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A PURE DISC-LIKE MOLECULE WITH CHOLESTERIC PROPERTIES

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Abstract

A cholesterogenic disc-like derivative of triphenylene is described. The N_D^* phase exhibits oily streaks from 192.5 to 246.5°C. That is the first evidence of a cholesteric phase in a pure disc-like molecule.

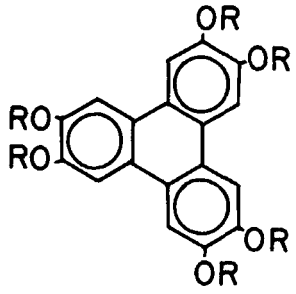
Introduction

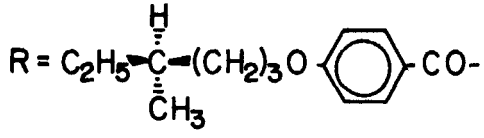
Recently, we have shown[1] that an optically active disc-like molecule, when dissolved in the N_D nematic phase (N_D : a nematic phase built up with disc-like molecule[2]) of 2,3,6,7,10,11-hexa(4-n-heptyloxy)benzoyloxytriphenylene, induced a torsion. This result suggested us to build up a pure chiral disc-like molecule with such a cholesteric behaviour.

We describe in the present letter the first example of a pure disc-like compound which exhibits "cholesteric" properties : (+)-2,3,6,7,10,11-hexa-[S-(4-methyl)-4-n-hexyloxybenzoyloxy] triphenylene 1 displays a twisted N_D (or N_D^*) phase in the range of 192.5°C ($K \rightarrow N_D^*$) to 246.5°C ($N_D^* \rightarrow I$).

Experimental

This compound 1 was prepared by reaction of the S-(+)-(4-methyl)-4-n-hexyloxybenzoyl chloride 2 with 2,3,6,7,10,11-hexahydroxytriphenylene in anhydrous pyridine and was purified by thin layer chromatography on silicagel (using 40% acetone/hexane mixture as an eluant) and recrystallized from ethanol/diethylether mixture[3].

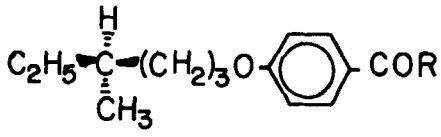




1

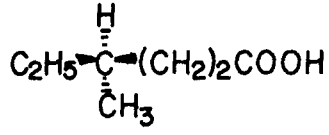
The acid chloride 2 was prepared from S-(-)-2-methylbutanol, the p-toluenesulfonate of which was condensed with sodium diethyl malonate to give S-(+)-4-methylhexanoic acid 4. 4 was reduced ($LiAlH_4$ in boiling THF) and the resulting alcohol was condensed, via its p-toluenesulfonate, with the di-sodium salt of 4-hydroxybenzoic acid in DMF (2 h, reflux). Saponification afforded S-(+)-(4-methyl)-4-n-hexyloxybenzoic acid 3, which was purified by crystallization from aqueous ethanol : K 116 S_C^* 126 I; $[\alpha]_{578}^{25}$: +9.0° (c≈1, $CHCl_3$). The reaction of 3 with thionyl chloride afforded 2.

Transition temperatures of 1 were determined by calorimetry using a DSC2 (Perkin Elmer). The textures were observed with a polarising microscope equipped with a heating and cooling stage (Mettler FP5).



R = Cl 2

= OH 3



4

Results

This compound 1 is mesogenic. The cholesteric range is K 192.5 N_D^* 246.5 I. Microscopic observations of optical textures of this fluid phase shown oily streaks (Fig. 1) similar to those observed from a 50/50 mixture in weight of C_7OHBT(*) and (+)-2,3,6,7,10,11-hexa-[S-(3-methyl)-nonanoyloxy] triphenylene[1].

This N_D^* phase is entirely miscible with the N_D nematic one of the C_6OHBT derivative (Fig. 2). In this contact, one can see the oily streaks of 1 overgrow the N_D nematic phase of C_6OHBT.

Let us point out that the existence of cholesteric properties seems to be very dependent to the structure of the chiral chain attached to the benzoic acid. We have observed that optically active compounds 1 with R = S-(+) n-C_6H_{13}-$CH(CH_3)(CH_2)_2O$-  -CO- and S-(+) n-C_4H_9-$CH(CH_3)$-CH_2-O-  -CO- exhibit respectively only a rectangular columnar phase D_{rd}, and none mesomorphic propertie. This behaviour recalls the hard dependence of the classical nematic stability toward the ramifications[5].

(*) C_7 OHBT is 2,3,6,7,10,11-hexa(4-n-heptyloxy)benzoyloxy-triphenylene.

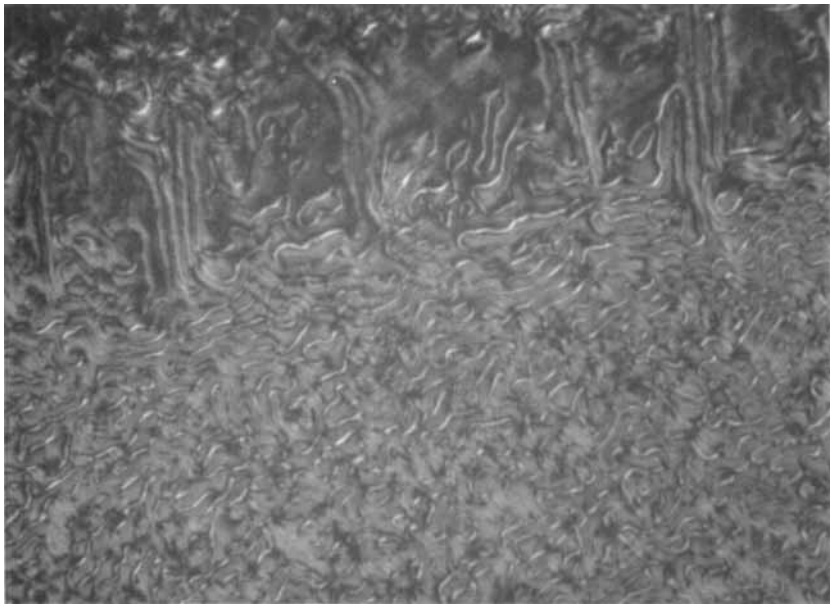


Fig. 1 : Optical texture observed from derivative 1 at 190°C : oily streaks.

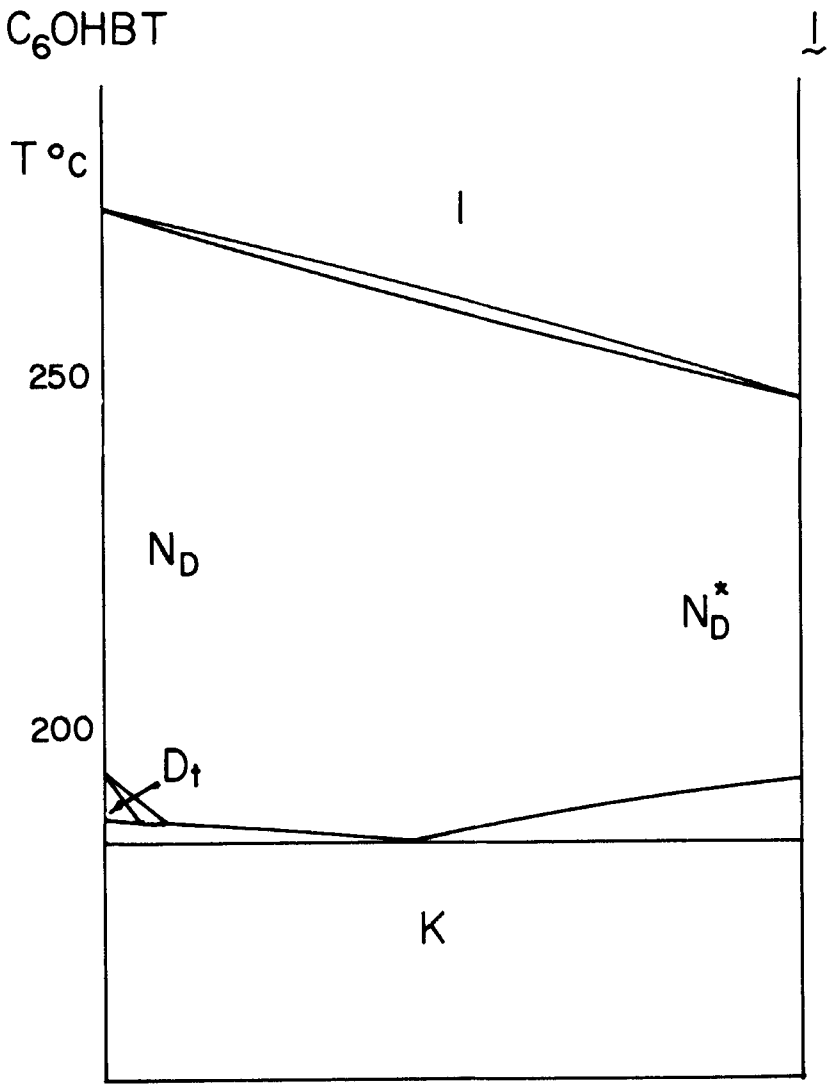


Fig. 2 : Isobaric phase diagram between C_6OHBT and $\underset{\sim}{1}$.

References

1 C. Destrade, Nguyen Huu Tinh, J. Malthête and J. Jacques, Physics Letters, 79A, 189 (1980)

2 Nguyen Huu Tinh, C. Destrade and H. Gasparoux, Physics Letters, 72A, 251 (1979)

3 $[\alpha]^{25}_{578}$ = +8.6° (c∿2, $CHCl_3$) ; IR (nujol) 1740-1610-1510-1250-1170 cm^{-1} ; H NMR ($CDCl_3$, TMS) δ0.7...1.8 (m, 78H), δ3.85 (t, 12H), 6.55 and 7.80 (2d, 24H), δ8.25 (s, 6H) ; Anal. Calcd for $C_{102}H_{120}O_{18}$: C, 74.97 ; H, 7.40 ; Found : C, 75.25 ; H, 7.46.

4 This N^*_D phase is right-handed with a comparatively large pitch (about 30 μm at ∿ 200°C). We are grateful to Prof. J. Billard for these preliminary measurements.

5 J. Malthête, J. Billard, J. Canceill, J. Gabard et J. Jacques, J. Physique Colloq. 37 C3, 1 (1976)