7. J. C. P. Broekhoff and J. H. deBoer, *J. Catalysis* **9**, 8 (1967).
8. W. Ahn, K. Shin, and S. Chang, *J. Colloid Interface Sci.* **51**, 232 (1975).
9. G. D. Halsey, *J. Chem. Phys.* **16**, 931 (1948).
10. S. J. Gregg and K. S. W. Sing, "Adsorption, Surface Area an Porosity (2nd ed.)" Chapt. 2, Academic Press (1982).
11. R. Sh. Mikhail, S. Brunauer, and E. E. Bodor, *J. Colloid Interface Sci.* **26**, 54 (1968).

A True Cholesteric Columnar Liquid Crystal

Iwhan Cho*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-650

Youngsoo Lim

Lucky Central Research Institute, 84 Changdong, Chung-ku, Daejeon 302-343. *Received December 14, 1987*

A pure columnar cholesterogen based on the octasubstituted phthalocyanine (PcH_2), S-(+)-2,3,9,10,16,17,23,24-octakis[5-(dodecyloxy)-2-oxa-pentyl]-phthalocyanine(**1a**), is described. To evaluate a cholesteric character of **1a**, the corresponding achiral PcH_2 **1b** and the copper complex of chiral PcH_2 **1a** (CuPc), S-(+)-2,3,9,10,16,17,23,24-octakis[4-(dodecyloxy)-2-oxa-pentyl]-phthalocyanine(**2a**) were also prepared. The chiral **1a** exhibited a typical cholesteric texture change in which the transition of platelet (blue phase) to fan-shape texture was observed (K — M — I), whereas the corresponding achiral **1b** showed only a focal conic texture (K — M — I). This is the first instance of a pure columnar cholesterogen observed with discotic liquid crystal systems.

Introduction

Since a new class of liquid crystals formed by disc-like molecules was first reported in 1977,[1] optically active discogens have been investigated in search for the discotic cholesterogens. Destrade *et al.* first reported the discotic cholesteric phase by mixing a known nematic discotic compound (N_D), triphenylene hexa-4-n-heptyloxybenzoate, with several chiral compounds which did not individually behave as cholesterogens.[2] They also reported the synthesis of the first genuine discotic cholesterogen, (-)-2,3,6,7,10,11-hexa-[S-(4-methyl)-4-n-hexyloxybenzoyloxy]-triphenylene.[3] However, it should be noted that the triphenylene derivatives mentioned above are all related to N_D phases (not columnar D-phase) and the resulting N_D^* phases exhtibited oily streak texture which were similar to those of classical nematic phases.

Since discogenic phthalocyanine derivatives (Pc) were characterized as columnar D-phases by Piechocki *et al.*,[4,5] we have focused our attention on these columnar phase and designed a structure of chiral PcH_2 **1a**(Figure 1). We now like to report the synthesis and the optical textures of a new genuine columnar cholesterogen.

The chiral PcH_2 **1a** was prepared according to the procedure[6] similar to that reported already from S-(+)-1,2-propane-diol (Scheme 1). For the purpose of comparison, achiral PcH_2 **1b** was also synthesized similarly from 1,2-propanediol.

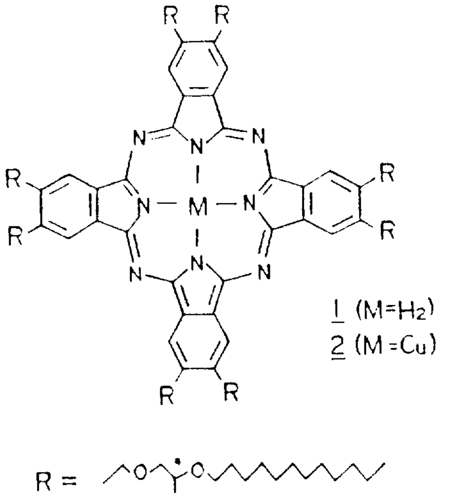
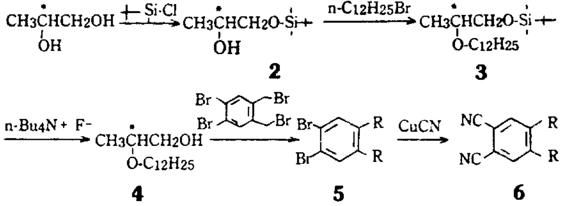
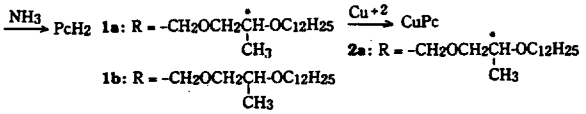


Figure 1. Chemical structure of chiral Pc derivatives: PcH_2 **1a** and CuPc **2a**.





$$\xrightarrow{NH_3} PcH_2\ \mathbf{1a}: R = -CH_2OCH_2\underset{CH_3}{\overset{\bullet}{C}}H\text{-}OC_{12}H_{25} \xrightarrow{Cu^{+2}} CuPc\ \mathbf{2a}: R = -CH_2OCH_2\underset{CH_3}{\overset{\bullet}{C}}H\text{-}OC_{12}H_{25}$$

$$\mathbf{1b}: R = -CH_2OCH_2\underset{CH_3}{C}H\text{-}OC_{12}H_{25}$$

Scheme 1

Experimental

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 FT80-A spectrometers. GLC analyses were performed on a Varian 2800 gas chromatograph using FID detectors. All analyses were carried out on 10ft × 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-butyldimethylsilyl 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-butyldimethylchlorosilane (18.5g, 120 mmol) in CH_2Cl_2 (100 m*l*) at room temperature for 5h. The reaction mixture was then diluted with a large volume of CH_2Cl_2, and washed with a cold 5% HCl solution, saturated $NaHCO_3$ solution, and finally with brine. The organic layer was dried over anhyd. $MgSO_4$ and the solvent was evaporated. The residue was then distilled under vacuum to obtaine 19.5g of the product (y = 90%), bp 75-7 °C/15 torr (GLC>99%). ^1H-NMR (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-butyldimethylsilyl ether(3). Silyl ether **2** (17.1g, 90mmol) in ether (100 m*l*) 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. $MgSO_4$, 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, ^1H-NMR (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 m*l*) 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, evaporated to dryness, and the oily residue was distilled under vacuum to obtain 6.5g of the product (y = 95%), bp 115-6°C/*l* torr. $[\alpha]_D^{17} = +5.8$ (c 0.8, EtOH). ^1H-NMR (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 (30m*l*) 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 then the reaction mixture was refluxed for 8h. After the solvent was removed, the residue was 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). ^1H-NMR ($CDCl_3$) $\delta = 1.25$ (m, 52H), 3.40 (m, 10H), 4.40 (s, 4H), 7.50 (s, 2H).

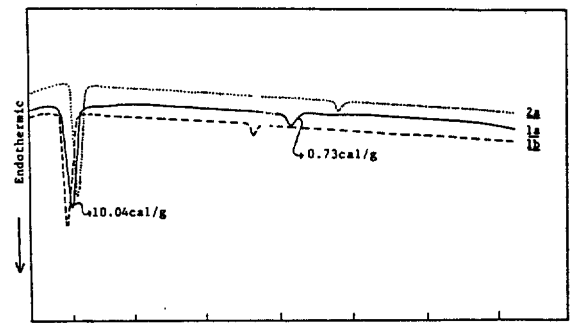


Figure 2. DSC curves of Pc derivatives: PcH_2 **1a**(—), PcH_2 **1b**(--) and CuPc **2a**(...).

S-(+)-1,2-Dicyano-4,5-bis[4-(dodecyloxy)-2-oxa-pentyl]-benzene(6). A mixture of dibromo-derivative **5**(6.2g, 8.3 mmol), CuCN (3g, 33.2 mmol) and DMF (35 m*l*) was refluxed for 8 h. Ammonia water (100 m*l*) 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, $CHCl_3$). IR(KBr) 2920, 2850, 2227, 1115 cm^{-1}. ^1H-NMR ($CDCl_3$) $\delta = 1.28$ (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 1.5m*l* 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 seperate 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: $CHCl_3$) to obtain the deep bluish product (y = 35%), K — M — I. IR(KBr) 3300, 2940, 2870, 1120, 1105 cm^{-1}. ^1H-NMR ($CDCl_3$) $\delta = 1.16$ (m, 208H), 3.82 (m, 40H), 5.25 (bs, 16H), 9.36 (bs, 8H). ^{13}C-NMR ($CDCl_3$) $\delta = 14.7$, 18.5, 23.2, 27.1, 30.3, 31.1, 32.6 (aliphatic), 70.3 ($-CH_2$-O-), 72.6 (chiral-C), 75.5 (Pc-CH_2-O-), 123.5, 136.2, 139.4, 149.9 (aromatic), Analysis, $C_{160}H_{274}N_8O_{16}$ (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). PcH_2 **1a** (200 mg, 0.078 mmol) was dissolved in pentanol (3 m*l*) 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-

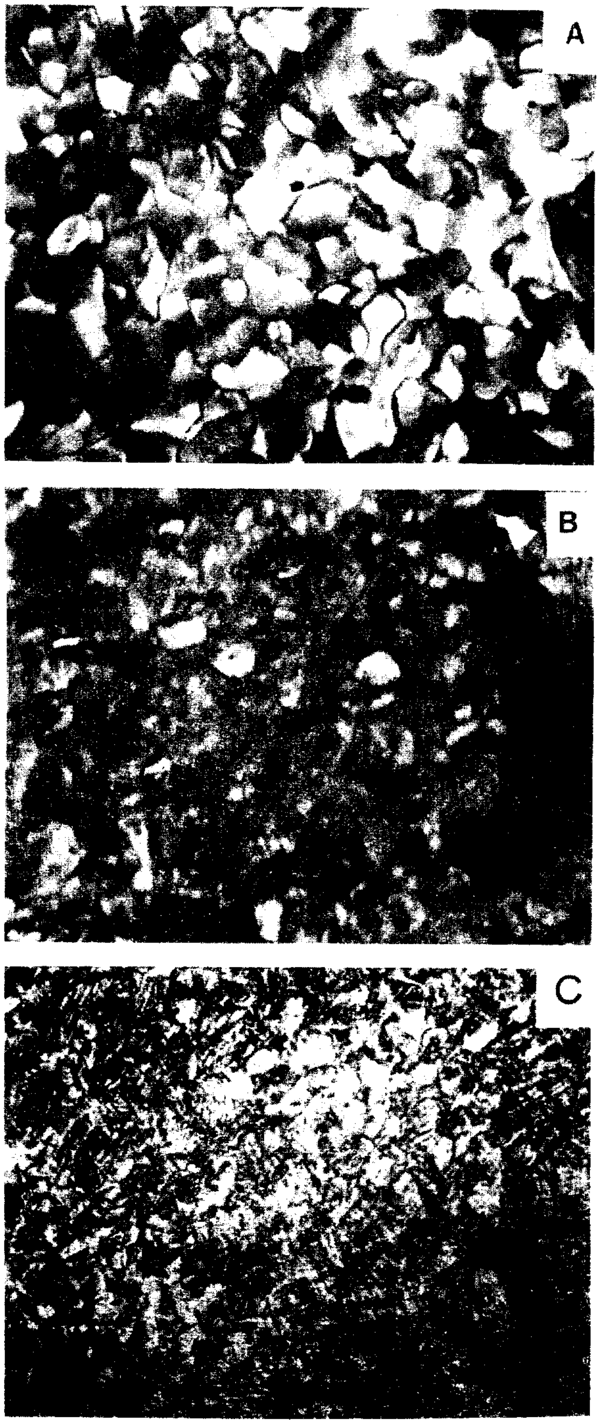


Figure 3. Optical textures of the chiral PcH_2 **1a**: (A) Platelet at 153°C, (B) texture change at 66°C, (C) Fan-shape at 60°C (X300).

sulting solid was purified by column chromatography over silica gel (eluent: $CHCl_3$) to obtain the deep bluish product (y = 90%). K – M – I. IR(KBr) 2930, 2850, 1120, 1100 cm^{-1}. Analysis, $C_{160}H_{272}N_8O_{10}Cu$ (2627.5): Calcd %, C73.1, H10.4, N4.3, Cu2.4. Found %, C73.5, H10.4, N4.3, Cu2.4.

Figure 4. Optical texture of the achiral PcH_2 **1b** at 45°C (X300).

Results and Discussion

Differential Scanning Calorimetry(DSC). All the thermograms of Pc derivatives recorded with increasing temperature showed clearly two endothermic peaks (Figure 2). In the case of the chiral PcH_2 **1a**, two peaks corresponded to the enthalpies of 10.04 cal/g at 23°C and 0.73 cal/g at 158°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 PcH_2 **1a** was different in transition temperature from the corresponding achiral 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°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.[1] However, the chiral 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°C (Figure 3A). On further cooling, however, texture change occurred at 66°C (Figure 3B) and typical "fan-shape" texture appeared at 60°C (Figure 3C), which was miantained down to room temperature, It is interesting to note that at this temperature (66°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.[7,8]

Contrary to the chiral 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°C, which was maintained without any texture change down to the first transition temperature (Figure 4). The results of the texture observations on PcH_2's (**1a** and

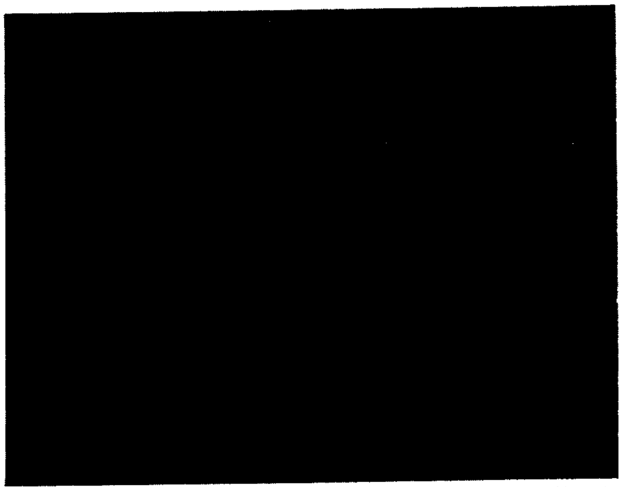


Figure 5. Optical texture of the chiral CuPc **2a** at 100°C (X300).

1b) suggest that the chiral PcH_2 **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_2's reported in literatures so far.[9] This result could be regarded as a another evidence that the chiral PcH_2 **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 A (characteristic van der Waals distance for aromatic compounds) for PcH_2 and CuPc, respectively.[4,10,11] 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_2 **1a**, and the difference in optical textures of the chiral PcH_2 **1a** and CuPc **2a**, the PcH_2 **1a** can be regarded as the first true columnar cholesteric phase displayed by the discotic liquid crystal systems.

Acknowledgement. The partial financial support of this work by Lucky Inc. is gratefully acknowledged.

References

1. S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, Pramana, **9**, 471 (1977).
2. C. Destrade, N. H. Tinh, J. Malthete, and J. Jacques, *Phys. Lett.*, **79A**, 189 (1980).
3. J. Malthete, C. Destrade, N. H. Tinh, and J. Jacques, *Mol. Cryst. Liq. Cryst. Lett.*, **64**, 233 (1981).
4. D. Guillon, A. Skoulios, C. Piechocki, J. Simon, and P. Weber, *Mol. Cryst. Liq. Cryst.*, **100**, 275 (1983).
5. C. Piechocki and J. Simon, *Nouveau J. de Chimie*, **9**, **No.3**, 159 (1958).
6. G. Pawlowski and M. Hanach, Synthesis, 287 (1980).
7. O. Lehman, *Z. Phys. Chem.*, **56**, 750 (1906).
8. D. Coates and G. W. Gray, *Phys. Lett.*, **51A**, 335 (1975).
9. I. Cho and Y. Lim, *Mol. Cryst. Liq. Cryst.* **154**, 9 (1988).
10. C. Piechocki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, *J. Am. Chem. Soc.*, **104**, 5245 (1982).
11. J. J. Andre, M. Bernard, C. Piechocki, and J. Simon, *J. Phys. Chem.*, **90**, 1327 (1986).

Dipole Moments of the OH, OH^+ and OH^- Valence States by *ab initio* Effective Valence Shell Hamiltonian Method

Hosung Sun

Department of Chemistry, Pusan National University, Pusan 609-735. *Received December 18, 1987*

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^+ and OH^- 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 quasidegenerate states of simple many-body perturbation theory (MBPT), a diagramatic representation of ordinary Rayleigh-Schrödinger perturbation theory for a reference nondegenerate single determinantal unperturbed wavefunction.[1-5]