

Temperature Dependent Sign Reversal of the Optical Anisotropy in Pyramidic Mesophases

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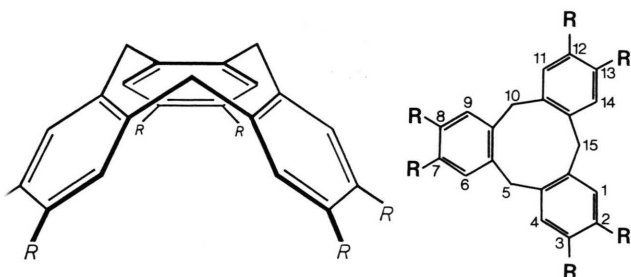
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Hexasubstituted tribenzocyclononene derivatives with $R = -OC(O)C_6H_4C_nH_{2n+1}$ and $R = -OC(O)C_6H_4OC_nH_{2n+1}$ possess enantiotropic pyramidic mesophases. These mesophases exhibit an uncommon feature in that their optical anisotropy changes sign as function of temperature within the mesophase region. It is suggested that this effect reflects conformational changes involving the side chain benzene ring.

Recently a new type of liquid crystalline mesophases was discovered consisting of pyramidal-shaped molecules which are piled together to form columnar phases similar to the classical discotics [1–3]. Since, however, the central core of the pyramidal molecules possesses an electric dipole moment parallel to their symmetry axis, the resulting columns acquire a macroscopic electric dipole moment, and consequently these pyramidal mesophases should be either ferro- or antiferroelectric [1, 4]. The compounds which were so far reported to exhibit pyramidal mesophases are all derivatives of tribenzocyclononene [5] (I) with R being either OC_nH_{2n+1} , $OC(O)C_nH_{2n+1}$ or $OC(O)C_6H_4OC_nH_{2n+1}$.



In the present note we report on an additional homologous series of substituted tribenzocyclononene which forms pyramidic mesophases, viz. hexa-*n*-alkylbenzoyloxytribenzocyclononene



These mesophases exhibit an uncommon optical behaviour in that their optical anisotropy changes sign as function of temperature.

Three members of this series with $n = 7, 8$ and 10 were studied. They were prepared by reacting hexahydroxytribenzocyclononene with the corresponding alkylbenzoylchlorides in pyridine [1] and purified over silica-gel with CH_2Cl_2/n -hexane as eluent. The phase transition temperatures and enthalpies, determined with a Mettler T.A. 3000 differential scanning calorimeter (DSC) are summarized in Table 1. These results refer to increasing of the temperature. Cooling from the isotropic liquid gives the same phases but only after considerable supercooling (by 20 to 30 °C) for both the liquid to mesophase and the mesophase to mesophase transitions. The room temperature mesophases are apparently monotropic and would crystallize only after very long durations. One sample of I-8, which was kept at -15 °C for fifteen days, gave crystals with the above reported melting point of 21.3 °C. Another sample that was kept at room temperature for about one year showed on first heating a strong single DSC peak at 45 °C ($\Delta H = 14.8$ kJ/mole). Attempts to crystallize the

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Table 1. Phase transition temperatures (in °C) and (in brackets) enthalpies (in kJ/mole) of the compounds I-*n* ($R=C_nH_{2n+1}C_6H_4C(O)O-$) and II ($R=C_{10}H_{21}OC_6H_4C(O)O-$) studied in the present work^a.

Com- pound	K	P ₁	P ₂	L	Tr ^b
I-7	– 33.0 (8.4)	– 57.3 (0.2–2) ^c	– 149.1 (9.6)	–	24.5
I-8	– 12.0	– 21.3 (8.2) ^d	– 156.5 (13.8)	–	– 3
I-10	–	– 43.0 (7.8)	– 162.0 (15.9)	–	40
II	– 50.6 (4.8)	– 100.0 (16.0)	– 190.2 (20.4)	–	≤ 0

^a In this table K stands for crystal, P for pyramidic mesophase and L for isotropic liquid. The data were obtained on a Mettler T.A. 3000 Differential Scanning Calorimeter upon heating.

^b Temperature at which optical anisotropy changes sign (in °C) within the high temperature monotropic mesophase.

^c The enthalpy change of this transition is not reproducible and sometimes is not detected at all.

^d The 12.0 and 21.3 transitions are not well resolved. The enthalpy of 8.2 refers therefore to the sum of both transitions.

mesophase by cooling to liquid nitrogen temperature for short periods were unsuccessful. At room temperature these compounds are colorless birefringent pastes. In the polarizing microscope they exhibit spherulite structures with radial rectilinear defects, similar to those observed in pyramidic liquid crystals (see Fig. 1) hence we assume that these mesophases too are columnar pyramidic. The mesophase → mesophase transitions of Table 1 have very small transition enthalpies and are not associated with discontinuities in the pattern observed in the polarizing microscope, except for the appearance of circular striations in the low temperature mesophase of I-7. This suggest that the various mesophases have very similar structures with perhaps small changes in the columnar arrangements. Miscibility studies on contact preparations have shown that the high temperature phases of the three homologues belong to the same class. Calculations [6, 7] for binary systems with nearly equal concentrations of homologues predict the existence of mixtures with a very wide range of thermodynamic stability for this phase.

A peculiar property of these compounds is the reversal of sign of the optical anisotropy. Using a

tungsten lamp as light source and a λ -plate we found that all three compounds of series I when in the high temperature monotropic mesophase change the sign of Δn from negative at high temperature to positive at low temperature. As an example we depict in Fig. 1 the pattern observed in the polarizing microscope above, around and below the sign reversal temperature (Tr) for compound I-10. The sign reversal temperature for this compound is completely reversible with respect to heating and cooling (Tr = 40 °C) and does not appear to be related to any transition between mesophases. A similar reversal of sign was observed for the compounds I-8 and I-7 (see Table 1), but for the latter the sign reversal temperature on heating and cooling was not the same (24.5 and 14.5 °C, respectively). In this compound the phase transition hysteresis, i.e. the supercooling was also more significant than in the other compounds. In contact preparations of I-8 and I-10 it was found that Tr changes monotonically with the mole fraction on going from one pure compound to the other.

In the absence of a λ -plate one observes a change in the color of the transmitted light from blue above Tr to brown-red below Tr, apparently due to change in the absorption spectrum (cf. right column of pictures in Fig. 1). Although no normally oriented areas have been observed, the vanishing of the birefringence at Tr strongly suggests that the mesophase is uniaxial. This is so since, while it is conceivable that the two refraction indices of such a phase will cross each other, it is very unlikely that the three indices of a biaxial phase will do so at the same temperature. The texture of the spherulite domains remains however the same on both sides of the sign-transition temperature. This suggests that the reversal of the optical anisotropy is associated with changes in the molecular conformation rather than in the molecular ordering of the mesophase. It is well known that the optical refraction of a compound is an additive property of the various molecular constituents with major contributions from highly polarizable units such as heavy atoms, multiple bonds and aromatic rings. In the present case the benzoyl groups of the side chains are probably the major contributors to Δn . The contribution depends, however, very delicately on their relative orientation with respect to the molecular frame. Small changes in the orientation of these groups may therefore change the overall Δn from positive to negative.

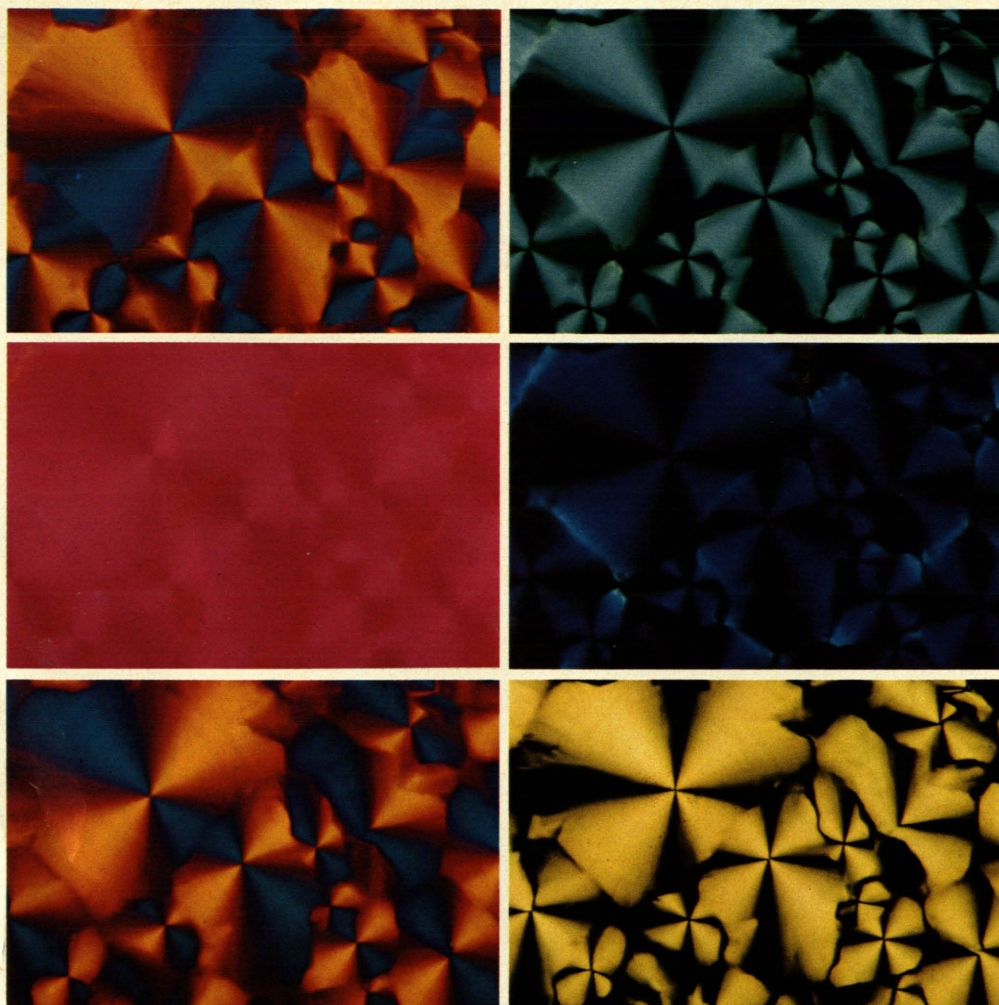


Fig. 1. Photomicroscopic pictures of the compared I-10 in the mesophase region obtained with a polarizing microscope (mag. $\times 160$). All pictures are of the same domains. Those on the left are with a λ -plate, while those on the right without. The temperatures from top to bottom are 70, 40, and 20 °C and correspond to above, about and below T_r .

Preliminary observations on hexadecyloxybenzoyloxytribenzocyclononene ($R=OC(O)C_6H_4OC_{10}H_{21}$) (compound II in Table 1) show that this compound too exhibits sign reversal of Δn . However, in this case the reversal is opposite to that of the alkylbenzoyloxy derivatives; here at room temperature Δn is positive, and it becomes negative on cooling. (The exact sign reversal temperature could not be determined but it is well below 0 °C.) Note that the only difference between II and I-10 is the presence of an oxygen atom in the side chain. These results support

the interpretation that the sign reversal results from a delicate balance of contributions from the various conformations and dipole moments.

We are not aware of other cases in which Δn of a neat phase reverses sign as function of temperature, although sign reversal as function of wave length in uniaxial crystals of silver gallium sulphide [8], and position [9] in inhomogeneous polymer preparation is known. Another related observation is that of Müller and Stegemeyer [10] who observed sign reversal of Δn at the compensation temperature of

cholesteric mixtures. This effect is, however, due to the spacial arrangement of molecules rather than to conformational changes as suggested above for pyramidic mesophases.

Acknowledgement

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