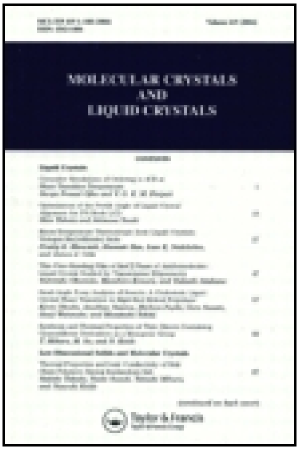

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Synthesis and Morphology of New Discogenic Phthalocyanine Derivatives

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New discogens based on the octasubstituted phthalocyanines (Pc) were synthesized: 2,3,9,10,16,17,23,24-octakis[dodecylthio-1-methyl]-phthalocyanine (1a), 2,3,9,10,16,17,23,24-octakis[4-(dodecylthio)-2-oxa-butyl]-phthalocyanine (1b), 2,3,9,10,16,17,23,24-octakis[dodecyloxy]-phthalocyanine (1c), phthalocyanine 2,3,9,10,16,17,23,24-octa-*n*-dodecanoate (1d), *S*-(+)-2,3,9,10,16,17,23,24-octakis[4-(dodecyloxy)-2-oxa-pentyl]-phthalocyanine (1e), as well as their corresponding copper complexes (CuPc) 2a, 2b, 2c and 2e. They were characterized by microanalysis, IR, ^1H and ^{13}C NMR spectroscopies, and their mesomorphic behaviors were examined with DSC and optical microscopic methods. The products exhibited the following optical textures and transition temperature ranges: focal conic (1a, 95–267°; 2a, 108–304°), linear default (1b, 52–247°; 2b, 70–255°; 1c, 75–269°; 2c, 78–310°), fan-shaped (1d, 58–303°; 2e, 29–191°). Chiral discogenic PcH_2 1e, however, showed a cholesteric-like texture (23–151°C) in which the transition of a platelet (blue phase) to a fan-shaped texture was observed.

I. Introduction

A new class of liquid crystals formed by disk-like molecules exhibiting discotic mesophases was first reported in 1977.[1] Since then various central cores have been introduced[2–5] and their discogenic derivatives were investigated, focusing on their polymorphic sequences, miscibilities and structures. However, continuous efforts are still being made to explore further different discogenic systems in the search for discotic mesophase systems which are stable at ambient temperatures.

Optically active discogens have also been investigated and attempts were made to obtain disk-like cholesterogens by mixing chiral compounds with known nematic discotic (N_D) materials.[6] The only known example of pure discotic cholesterogen is an optically active triphenylene derivative, and it has been indicated that the occurrence of the cholesteric phase depends rather critically on the structure of the chiral chains.[7]

Recently, C. Piechocki et al. have reported the synthesis of discotic liquid crystals based on the phthalocyanine subunit (Pc).[5,8-9] They synthesized three metal-free PcH_2's and a CuPc. Only on one PcH_2, however, were the optical textures and the phase transition temperatures described.

In the present paper we would like to report the synthesis of various new octasubstituted Pc derivatives which exhibit thermotropic mesomorphic behavior, particularly the discophase at room temperature, and we also report on a pure disk-like cholesterogen which is the first example with phthalocyanine derivatives.

II. Results and Discussion

1. Synthesis

The new derivatives of synthesized PcH_2 and CuPc are shown in Figure 1.

Common synthetic methods of octasubstituted Pc derivatives have been described[10-11] and the modified synthetic pathways employed in the present research are represented in Figures 2, 3 and 4.

The syntheses of PcH_2's (1a and 1b) and CuPc's (2a and 2b), as shown in Fig. 2, were similarly carried out according to the literature procedure.[8]

Nuclear bromination of pyrocatechol to 1,2-dibromo-4,5-catechol (3a)[12] and the introduction of paraffinic tails by the reaction of 3a with the corresponding alkyl bromide gave the aryl-alkyl ether derivative 5c. The protection of vicinal diol-group in 3a with acetone gave dibromo-acetonide 5d. Thus, the possible formation of a copper complex during the substitution reaction of by cuprous cyanide was avoided.

The chiral alkyl chains were introduced by the scheme as shown in Figure 4. Primary alcohol of *S*-(+)-propane-1,2-diol selectively reacted with *t*-butyldimethylchlorosilane(TBDCS) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) catalyst to obtain mono-protected alcohol 8.[13] Long aliphatic tails were introduced by mixing 8 with the corresponding alkyl bromide after the formation of sodium

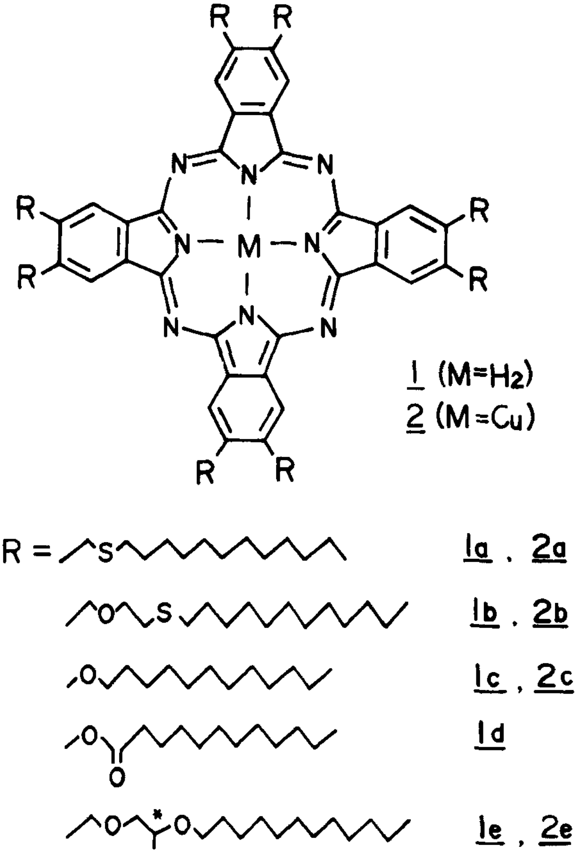

FIGURE 1 Chemical structures of the different octasubstituted synthesized discogenic phthalocyanine.

or potassium alkoxide of 8, obtaining ether type derivative 9. The silyl protecting group of 9 was removed by stirring with tetra-*n*-butylammonium fluoride at room temperature, producing chiral alcohol 10. The dibromo-derivative 5e with chiral long chains was obtained by mixing chiral alkoxide with the tetrabromo-derivative 4. This reaction required the use of protic anhydrous solvents in order to avoid elimination reactions. The dicyano-derivatives 6a–e were obtained by treating the corresponding dibromo-derivatives with a small excess of cuprous cyanide (below 2.0 equivalent) in diluted DMF. It is to be noted that working at high concentrations with a large excess of cuprous cyanide led directly to the formation of CuPc.[10]

Many synthetic pathways for the conversion of dicyano-derivative

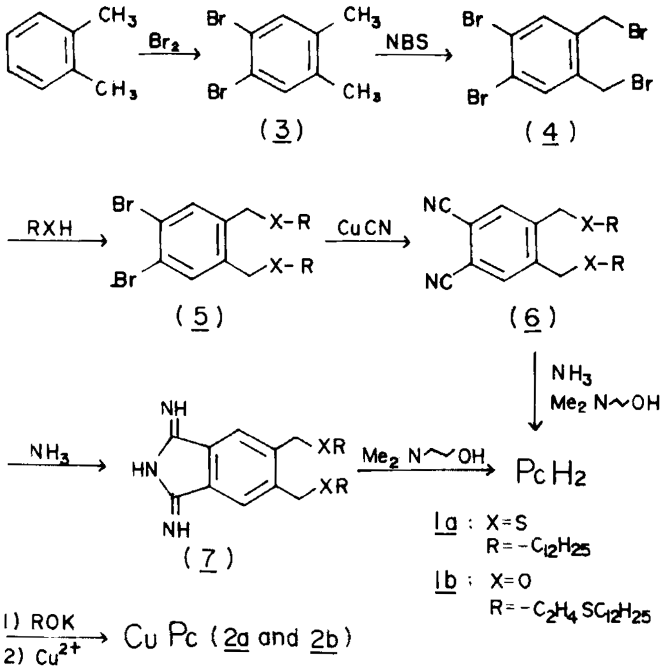

FIGURE 2 General pathway to synthesize PcH_2's (1a and 1b) and CuPc's (2a and 2b).

6 to PcH_2 have been established.[14–17] In the present work PcH_2's were obtained with similar percent yields either directly from dicyano-derivatives 6a, e or via diimino-derivatives 7b–d. The diimino-derivatives 7b–d were obtained in a quantitative yield of 6b–d by passing gaseous ammonia through their methanolic solutions in the presence of sodium methoxide. The PcH_2's were obtained either in 40–50% yields by refluxing 7b–d in dimethylaminoethanol, or in 35–45% yields from 6a,e. The CuPc's were readily obtained by treating first the corresponding PcH_2's with sodium or potassium alkoxide to obtain the dianion, followed by the reaction at 100°C with anhydrous cupric acetate. The Pc derivatives were purified by column chromatography over silica gel (eluent; $CHCl_3$), and characterized by microanalysis and spectroscopic data. All the new intermediates and Pc derivatives are summarized in Table I.

2. Differential scanning calorimetry (DSC)

Detection of phase transitions and measurement of transition temperatures were made using a Du Pont 990 TA 910 cellbase differential

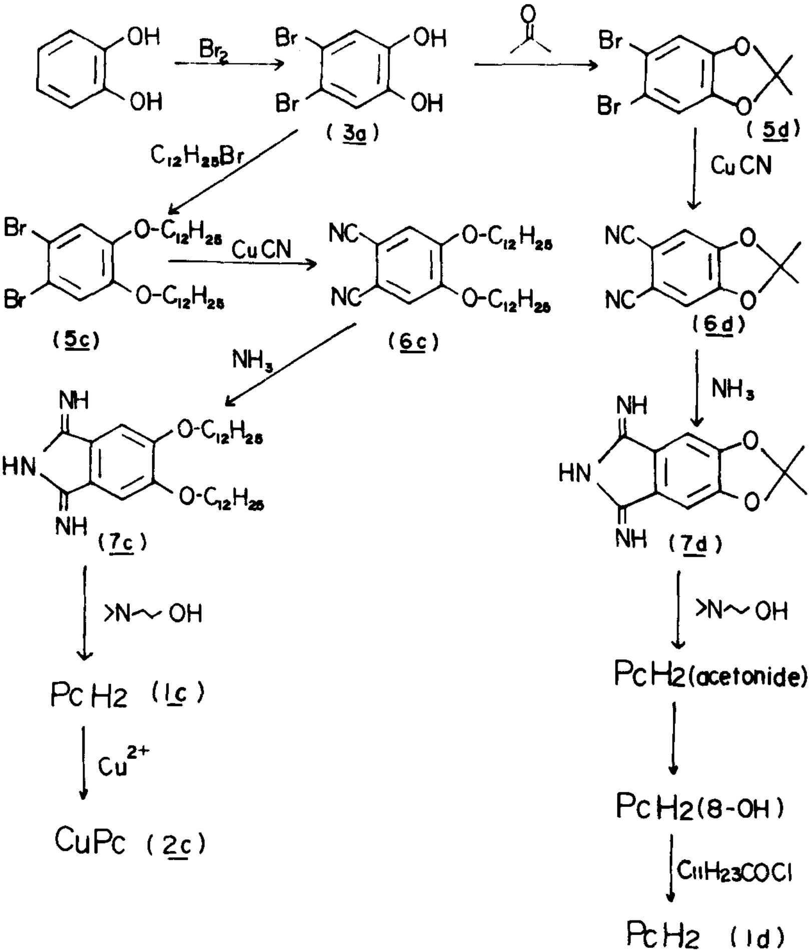

FIGURE 3 Synthetic pathway to prepare PcH_2's (1c and 1d) and CuPc (2c).

scanning calorimeter, with a heating rate 10°C/min. The phase transition temperatures of Pc derivatives synthesized in the present work are given in Table II.

All the thermograms of Pc derivatives recorded with increasing temperature showed clearly two endothermic peaks. The first ones appearing mostly below 100°C showed a very large enthalpy compared with the second ones. As suggested by C. Piechocki et al.,[9] we assume that the first peaks are related to the transitions from crystal phases to discotic mesophases, and the second ones to the transitions from discotic mesophases to isotropic liquid phases.

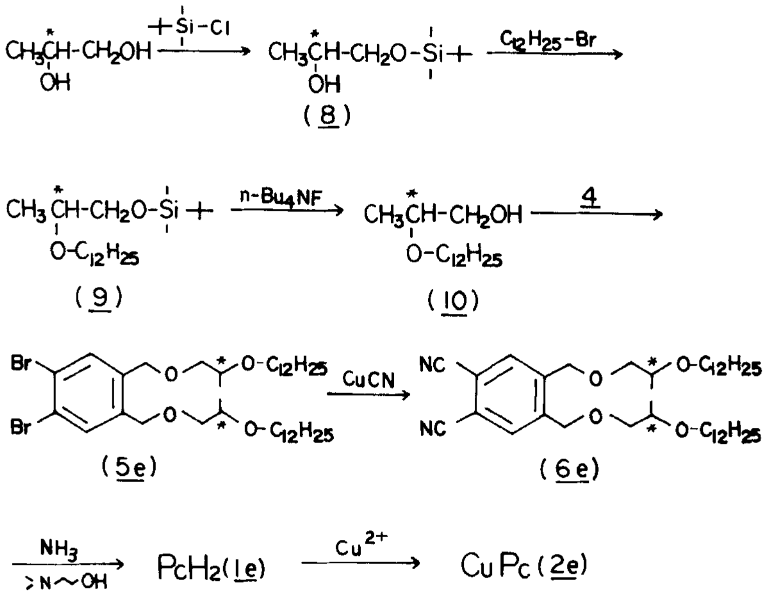

FIGURE 4 Synthetic pathway to prepare PcH_2 (1c) and CuPc (2c).

It is interesting to note that the chemically less stable ester PcH_2 (1d) exhibited better thermal stability and a wider discogenic range compared with various ether-type PcH_2's (1a–c, e). The introduction of branching on the aliphatic chains lowered the melting temperatures of PcH_2's (1b and 1e), and we were finally able to obtain the Pc derivatives 1e and 2e which exhibited the discotic mesophase in the room temperature range.

3. Optical microscopy

Observations of microscopic textures and transition temperatures were carried out using a Leitz polarizing microscope equipped with a Mettler FP 52 hot stage.

The only discotic Pc texture reported so far in literature is a "flower like" texture[9] which is identical to those described primarily by S. Chandrasekhar et al.[1] for the discotic mesophase. The compounds PcH_2 (1a) and CuPc (2a), upon cooling the isotropic liquid below the second transition temperatures, exhibited anisotropic phases reappearing at 265°C with 1a and at 300°C with 2a. In the anisotropic phases, both exhibited typical "focal conic" texture without any change in texture down to the temperatures corresponding to the first tran-

TABLE I

Selected Data of Compounds 1, 2, 5, 6 and 7[a]

Compds	Yield (%)	Mp (°C)	Molecular formula	IR (cm^{-1})	^1H-NMR (p.p.m.)	^{13}C-NMR (p.p.m.)	Elemental analysis; Calcd. % (Found %)					
							C	H	Br	N	S	Cu
1a	43	—	$C_{136}H_{226}N_8$ S_8 (2229.8)	1020	1.15 (*m*, 184 H), 3.05 (*bs*, 16 H) 4.65 (*bs*, 16 H), 8.75 (*bs*, 8 H)[b]	13.8, 21.5, 24.6 28.3, 29.1, 30.9 35.5, 58.4, 120.8 134.1, 138.5, 147.4[b]	73.26 (73.4)	10.22 (10.4)		5.03 (4.91)	11.5 (11.39)	
1b	45	—	$C_{152}H_{258}N_8$ O_8S_8 (2582.2)	1095	1.22 (*m*, 184 H), 2.83 (*m*, 32 H) 4.1 (*bs*, 16 H), 5.17 (*bs*, 16 H) 8.97 (*bs*, 8 H)[b]	14.6, 21.2, 23.1 28.4, 30.6, 34.5 48.5, 64.2, 75.7 122.1, 136.2, 137.9 149.1[b]	70.7 (70.62)	10.07 (10.14)		4.34 (4.41)	9.93 (9.78)	
1c	42	—	$C_{128}H_{210}N_8$ O_8(1989.1)	1280 1220 1090	1.39 (*m*, 184 H), 4.5 (*bs*, 16 H) 8.2 (*bs*, 8 H)[b]	13.2, 21.9, 25.9 28.7, 29.2, 31.2 68.7, 104.2, 128.8 147, 150.7[b]	77.29 (77.26)	10.64 (10.69)		5.63 (5.58)		
1d	35	—	$C_{128}H_{194}N_8$ O_{16}(2101.0)	1775 1135 1090 1010	1.4 (*m*, 168 H), 2.86 (*bt*, 16 H) 8.5 (*s*, 8 H)[b]	13.6, 21.7, 22.9 28.7, 29.6, 30.1 34.8, 115.2, 127.6 142.5, 150.1, 181.5[b]	73.18 (73.25)	9.31 (9.26)		5.33 (5.29)		
2a	82	—	$C_{136}H_{224}Cu$ N_8S_8 (2291.3)	1010	[d]	—	71.29 (71.25)	9.85 (9.90)		4.89 (4.19)	11.19 (11.19)	2.77 (2.77)

TABLE I (*Con't.*)

Selected Data of Compounds 1, 2, 5, 6 and 7[a]

Compds	Yield (%)	Mp (°C)	Molecular formula	IR (cm^{-1})	^{1}H-NMR (p.p.m.)	^{13}C-NMR (p.p.m.)	Elemental analysis; Calcd. % (Found %)					
							C	H	Br	N	S	Cu
2b	85	—	$C_{152}H_{256}Cu$ $N_8O_8S_8$ (2643.8)	1080	[d]	—	69.05 (69.37)	9.76 (9.91)		4.24 (4.08)	9.7 (9.52)	2.4 (2.28)
2c	92	—	$C_{128}H_{208}Cu$ N_8O_8 (2050.6)	1270 1200 1080	[d]	—	74.97 (75.08)	10.22 (10.29)		5.46 (5.38)		3.1 (3.02)
5a	84	50	$C_{32}H_{56}Br_2$ S_2 (664.7)	1020 650	1.3 (*m*, 46 H), 2.45 (*t*, 4 H) 3.75 (*s*, 4 H), 7.5 (*s*, 2 H)[c]	—	57.82 (56.94)	8.49 (8.05)	24.04 (24.71)		9.65 (10.26)	
5b	64	46	$C_{36}H_{64}Br_2$ O_2S_2 (752.8)	1100 650	1.35 (*m*, 46 H), 2.72 (*m*, 8 H) 3.73 (*t*, 4 H), 4.6 (*s*, 4 H) 7.7 (*s*, 2 H)[b]	—	57.44 (57.75)	8.57 (8.68)	21.23 (20.84)		8.52 (8.41)	
5c	60	54	$C_{30}H_{52}Br_2$ O_2 (604.5)	1030 650	1.25 (*m*, 46 H), 3.92 (*t*, 4 H) 7.03 (*s*, 2 H)[b]	—	59.61 (60.13)	8.67 (8.82)	26.44 (25.83)			
5d	61	86	$C_9H_8Br_2O_2$ (308.0)	1235 1202 650	1.65 (*s*, 6 H), 6.92 (*s*, 2 H)[b]	—	35.1 (34.86)	2.62 (2.74)	51.89 (52.09)			

6a	65	61	$C_{34}H_{56}N_2S_2$ (556.9)	2240 1030	1.25 (*m*, 46 H), 2.4 (*bt*, 4 H) 3.85 (*bs*, 4 H), 7.75 (*s*, 2 H)[b]	—	73.33 (72.76)	10.14 (10.52)	5.03 (5.26)	11.51 (11.25)
6b	66	51	$C_{38}H_{64}N_2O_2$ S_2 (645.1)	2240 1110	1.32 (*m*, 46 H), 2.68 (*bs*, 8 H) 3.77 (*bt*, 4 H), 4.65 (*s*, 4 H) 7.92 (*s*, 2 H)[b]	—	70.75 (71.36)	10.0 (10.61)	4.34 (4.18)	9.94 (9.82)
6c	62	104	$C_{32}H_{52}N_2O_2$ (496.8)	2235 1300 1230 1090	1.26 (*m*, 46 H), 4.04 (*t*, 4 H) 7.1 (*s*, 2 H)[b]	—	77.37 (77.28)	10.55 (10.48)	5.64 (5.61)	
6d	45	193	$C_{11}H_8N_2O_2$ (200.2)	2225 1280 1215	1.8 (*s*, 6 H), 7.1 (*s*, 2 H)[b]	—	65.99 (65.91)	4.03 (4.12)	13.99 (13.87)	
7b	93	97	$C_{38}H_{67}N_3O_2$ S_2 (662.1)	3300 3180 1650 1100	1.3 (*m*, 46 H), 2.63 (*m*, 8 H) 3.68 (*t*, 4 H), 4.65 (*bs*, 4 H) 7.5 (*br*, 3 H), 7.75 (*bs*, 2 H)[b]	—	68.93 (68.89)	10.2 (10.02)	6.35 (6.47)	9.68 (9.62)
7c	91	105	$C_{32}H_{55}N_3O_2$ (513.8)	3300 1640 1305 1220 1100	1.3 (*m*, 46 H), 4.23 (*t*, 4 H) 6.65 (*br*, 3 H), 7.3 (*s*, 2 H)[b]	—	74.81 (75.05)	10.79 (10.64)	8.18 (8.04)	
7d	90	152 (dec)	$C_{11}H_{11}N_3O_2$ (217.2)	3300 1650 1290 1215	1.85 (*s*, 6 H), 6.65 (*br*, 3 H) 7.3 (*s*, 2 H)[b]	—	60.83 (60.78)	5.1 (5.02)	19.35 (18.96)	

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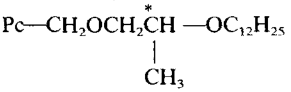
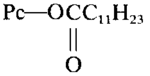
[a] For data of compounds 1e, 2e, 5e and 6e, see experimental procedures.

[b] $CDCl_3$

[c] CCl_4

[d] Only paraffinic protons appear and other protons are not observed due to paramagnetic copper ion.

TABLE II
Phase Transition Behavior[a]

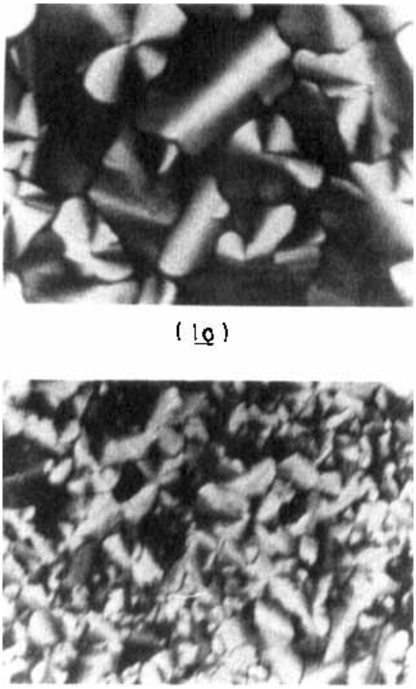
	K ⟶ M ⟶ I (°C)	
Pc-derivatives	PcH_2 (1)	CuPc (2)
$Pc—CH_2SC_{12}H_{25}$	95,267	108,304
$Pc—CH_2OC_2H_4SC_{12}H_{25}$	52,247	70,255
$Pc—OC_{12}H_{25}$	75,269	78,310
 $Pc—CH_2OCH_2\overset{*}{C}H(CH_3)—OC_{12}H_{25}$	23,158	29,191
 $Pc—OC(=O)C_{11}H_{23}$	58,303	

[a]Instrument: Du Pont 990 TA 910 cellbase; Scan range: 0–350°C; Heating rate: 10°C/min

sition (Figure 5). Such a focal conic texture that is common with those of smectic E, B or A was also observed with hexa-*n*-dodecanoate of triphenylene (Drd).[18–19] With PcH_2(1b) and CuPc(2b), however, we observed only a typical "linear default" texture reappearing at 242°C for 1b and at 250°C for 2b. The textures were again prolonged without notable change down to the temperatures of the first transition (Figure 6). Also in the case of PcH_2(1c) and CuPc(2c), only a clear "linear default" was exhibited reversibly at 265°C with 1c and 307°C with 2c (Figure 7). This texture was also observed in the discophase formed by hexa-*n*-alkoxy triphenylene(Dho). It is notable that these different aryl-alkyl ether systems (phthalocyanine and triphenylene systems) showed the same texture—linear default.

The compound PcH_2 (1d) exhibited reversibly only a "fan-shaped"(?) texture at 300°C as shown in Figure 8, and maintained it down to the first transition temperature (58°C). This texture is quite different from those observed with usual discophases, being very similar to those of common smectics.

Chiral PcH_2 (1e) exhibited quite a different mesomorphic behavior. Upon cooling below the second transition temperature, the "platelet" texture appeared first at 153°C. However, the texture changed at 66°C to "fan-shaped", and was maintained down to room temperature (Figure 9). It should be noted that at this temperature (66°C) no transition could be detected by DSC, and this transition of the platelet texture to the fan-shaped was attributable to the cholesteric liquid crystal character of 1e.[20–21] It is possible that PcH_2 (1e) may be the



(1a)

(2a)

FIGURE 5 Optical textures observed from PcH_2 (1a: $Pc—CH_2SC_{12}H_{25}$) at 220°C and CuPc (2a) at 200°C (× 300).

first genuine cholesteric liquid crystal phase exhibited by Pc systems. In the case of CuPc (2e), however, on cooling below 190°C the anisotropic phase began to appear at 187°C, showing a texture similar to a small "fan-shaped" one, and remained without any change down to room temperature (Figure 10). We wish to point out that this is the only case in which the texture of CuPc (2e) is different from that of the corresponding PcH_2 (1e).

III. Experimental

Melting points were measured with a Thomas-Hoover melting point apparatus and were uncorrected. Boiling points were those observed during the distillation with a Kugelrohr apparatus and were uncorrected. Infrared spectra were taken on a Perkin–Elmer Model 283B spectrometer. ^1H and ^{13}C NMR spectra were obtained on Varian Model T60-A and Varian FT 80-A spectrometers. GLC analysis was

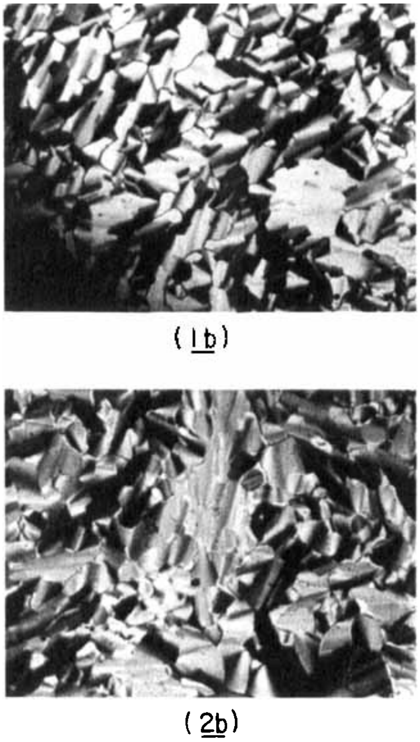
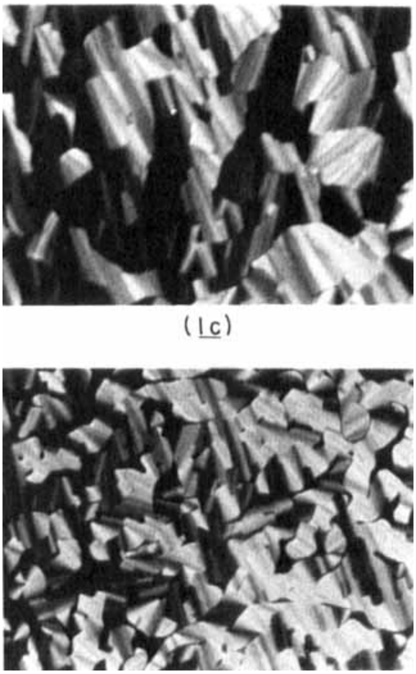


FIGURE 6 Optical textures observed from PcH$_2$ (1b: Pc—CH$_2$OC$_2$H$_4$S—C$_{12}$H$_{25}$) and CuPc (2b) at 200°C (× 300).

performed on a Varian 2800 gas chromatograph using FID detectors. All analyses were carried out on 10 ft × 0.125 in 10% Carbowax 20M. Optical rotations were recorded on an Autopol III automatic polarimeter. Elemental analyses were performed at Lucky Central Research Institute in Korea.

1. Preparation of S-(+)-2-hydroxypropyl *t*-butyldimethylsilyl ether (8).

S-(+)-1,2-Propanediol (9.1 g, 120 mmol), DBU (5.4 g, 36 mmol), and triethylamine (12.3 g, 120 mmol) were mixed with TBDCS (18.5 g, 120 mmol) in CH$_2$Cl$_2$ (100 ml) at room temperature for 5 h. The reaction mixture was then diluted with a large volume of CH$_2$Cl$_2$, and washed with a cold 5% HCl solution, saturated NaHCO$_3$ solution, and finally with brine. The organic layer was dried over anhydrous MgSO$_4$ and the solvent was evaporated. The residue was then distilled



(1c)

(2c)

FIGURE 7 Optical textures observed from PcH_2(1c: $Pc{-}OC_{12}H_{25}$) at 250°C and CuPc (2c) at 220°C (× 300).

FIGURE 8 Optical texture observed from PcH_2 (1d: $Pc{-}O\underset{\overset{\|}{O}}{C}C_{11}H_{23}$) at 210°C (× 300).

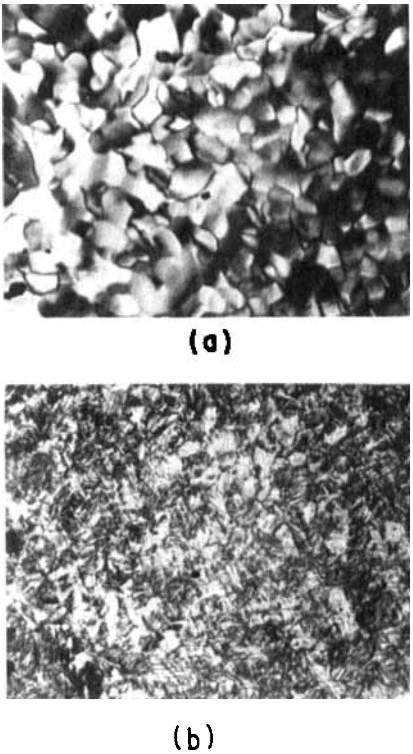


FIGURE 9 Optical textures observed from PcH_2 (1e) (× 300): a) Platelet texture at 130°C; b) Fan-shaped texture at 25°C.

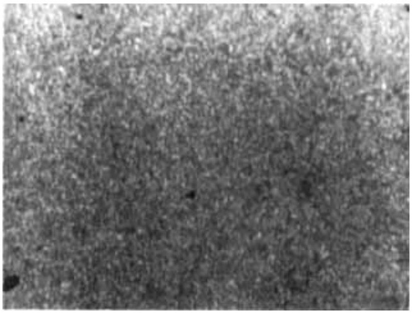


FIGURE 10 Optical texture observed from CuPc (2e) at 180°C (× 300).

in a vacuum to give 19.5 g of the product (y = 90%), bp 75–7°C/15 Torr (GLC > 99%). ^{1}H-NMR(CCl_4) δ = 0.15 (*s*, 6H), 1.10 (*s*, 9H), 1.26 (*d*, 3H), 2.75 (*s*, –OH), 3.67 (*m*, 3H).

2. Preparation of S-(+)-2-(dodecyloxy)-propyl *t*-butyldimethylsilyl ether (9).

Silyl ether 8 (17.1 g, 90 mmol) in ethyl ether (100 ml) reacted overnight with Na metal (2.1 g, 90 mmol) under reflux. After all the metal Na reacted, 1-dodecylbromide (27 g, 108 mmol) was added dropwise for the time period of 30 min, and then refluxed for 12 h. The reaction mixture was washed with water, dried over anhyd. $MgSO_4$, and the solvent was removed. The oily residue was distilled in a vacuum to give 25.5 g of the product (y = 79%), bp 130–2°C/1 Torr. ^{1}H-NMR(CCl_4) δ = 0.1 (*s*, 6H), 1.0 (*s*, 9H), 1.32 (*m*, 26H), 3.55 (*m*, 5H).

3. Preparation of S-(+)-2-(dodecyloxy)-propanol (10).

Alkylsilyl ether 9 (10 g, 28 mmol) in THF (120 ml) reacted with tetra-*n*-butylammonium fluoride (22 g, 70 mmol) at room temperature for 1 h. The mixture was then evaporated, diluted with water, and extracted with ether. The ether extracts were dried, evaporated to dryness, and the oily residue was distilled in a vacuum to give 6.5 g of the product (y = 95%), bp 115–6°C/1 Torr. $[\alpha]_D^{17}$ = +5.8 (*c* 0.8, EtOH). ^{1}H-NMR(CCl_4) δ = 1.30 (*m*, 26H), 2.90 (*s*, –OH), 3.54 (*m*, 5H).

Analysis, $C_{15}H_{32}O_2$ (244.4): Calcd. (%) C73.72, H13.20. Found(%) C73.69, H13.18.

4. Preparation of S-(+)-1,2-dibromo-4,5-bis[4-(dodecyloxy)-2-oxa-pentyl]-benzene (5e).

Dodecyloxypropanol 10 (6.5 g, 26.6 mmol) in *t*-butanol (30 ml) reacted with Na metal (0.735 g, 32 mmol) at 60°C for 2 h until all the metal Na was reacted. Tetrabromo-derivative 4 (5.62 g, 13.3 mmol) was then added in small portions at room temperature and then the reaction mixture was refluxed for 8 h. The mixture was evaporated, diluted with water, extracted with $CHCl_3$, and the extracts were dried over anhyd. $MgSO_4$ and evaporated to dryness. The residual oil was purified by column chromatography over silica gel (eluent; $CHCl_3$) to obtain the product (y = 58%), mp –5.5°C. $[\alpha]_D^{17}$ = +9.2 (c 1.0, EtOH). ^{1}H-NMR($CDCl_3$) δ = 1.25 (*m*, 52 H), 3.40 (*m*, 10 H), 4.40 (*s*, 4 H), 7.50 (*s*, 2 H).

Analysis, $C_{38}H_{68}Br_2O_4$(748.8): Calcd. (%) C60.95, H9.15, Br21.34. Found(%) C61.03, H9.19, Br21.22.

5. Preparation of S-(+)-1,2-dicyano-4,5-bis[4-(dodecyloxy)-2-oxa-pentyl]-benzene (6e).

A mixture of dibromo derivative 5e (6.2 g, 8.3 mmol), CuCN (3 g, 33.2 mmol) and DMF (35 ml) was refluxed for 8 h. Ammonia water (100 ml) was then added and stirred further for 30 min at room temperature. The mixture was filtered, washed with water, and dried in air. The solids were extracted with ether for 24 h using a Soxhlet apparatus and the extract was evaporated to dryness. Recrystallization of the residual solids from methanol gave 2.65 g of the product (y = 50%), mp 40.5–41°C. $[\alpha]_D^{17}$ = +7.2 (c 1.0, $CHCl_3$). IR(KBr) 2920, 2850, 2227, 1115 cm^{-1}. ^{1}H-NMR($CDCl_3$) δ = 1.28 (m, 52 H), 3.55 (m, 10 H), 4.63 (s, 4 H), 7.88 (s, 2 H).

Analysis, $C_{40}H_{68}N_2O_4$(641.0): Calcd. (%) C74.95, H10.69, N4.37. Found (%) C74.91, H10.58, N4.43.

6. Preparation of S-(+)-2,3,9,10,16,17,23,24-octakis[4-(dodecyloxy)-2-oxa-pentyl]-phthalocyanine (1e).

Dicyano-derivative 6e (1.92 g, 3 mmol) was dissolved in 1.5 ml of N,N-dimethylaminoethanol and gaseous ammonia was bubbled through the mixture. The resulting reaction mixture was then heated under reflux for 72 h. The reaction mixture was extracted with acetone to separate the product from the unreacted starting material and by-products. After the removal of acetone, the residual solid was purified by column chromatography over silica gel (eluent: $CHCl_3$) to obtain the deep bluish product (y = 35%), $K \xrightarrow{23^\circ} M \xrightarrow{158^\circ} I$. IR(KBr) 3300, 2940, 2870, 1120, 1105 cm^{-1}. ^{1}H-NMR($CDCl_3$) δ = 1.16 (m, 208 H), 3.82 (m, 40 H), 5.25 (bs, 16 H), 9.36 (bs, 8 H). ^{13}C-NMR($CDCl_3$) δ = 14.7, 18.5, 23.2, 27.1, 30.3, 31.1, 32.6 (aliphatic), 70.3 (—CH_2—O—), 72.6 (chiral—C), 75.5 (Ar—CH_2—O—), 123.5, 136.2, 139.4, 149.9 (aromatic).

Analysis, $C_{160}H_{274}N_8O_{16}$ (2566.0): Calcd. (%) C74.89, H10.76, N4.37. Found (%) C75.1, H10.68, N4.45.

7. Preparation of S-(+)-2,3,9,10,16,17,23,24-octakis[4-(dodecyloxy)-2-oxa-pentyl]-phthalocyaninatocopper (2e).

PCH_2 1e (200 mg, 0.078 mmol) was dissolved in pentanol (3 ml) containing K metal (9.1 mg, 0.234 mmol) under N_2 atmosphere. The reaction mixture was then heated at 100°C for 1 h and cooled. $Cu(OAc)_2$

(17.6 mg, 0.117 mmol) was added at room temperature and the reaction was continued for a further 3 h at 100°C. The solvent was evaporated and the resulting solid was purified by column chromatography over silica gel (eluent; $CHCl_3$) to obtain the deep bluish product (y = 90%). $K \xrightarrow{29°} M \xrightarrow{191°} I$. IR(KBr) 2930, 2850, 1120, 1100 cm^{-1}.

Analysis, $C_{160}H_{272}N_8O_{16}Cu$ (2627.5): Calcd. (%) C73.14, H10.43, N4.26, Cu2.42. Found (%) C73.54, H10.38, N4.31, Cu2.38.

IV. Conclusions

Various types of new discogenic PcH_2's (1a–e) and corresponding copper complexes (2a–c, e) were prepared in the present work and it is notable that introduction of ramification in the aliphatic chains enabled us to obtain the Pc derivatives 1e and 2e which exhibit discotic mesophases at room temperature. It is also interesting to observe that the optical textures of Pc derivatives exhibited only single simple mesomorphic behavior except PcH_2(1e). This is not common in most discogenic compounds.

With chiral PcH_2(1e), we observed a cholesteric-like texture which could be considered by the transition of the platelet texture into the fan-shaped texture. This result is, we believe, the first instance in which a pure cholesteric discogen was observed with a phthalocyanine system.

We will continue to work on other cholesteric discogens based mainly on the phthalocyanine system and the results will be published in forthcoming reports.

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