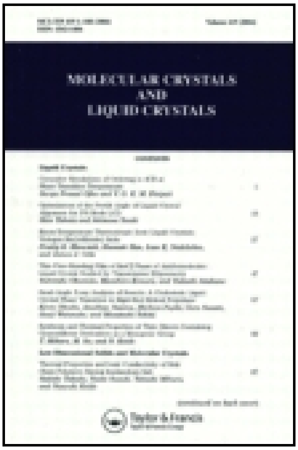

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The Liquid Crystal Properties of 1-(4-Cyanophenyl)-*trans*-4-n-dodecylcyclohexane (PCH-12)

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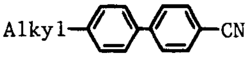
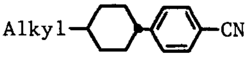
1-(4-Cyanophenyl)-*trans*-4-*n*-dodecylcyclohexane, a long chain member of the PCH series of liquid crystal materials has been prepared and its phase behavior established by optical microscopy and DSC. In comparison with the purely smectic (S_A) biphenyl analogue (K36), PCH-12 maintains an enantiotropic nematic phase range of about 9°C above its monotropic smectic A phase, allowing a clearer comparison to be made between the smectic tendencies of the PCH and the K series.

INTRODUCTION

In recent years, two series of compounds forming liquid crystal phases have been the centres of particular interest from both an academic and a commercial standpoint. These materials belong to the series of 4-alkyl-4′-cyanobiphenyls (I)[1] and 1-(4-cyanophenyl)-*trans*-4-alkylcyclohexanes (II)[2]—known respectively as the K and PCH series.



((I) - K series)



((II) - PCH series)

These compounds have featured strongly in applications in various forms of electro-optical display and their properties are often the subject of comparison, the PCH series having higher clearing points, and a lower birefringence, dielectric anisotropy, and viscosity. Another factor of significance relates to the smectic tendencies of these materials. The K-series introduces smectic properties at the n-octyl (C_8) homologue; this is an advantage in some respects, eg, materials[3] are provided that are of interest for laser-addressed smectic displays, but a disadvantage in others. On the other hand, in the PCH series, one of the highest homologues to be studied (n-nonyl, C_9) was found to exhibit purely nematic properties.

The PCH series has therefore always been regarded as considerably less smectogenic than the K series, but until now no more clearly defined comparison has been possible.

RESULTS AND DISCUSSION

The C_{12} homologue of the PCH series has now been made. 1-(4-Cyanophenyl)-*trans*-4-*n*-dodecyclcyclohexane (III) exhibits a smectic A phase *and* a nematic phase,

(III)

whereas the C_{12} homologue of the K series is *purely* smectic. The relevant $T_{S_A\text{-}N}$, $T_{S_A\text{-}I}$ and $T_{N\text{-}I}$ values are given below for comparison.

Compound (III)	S_A-N 52°C N-I 61.1°C
Compound (I) (alkyl = C_{12})	S_A-I 58.5°C

The maintenance of nematic properties in the PCH material (III) clearly demonstrates that even with this long alkyl substituent, the nematic thermal stability still exceeds that of the smectic phase, whereas in the biphenyl analogue, purely smectic properties have taken over.

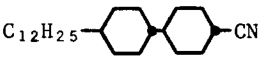
The lower clearing temperatures of the K series make stricter comparisons more difficult, but if we compare the transition temperatures for:

a. the C_7 homologue of the K series (I), N-I 42.8°C, and
b. the C_7 homologue of the PCH series (II), N-I 57°C,

we see that the nematic thermal stability has *decreased* on passing from PCH to K series by 14.2°C.

A similar comparison for the C_{12} homologues shows however that from the PCH to the K series, the smectic thermal stability has *increased* by 6.5°C. This puts the relative smectic tendencies of the two series on a clearer numerical basis for the first time.

Finally, we note that the liquid crystal properties of the CCH compound (IV) have also been established.[4] The material is purely nematic



(IV)

C-N 68°C N-I 78°C

and the nematic phase supercools to room temperature. Therefore on passing along the sequence

K 36 → PCH 12 → CCH 12

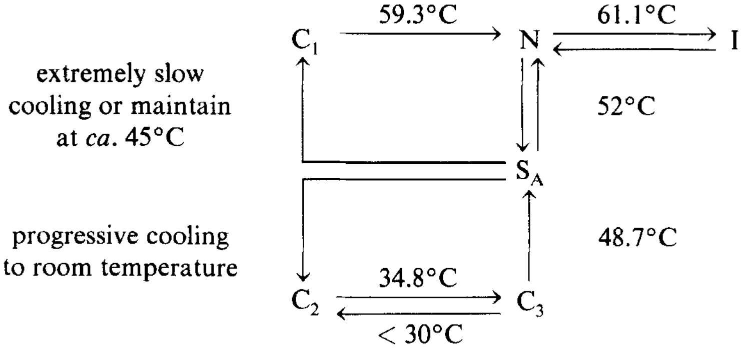
$T_{N\text{-}I}$ increases and the smectic properties diminish.

The smectic phase of PCH 12

The smectic phase of the compound PCH-12 was proved to be smectic A by miscibility experiments using 4-cyano-4′-*n*-octylbiphenyl which has $T_{S_A\text{-}N}$ 33.5°C and $T_{N\text{-}I}$ 40.5°C. The transition temperatures for a 50 : 50 (w : w) mixture with PCH-12 were $T_{S_A\text{-}N}$ 37.8°C and $T_{N\text{-}I}$ 50°C. The mean of the $T_{S_A\text{-}N}$ values of the C_8 homologues of the K and PCH series is 42.8°C. The $T_{S_A\text{-}N}$ curve connecting the two C_8 homologues across the diagram of state therefore has a slight concavity. The mean of the two $T_{N\text{-}I}$ values is 50.8°C and the $T_{N\text{-}I}$ curve is by contrast almost a straight line.

Transition temperatures for PCH-12

The overall melting behavior of PCH-12 is complicated by the occurrence of polymorphic crystal forms. The position has been elucidated by a combination of optical microscopy and DSC. The sequence of transitions is illustrated below:



The stable crystal form C_1 (obtained by crystallisation from a solvent) melts at 59.3°C giving a short enantiotropic nematic phase. On cooling this forms the S_A phase which is monotropic with respect to C_1. If the smectic A phase is cooled very, very slowly so that crystallisation occurs above about 40°C or is kept at say 45°C till crystallisation occurs, C_1 is formed. Steady progressive cooling gives another crystal form C_2 which on heating converts into C_3; this transition is reversible on cooling. C_3 then melts to form the S_A phase at 48.7°C. Both nematic and smectic A phases are therefore enantiotropic with respect to C_3 and C_2. The S_A phase never forms C_3 directly on cooling.

These observations made by optical microscopy were confirmed by DSC. A fresh sample of PCH-12 gives a single, large endotherm corresponding to the C_1-N transition at 59.3°C; this peak carries a weak shoulder corresponding to the N-I transition at 61.1°C (heating rate 10°C/min). At slower heating rates, the N-I peak is clearly resolved from the C_1-N peak. The enthalpy values obtained (see Fig. 1) at a heating rate of 2°C/min are:

C_1-N	29.19 cal g^{-1}
N-I	0.73 cal g^{-1}

If the sample is cooled and maintained at about 45°C until crystallisation occurs, the above events are reproduced on heating.

Rapid, progressive cooling at 10°C/min to room temperature followed by heating produces different responses, dependent upon the rate of heating.

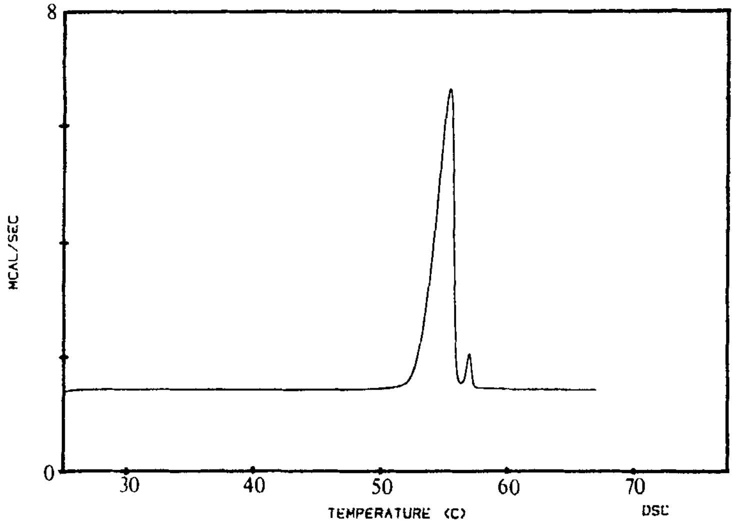


FIGURE 1 DSC trace for PCH-12 (C_1 form); heating rate 2°C/min; $C_1 \rightarrow N \rightarrow I$.

Fast heating rates (20°C/min) allow the sequence below to be observed:

$$C_2 \rightarrow C_3 \rightarrow N \rightarrow I$$

The C_3-S_A and S_A-N peaks are not then resolved.

Slow heating rates (< 10°C/min) give the S_A phase formed from C_3 time to convert into the stable crystal form C_1 which then melts at a higher temperature forming the nematic phase. The formation of C_1 is shown as an exotherm.

At a heating rate of 10°C/min, it seems that either of the two possibilities mentioned above may be observed. Fig. 2 shows the case in which the $C_2 \rightarrow C_3 \rightarrow N \rightarrow I$ sequence occurs. The enthalpies for the transitions are:

C_2-C_3	2.0 cal g^{-1}
C_3-(S_A)-N	22.6 cal g^{-1}
N-I	1.12 cal g^{-1}

Fig. 3 shows a case (again at a heating rate of 10°C/min) where the C_2-C_3 transition occurs, but immediately after the peak associated with melting of C_3 there is an exotherm denoting formation of C_1

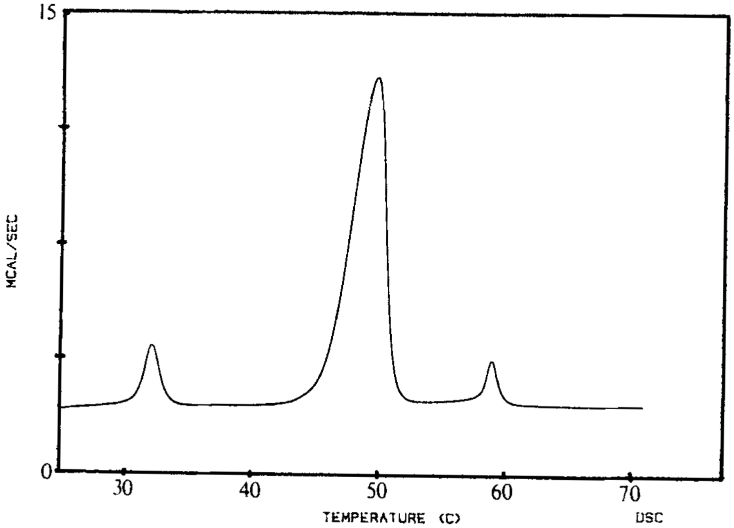


FIGURE 2 DSC trace for PCH-12 (C_2 form); heating rate ≥ 10°C/min; $C_2 \rightarrow C_3 \rightarrow N \rightarrow I$.

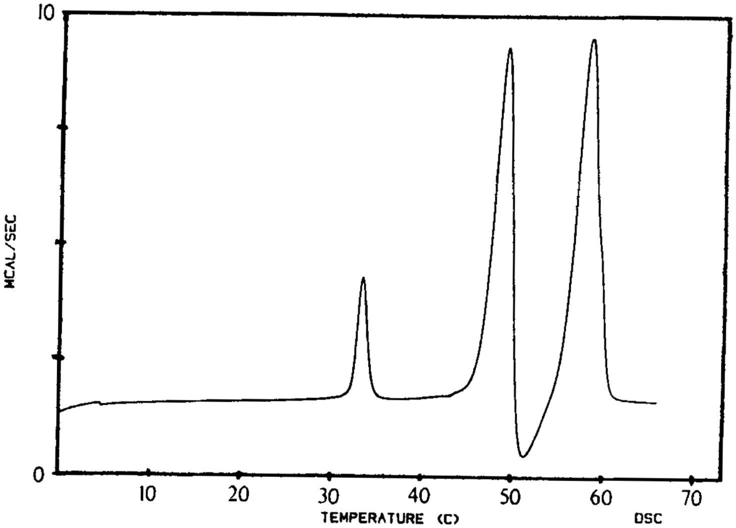


FIGURE 3 DSC trace for PCH-12 (C_2 form); heating rate 10°C/min; $C_2 \rightarrow C_3 \rightarrow S_A$ (unresolved) $\longrightarrow C_1$ (exotherm) $\rightarrow$ I (N-I unresolved).

which then melts at a higher temperature to form the isotropic liquid (T_{N-I} unresolved).

It is noted that the total enthalpy measured for the change $C_1 \rightarrow N \rightarrow I$ at a heating rate of 10°C/min is 30.72 cal g^{-1}. The total enthalpy of transition from $C_2 \rightarrow C_3$-(S_A)-N-I is 25.72 cal g^{-1}. Therefore the stable crystal form C_1 is more stable than the other crystal form C_2 that may exist at room temperature by 5.0 cal g^{-1}.

The enthalpy of the S_A-N transition can be evaluated readily from cooling cycles. However, if a sample is cooled to give the S_A phase and reheated before crystallisation occurs, the enthalpy of the S_A-N transition is obtained on heating. The enthalpy in either case is about 0.02 cal g^{-1}. This low value is typical of S_A materials involving pairwise anti-parallel correlation of cyano-substituted molecules, and a similar situation arises for the S_A-N transitions of the 4-alkyl-4′-cyanobiphenyls.

The above behavior diagnosed from DSC was confirmed by optical microscopy. The growth of the stable crystal form C_1 in the smectic A phase formed from crystal form C_3 could readily be observed. The S_A phase is texturally typical—largely homeotropic, but with some characteristic focal-conic areas. Only by optical microscopy can the change $C_3 \rightarrow C_2$ be observed on cooling.

EXPERIMENTAL

1-(4-Cyanophenyl)-*trans*-4-n-dodecylcyclohexane (PCH-12) was prepared by procedures already published for lower homologues of the series. Spectroscopic data were in accordance with the required structure and the purity of the material as assessed by capillary g.l.c. was 99.7%.

Optical Microscopy was carried out using a Nikon LKe polarising microscope in conjunction with a Mettler FP 52 heating stage and control system FP 5.

Thermal Analysis: Data were obtained using a Perkin-Elmer DSC-2C instrument.

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