp.}\ddagger \xrightarrow{388} \text{2nd decomp.}\ddagger$
9c	$C_1 \xrightarrow[\P]{77} C_2 \xrightarrow[17\cdot6]{165} C_3 \xrightarrow{222} \text{1st decomp.}\ddagger \xrightarrow{381} \text{2nd decomp.}\ddagger$

† Phase nomenclature: C = crystal, D_{hd} = hexagonal disordered columnar mesophase, D_{rd} = rectangular disordered columnar mesophase.

‡ See text.

§ The phase M could not be assigned.

¶ This enthalpy change was too small to be determined.

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no mesomorphism. The relationship between the transition temperature and the alkyl chain length can be derived as follows. $(C_nOph)_8PcH_2$ leads to a mesophase for chain lengths with $n \geqslant 10$, and the crystal–mesophase transition temperatures decrease with increasing chain length. $(2Et\text{-}C_6Oph)_8PcH_2$ (**8e**) shows no mesomorphism whereas the corresponding alkyloxy derivative has been said to form a nematic mesophase [8].

The copper complexes lead to rectangular disordered columnar mesophases (D_{rd}) instead of hexagonal ones for the metal free derivatives (see table 3). However, the structural rearrangements needed to transform the mesophases in one another are very small. For $(C_{12}Oph)_8PcCu$ (**9b**), for example, the rectangular parameters are $a = 61\cdot0$ Å and $b = 28\cdot6$ Å. A rectangular symmetry may be obtained while preserving a hexagonal packing of the molecular units within the molecular plane by shifting the layers relative to each other (see figure 5). From the lattice parameters, an angle of 35·7° can be calculated between the c axis of the columns and the normal to the macrocyclic planes. This leads to a shift of the molecular units by about 2·5 Å. This shift is very probably due to the strong tendency of the copper ions to have axially coordinated ligands. In the X-ray structure of single crystals of unsubstituted PcCu [22], the copper ion is axially coordinated with the *meso*-nitrogen atoms of the neighbouring phthalocyanine molecules (see figure 6). In the single crystals, a shift of approximately 3·3 Å occurs, this must be compared with the value of 2·5 Å found in the mesophases.

Table 3. X-ray diffraction data of the octakis(alkyloxyphenyl)PcH_2 derivatives (**8a, b**) and their copper (II) complexes (**9a, b**). The halos observed at 4·8 Å correspond to the molten aliphatic side chains.

Compound	Lattice constants/Å		Observed spacings/Å	Miller indices (*hkl*)
8a	D_{hd}	$a=43·1$	37·3	(100)
$(C_{18}Oph)_8PcH_2$	at 150°C		21·8	(110)
			19·0	(200)
			c. 4·8	—
8b	D_{hd}	$a=38·3$	33·2	(100)
$(C_{12}Oph)_8PcH_2$	at 120°C		19·3	(110)
			16·9	(200)
			c. 4·8	—
9a	D_{rd}(C2/m)	$a=71·1$	35·6	(200)
$(C_{18}Oph)_8PcCu$	at 100°C	$b=35·8$	31·9	(110)
			19·2	(310)
			16·3	(220)
			c. 4·8	—
9b	D_{rd}(C2/m)	$a=61·0$	30·5	(200)
$(C_{12}Oph)_8PcCu$	at 150°C	$b=28·6$	25·9	(110)
			16·2	(310)
			12·7	(220)
			c. 4·8	—
10	D_{ho}	$a=39·9$	34·6	(100)
$(C_{12}phOCH_2)_8PcH_2$	at 250°C		20·0	(110)
			17·3	(200)
			13·0	(210)
			c. 4·9	—
			3·4	—

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As far as we know, the complexes (**9a, b**) are the first examples of D_{rd} mesogens in the phthalocyanine metal complex series. The comparison of the lattice parameters with the molecular dimensions leads us to postulate either an important intracolumnar synclinal interlacing or a large intercolumnar interlacing of the paraffinic chains [23] (see figure 5).

The compound **10** $(C_{12}phOCH_2)_8PcH_2$ shows no phase transition from room temperature to 300°C by DSC. X-ray diffraction at 100°C and at 250°C shows, in both cases, an ordered hexagonal columnar structure. The phenyl rings pobably adopt a coplanar arrangement with the phthalocyanine macrocycle leading to the formation of an extremely large central aromatic core. This is probably the reason for the enhanced stability of the mesophase.

The peculiar decomposition behaviour of the mesogens was noted in table 2. The decomposition of $(C_{18}Oph)_8PcH_2$ (**8a**) may be described as follows. $(C_{18}Oph)_8PcH_2$ (**8a**) gives an exothermic peak at 253°C corresponding to the first decomposition. On further heating, the thermogram shows a gradual slight weight loss up to 349°C where a second decomposition occurs accompanied by a large weight loss. The visible absorption spectra were measured after the first decomposition (solvent cast thin films)

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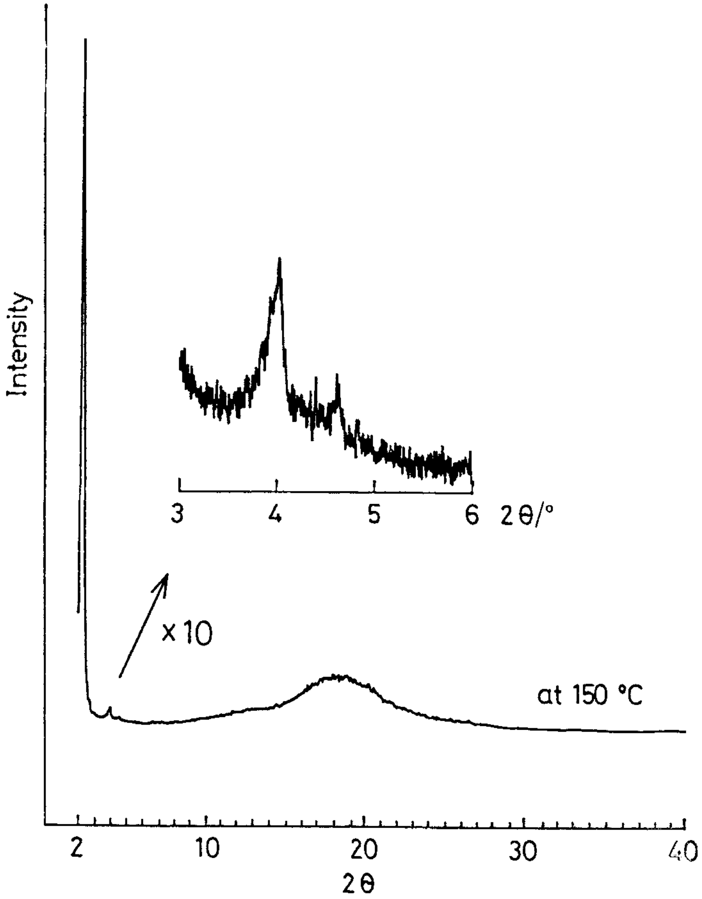

Figure 3. X-ray diffraction pattern of $(C_{18}Oph)_8PcH_2$ (**8a**) at 150°C (D_{hd} mesophase).

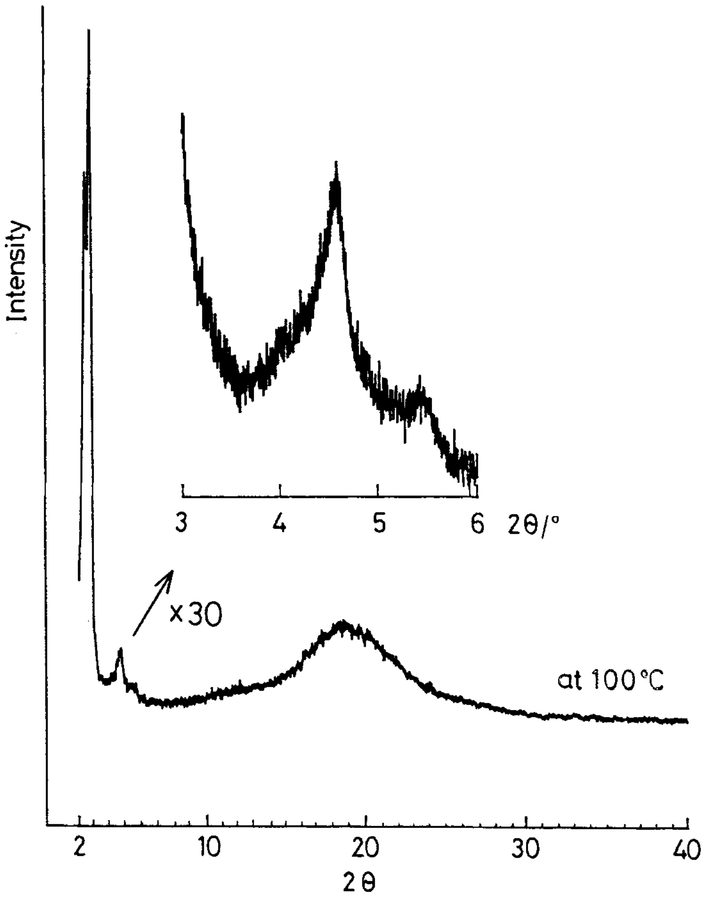

Figure 4. X-ray diffraction pattern of $(C_{18}Oph)_8PcCu$ (**9a**) at 100°C (D_{rd} mesophase).

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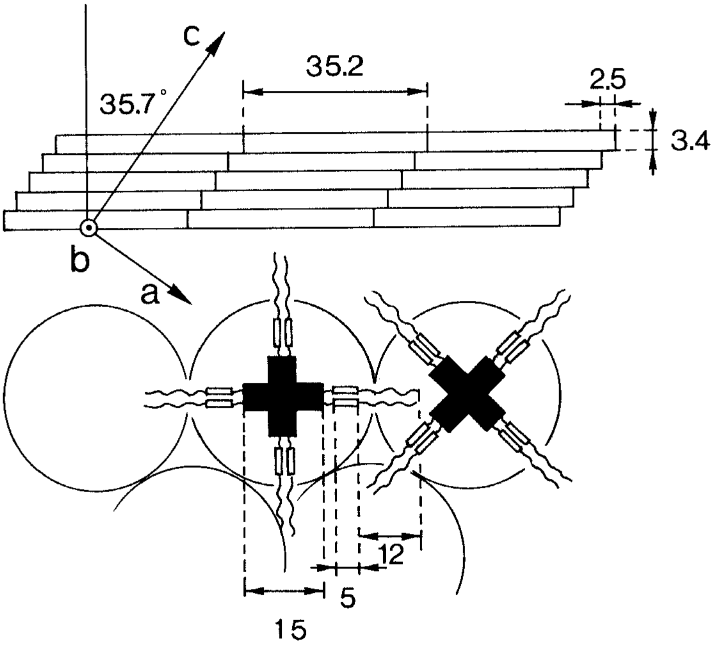

Figure 5. Schematic representation of the mesophase (D_{rd}, C2/m) of $(C_{12}Oph)_8PcCu$ ($a=61{\cdot}0$ Å; $b=28{\cdot}6$ Å). The dimensions of the molecular unit are derived from CPK models and from the length of molten aliphatic chains [2].

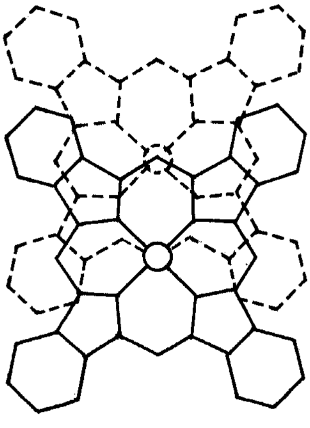

Figure 6. Superposition of the phthalocyanine macrocycles permitting axial coordination of the copper ion in PcCu single crystals.

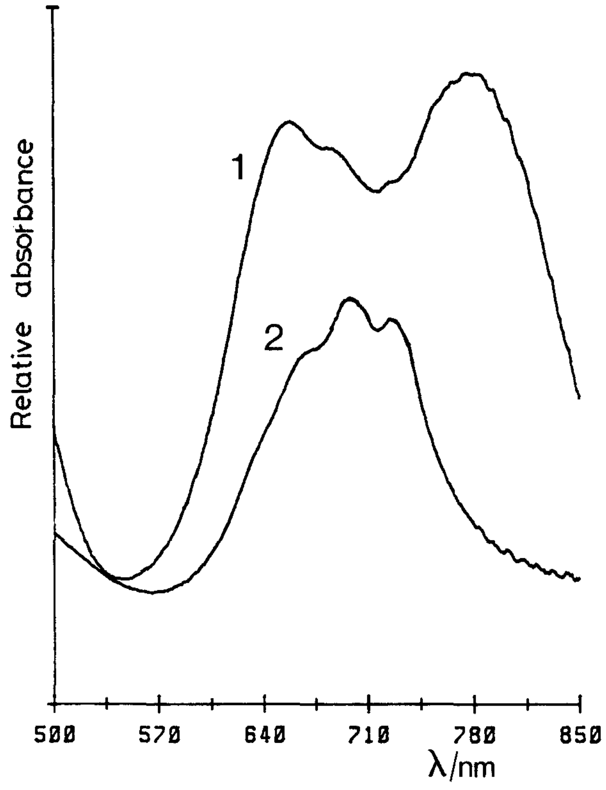

Figure 7. Effect of heat treatment on the visible absorption spectrum of $(C_{18}Oph)_8PcH_2$ (chloroform cast thin films). 1, untreated $(C_{18}Oph)_8PcH_2$. 2, after heat treatment at 280°C for 10 min and then washed with $CHCl_3$ in which the starting material is soluble.

(see figure 7). The compounds when heated around 280°C become insoluble in most organic solvents. The absorption spectra could indicate that the transformation involves the formation of triphenylene rings from the terphenyl-like substituted side groups. Further evidence is needed to substantiate this point.

4. Conclusion

A new type of side chains has been used in the series of the phthalocyanine mesogens. The use of *n*-alkyloxyphenyl side chains leads to the formation of rectangular disordered columnar mesophases for the copper complexes. Both axial coordination of the copper ion and the presence of bulky non-planar phenyl groups seem necessary to favour the appearance of these mesophases. Further studies are in progress to determine the factors allowing the formation of lenticular nematic mesophases from the disordered rectangular columnar mesophases obtained in the present study.

This international collaboration was supported by a grant-in-aid for scientific research (No. 02044060) from the Japanese Ministry of Education, Science and Culture.

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