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A Columnar Cholesteric Liquid Crystal Based on Phthalocyanine Core

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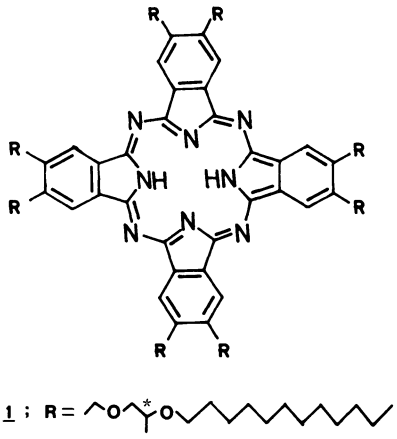
A new columnar cholesterogen based on the octasubstituted phthalocyanine(PcH_2), (+)-2,3,9,10,16,17,23,24-octakis[4-(dodecyloxy)-2-oxa-pentyl]-phthalocyanine(1), is described. The chiral PcH_2 1 exhibited classical cholesteric textures in which the transition of platelet to fan-shaped texture was observed ($K \xrightarrow{23\ ^{\circ}C} M \xrightarrow{158\ ^{\circ}C} I$). This is the first instance of columnar cholesterogen observed with disc-like liquid crystal systems.

In recent years, optically active discotic liquid crystals have been investigated in search for the disc-like cholesterogens. Destrade et al. have first reported the cholesteric phase in disc-like mesogens 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.[1] They have also synthesized the first genuine disc-like molecule with cholesteric properties, (-)-2,3,6,7,10,11-hexa-[S-(4-methyl)-4-n-hexyloxybenzoyloxy]-triphenylene.[2] However it should be noted that the triphenylene derivatives mentioned above are related to N_D phases (not columnar D-phase) and the resulting N_D^* phases exibited oily streak textures.

Since phthalocyanine derivatives were characterized as columnar D-phases by Piechocki et al.,[3,4] we have focused our attention on these columnar discogens and designed a structure of chiral PcH_2 1 (Fig. 1). We now like to report the synthesis and properties of a new genuine columnar cholesterogen. The deep bluish 1 was synthesized from S-(+)-1,2-propanediol and characterized by IR, ^1H and ^{13}C NMR spectroscopic data, and microanalysis.[5]



1 ; R=

Fig. 1. Chemical structure of PcH_2 1.

Observations of phase transition temperatures and microscopic textures were carried out using DSC (Du Pont 990TA 910 DSC; heating rate 10 °C/min) and Leitz polarizing microscope equipped with Mettler FP 52 hot stage. The thermograms of 1 showed clearly two endothermic peaks at 23 and 158 °C. Upon heating above 155 °C, 1 gave highly fluid isotropic phase at 160 °C. Upon cooling below 155 °C, an anisotropic phase began to reappear at 153 °C, showing the texture similar to

platelet(blue phase) (Fig. 2a). However, the texture changed at 66 °C to typical cholesteric fan-shape and remained without further change down to room temperature (Fig. 2b). It should be noted that at this temperature(66 °C) no transition could be detected by DSC. This transition of platelet texture to fan-shape is commonly observed in twisted smectic C phases,[6,7] and can be attributed to the discotic cholesterogen character of 1. This result was, we believe, the first instance in that pure columnar cholesterogen was observed with discotic liquid crystal systems. Continuous endeavor with this type of liquid crystals may lead to interesting practical applications. Further investigations for the related cholesteric systems are now in progress and the results will be published in forthcoming papers.

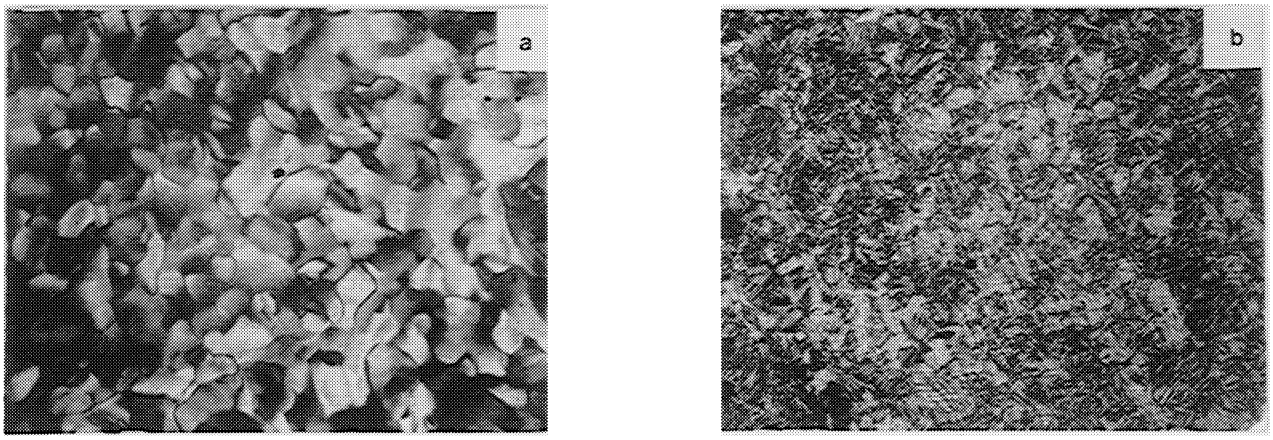


Fig. 2. Optical textures observed with 1: (a) Platelet texture observed at 130 °C; (b) Fan-shaped texture at 25 °C (x 300).

References

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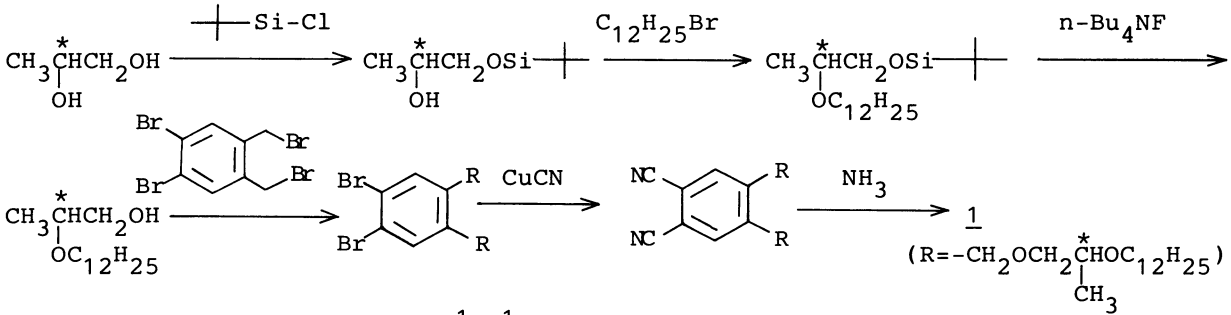

1 : IR(KBr) 3300, 1120, 1105 cm^{-1}; ^{1}H-NMR($CDCl_3$) 1.16(m, 208H), 3.82(m, 40H), 5.25 (bs, 16H), 9.36(bs, 8H); ^{13}C-NMR($CDCl_3$) 14.7, 18.5, 23.2, 27.1, 30.3, 31.1, 32.6(aliphatic), 70.3(-CH_2-O), 72.6(chiral-C), 75.5(Ar-CH_2-O), 123.5, 136.2, 139.4, 149.9(aromatic); Analysis for $C_{160}H_{274}N_8O_{16}$(2566.0), Calcd % (Found %) C 74.8(75.1), H 10.76(10.68), N 4.37(4.45).

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