

### Experimental

Infrared spectra were taken on a Perkin-Elmer Model 283B spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian Model T60-A and Varian FT80-A spectrometers. GLC analyses were performed on a Varian 2800 gas chromatograph using FID detectors. All analyses were carried out on 10ft  $\times$  0.125in 10% Carbowax 20M. Optical rotations were recorded on an Autopol III automatic polarimeter. Elemental analyses were performed at Lucky Central Research Institute in Korea. Detection of phase transitions and measurement of transition temperatures were made using a Du Pont 990TA 910 cellbase differential scanning calorimeter (DSC) with a heating rate 10°C/min. Observations of microscopic textures were carried out using a Leitz polarizing microscope equipped with a Mettler FP52 hot stage.

**S-(+)-2-Hydroxypropyl t-butylidimethylsilyl ether(2).** S-(+)-1,2-propanediol (9.1g, 120 mmol), DBU (5.4g, 36 mmol), and triethylamine (12.3g, 120 mmol) were reacted with t-butylidimethylchlorosilane (18.5g, 120 mmol) in  $\text{CH}_2\text{Cl}_2$  (100 ml) at room temperature for 5h. The reaction mixture was then diluted with a large volume of  $\text{CH}_2\text{Cl}_2$ , and washed with a cold 5% HCl solution, saturated  $\text{NaHCO}_3$  solution, and finally with brine. The organic layer was dried over anhyd.  $\text{MgSO}_4$  and the solvent was evaporated. The residue was then distilled under vacuum to obtain 19.5g of the product ( $y = 90\%$ ), bp 75-7 °C/15 torr (GLC >99%).  $^1\text{H-NMR}$  ( $\text{CCl}_4$ )  $\delta = 0.15$  (s, 6H), 1.10 (s, 9H), 1.26 (d, 3H), 2.75 (s, -OH), 3.67 (m, 3H).

**S-(+)-2-(Dodecyloxy)-propyl t-butylidimethylsilyl ether(3).** Silyl ether 2 (17.1g, 90mmol) in ether (100 ml) was reacted overnight with Na metal (2.1g, 90 mmol) under reflux. After all the metal reacted, 1-dodecylbromide (27g, 108 mmol) was added dropwise for the time period of 30 min, and the reaction mixture was then refluxed for 12h. The reaction was worked up by washing with water, dried over anhyd.  $\text{MgSO}_4$ , and the solvent was removed. The oily residue was distilled under vacuum to obtain 25.5g of the product ( $y = 79\%$ ), bp 130-2°C/1 torr,  $^1\text{H-NMR}$  ( $\text{CCl}_4$ )  $\delta = 0.1$  (s, 6H), 1.0 (s, 9H), 1.32 (m, 26H), 3.55 (m, 5H).

**S-(+)-2-(Dodecyloxy)-propanol(4).** Alkylsilyl ether 3 (10g, 28mmol) in THF (120 ml) reacted with tetra-n-butylammonium fluoride (22g, 70 mmol) at room temperature for 1h. Solvent was then evaporated, and the residue was diluted with water and extracted with ether. The ether extracts were dried, evaporated to dryness, and the oily residue was distilled under vacuum to obtain 6.5g of the product ( $y = 95\%$ ), bp 115-6°C/1 torr.  $[\alpha]_D^{17} = +5.8$  (c 0.8, EtOH).  $^1\text{H-NMR}$  ( $\text{CCl}_4$ )  $\delta = 1.30$  (m, 26H), 2.90 (s, -OH), 3.54 (m, 5H).

**S-(+)-1,2-Dibromo-4,5-bis[4-(dodecyloxy)-2-oxapentyl]-benzene(5).** Dodecyloxypropanol 4 (6.5g, 26.6 mmol) in t-butanol (30ml) was reacted with Na metal (0.735g, 32 mmol) at 60°C for 2 until all the metal Na was reacted, 1,2-Dibromo-4,5-bis(bromomethyl)-benzene (5.62g, 13.3 mmol) was then added in small portions at room temperature and

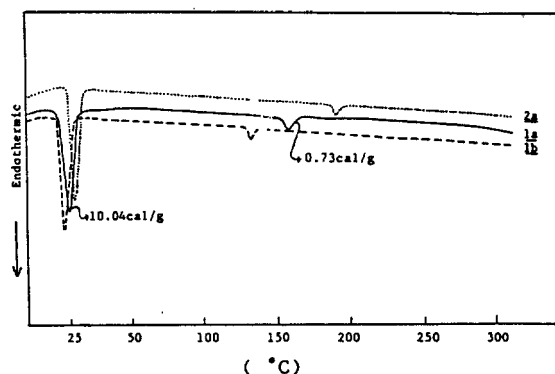


Figure 2. DSC curves of Pc derivatives:  $\text{PcH}_2$  **1a**(—),  $\text{PcH}_2$  **1b**(---) and  $\text{CuPc}$  **2a**(...).

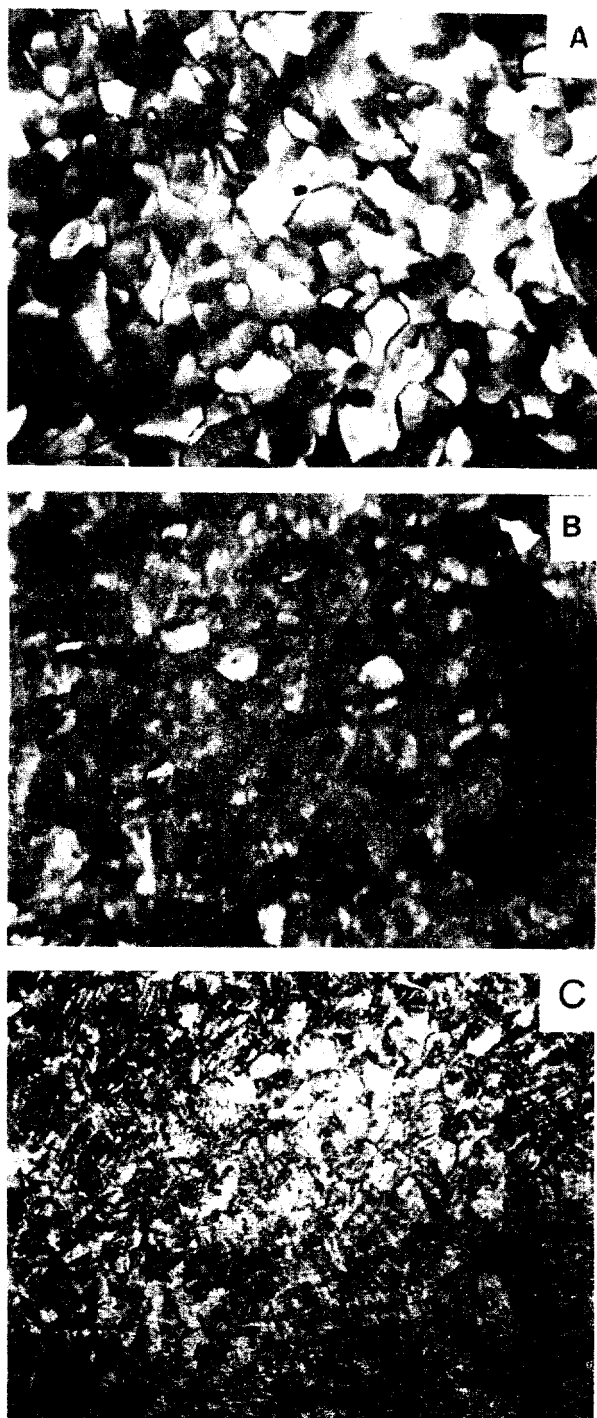
then the reaction mixture was refluxed for 8h. After the solvent was removed, the residue was diluted with water, extracted with  $\text{CHCl}_3$ , and the extracts were dried over anhyd.  $\text{MgSO}_4$  and evaporated to dryness. The residual oil was purified by column chromatography over silica gel (eluent:  $\text{CHCl}_3$ ) to obtain the product ( $y = 58\%$ ), mp -5.5°C.  $[\alpha]_D^{17} = +9.2$  (c 1.0, EtOH).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta = 1.25$  (m, 52H), 3.40 (m, 10H), 4.40 (s, 4H), 7.50 (s, 2H).

**S-(+)-1,2-Dicyano-4,5-bis[4-(dodecyloxy)-2-oxapentyl]-benzene(6).** A mixture of dibromo-derivative **5** (6.2g, 8.3 mmol),  $\text{CuCN}$  (3g, 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 extracts was evaporated to dryness. Recrystallization of the residual solids from MeOH gave 2.65g of the product ( $y = 50\%$ ), mp 40.5-41°C.  $[\alpha]_D^{17} = +7.2$  (c 1.0,  $\text{CHCl}_3$ ). IR(KBr) 2920, 2850, 2227, 1115  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta = 1.28$  (m, 52H), 3.55 (m, 10H), 4.63 (s, 4H), 7.88 (s, 2H).

**S-(+)-2,3,9,10,16,17,23,24-Octakis[4-(dodecyloxy)-2-oxapentyl]-phthalocyanine(1a).** Dicyano-derivative **6** (1.92g, 3 mmol) was dissolved in 1.5ml of N,N-dimethylaminoethanol and gaseous ammonia was bubbled through the mixture. The resulting 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 side products. After the removal of acetone, the residual solids were purified by column chromatography over silica gel (eluent:  $\text{CHCl}_3$ ) to obtain the deep bluish product

( $y = 35\%$ ), K - M - I. IR(KBr) 3300, 2940, 2870, 1120, 1105  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta = 1.16$  (m, 208H), 3.82 (m, 40H), 5.25 (bs, 16H), 9.36 (bs, 8H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta = 14.7$ , 18.5, 23.2, 27.1, 30.3, 31.1, 32.6 (aliphatic), 70.3 (- $\text{CH}_2\text{-O}$ ), 72.6 (chiral-C), 75.5 (Pc- $\text{CH}_2\text{-O}$ ), 123.5, 136.2, 139.4, 149.9 (aromatic). Analysis,  $\text{C}_{160}\text{H}_{274}\text{N}_8\text{O}_{16}$  (2566.0): Calcd %, C74.9, H10.8, N4.47. Found % C75.1, H10.7, N4.5.

**S-(+)-2,3,9,10,16,17,23,24-Octakis[4-(dodecyloxy)-2-oxapentyl]-phthalocyaninatocopper(2a).**  $\text{PcH}_2$  **1a** (200 mg, 0.078 mmol) was dissolved in pentanol (3 ml) containing K metal (9.1 mg, 0.234 mmol) under nitrogen atmosphere. The reaction mixture was then heated at 100°C for 1h and cooled. Cupric acetate (17.6mg, 0.117 mmol) was added at room temperature and the reaction was continued for additional 3h at 100°C. The solvent was evaporated and the re-



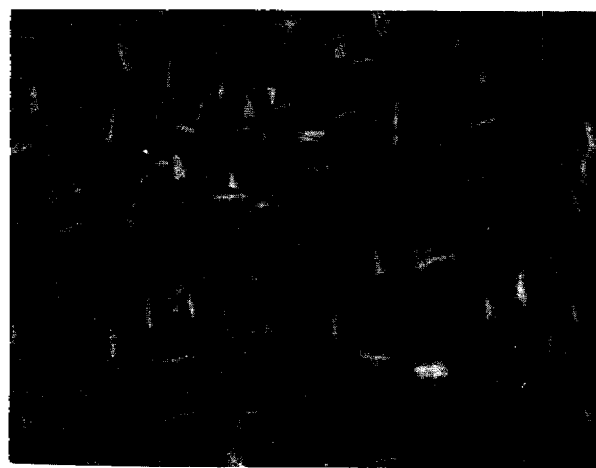
**Figure 3.** Optical textures of the chiral  $\text{PcH}_2$  **1a**: (A) Platelet at  $153^\circ\text{C}$ , (B) texture change at  $66^\circ\text{C}$ , (C) Fan-shape at  $60^\circ\text{C}$  (X300).

sulting solid was purified by column chromatography over silica gel (eluent:  $\text{CHCl}_3$ ) to obtain the deep bluish product

( $y = 90\%$ ).  $K - M - I$ . IR(KBr) 2930, 2850, 1120, 1100  $\text{cm}^{-1}$ . Analysis,  $\text{C}_{100}\text{H}_{120}\text{N}_8\text{O}_6\text{Cu}$  (2627.5): Calcd %, C73.1, H10.4, N4.3, Cu2.4. Found %, C73.5, H10.1, N4.3, Cu2.4.

## Results and Discussion

**Differential Scanning Calorimetry(DSC).** All the ther-



**Figure 4.** Optical texture of the achiral  $\text{PcH}_2$  **1b** at  $45^\circ\text{C}$  (X300).

mograms of Pc derivatives recorded with increasing temperature showed clearly two endothermic peaks (Figure 2). In the case of the chiral  $\text{PcH}_2$  **1a**, two peaks corresponded to the enthalpies of 10.04 cal/g at  $23^\circ\text{C}$  and 0.73 cal/g at  $158^\circ\text{C}$ , respectively. It is reasonable to assume that the first peaks are related to the transition from the crystal into discotic mesophase and can be interpreted to correspond essentially to the melting of the flexible side chains which comprise the important weight portion (ca. 80%) of the compound. The second peaks are related to the transition between discotic mesophase and isotropic liquid.

It is to note that the chiral  $\text{PcH}_2$  **1a** was different in transition temperature from the corresponding achiral  $\text{PcH}_2$  **1b**, implying that chirality in the side chains has significant effect on the morphology of the system.

It is also notable that all the Pc derivatives which exhibited discotic mesophases in room temperature range and were chemically stable up to  $300^\circ\text{C}$  may be useful in many applied fields.

Interesting to observe was that all the Pc derivatives showed only single mesomorphic transition, whereas most of other discogenic systems exhibited rather complex polymorphisms.

**Optical Microscopy.** The only discogenic Pc texture reported so far in literature was "flower like" texture which was identical to that described primarily by Chandrasekhar *et al.* as a discotic texture.<sup>1</sup> However, the chiral  $\text{PcH}_2$  **1a** exhibited quite different mesomorphic behavior. Upon cooling the isotropic liquid below the second transition temperature, a "platelet" (blue phase) texture appeared first at  $153^\circ\text{C}$  (Figure 3A). On further cooling, however, texture change occurred at  $66^\circ\text{C}$  (Figure 3B) and typical "fan-shape" texture appeared at  $60^\circ\text{C}$  (Figure 3C), which was maintained down to room temperature. It is interesting to note that at this temperature ( $66^\circ\text{C}$ ) no transition could be detected by DSC. This transition of the platelet (blue phase) to the fanshape texture was one of typical characters observed with classical cholesteric liquid crystal systems.<sup>7,8</sup>

Contrary to the chiral  $\text{PcH}_2$  **1a**, the achiral **1b** showed single mesomorphic behavior. Upon cooling below the second transition temperature, a small "focal conic" texture began to appear at  $128^\circ\text{C}$ , which was maintained without any texture change down to the first transition temperature (Figure 4). The results of the texture observations on  $\text{PcH}_2$ 's (**1a** and

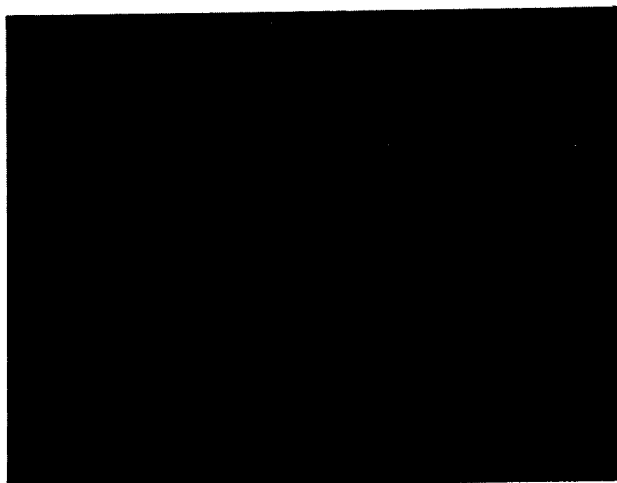


Figure 5. Optical texture of the chiral CuPc **2a** at 100°C (X300).

**1b**) suggest that the chiral PcH<sub>2</sub> **1a** could be a true disc-like cholesteric liquid crystal.

In the case of the chiral CuPc **2a**, however, an anisotropic phase began to appear at 187°C, showing the texture similar to small "fan-shape" texture in mesophase ranges (Figure 5). It should be pointed out that this was the only case in which the optical textures of CuPc's were different from those of the corresponding PcH<sub>2</sub>'s reported in literatures so far.<sup>9</sup> This result could be regarded as another evidence that the chiral PcH<sub>2</sub> **1a** is a columnar liquid crystal exhibiting cholesteric phase. It has been known by X-ray studies that the mean stacking distances of known discogenic Pc derivatives were about 4.6 ± 0.2 and 3.4 Å (characteristic van der Waals distance for aromatic compounds) for PcH<sub>2</sub> and CuPc, respectively.<sup>4,10,11</sup> From these values it can be assumed that the chiral CuPc **2a** is difficult to form a "helical structure", but the columnar structure may be "tilted" due to interatomic

repulsions of the side chains.

### Conclusion

From the results of the differences in the transition behaviors and the optical textures generated by chiral effect, i.e., a cholesteric-like texture (from platelet to fan-shape) of the chiral PcH<sub>2</sub> **1a**, and the difference in optical textures of the chiral PcH<sub>2</sub> **1a** and CuPc **2a**, the PcH<sub>2</sub> **1a** can be regarded as the first true columnar cholesteric phase displayed by the discotic liquid crystal systems.

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## Dipole Moments of the OH, OH<sup>+</sup> and OH<sup>-</sup> Valence States by *ab initio* Effective Valence Shell Hamiltonian Method

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The *ab initio* effective valence shell Hamiltonian method, based on quasidegenerate many-body perturbation theory, is generalized to calculate molecular properties as well as the valence state energies which have previously been determined for atoms and small molecules. The procedure requires the evaluation of effective operator for each molecular property. Effective operators are perturbatively expanded in powers of correlation and contain contributions from excitations outside of the multireference valence space. To demonstrate the validity of this method, calculations for dipole moments of several low lying valence states of OH, OH<sup>+</sup> and OH<sup>-</sup> to first order in the correlations have been performed and compared with configuration interaction calculations.

### Introduction

The quasidegenerate many-body perturbation theory (QDMBPT) is a generalization to multiple reference quaside-

generate states of simple many-body perturbation theory (MBPT), a diagrammatic representation of ordinary Rayleigh-Schrödinger perturbation theory for a reference nondegenerate single determinantal unperturbed wavefunction.<sup>1-5</sup>