Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: I. C. Lewis & C. A. Kovac (1979): Liquid Crystal Transitions of p-Sexiphenyl, Molecular Crystals and Liquid Crystals, 51:3-4, 173-178

To link to this article: http://dx.doi.org/10.1080/00268947908084703

Mol. Cryst. Liq. Cryst., 1979, Vol. 51, pp. 173–178

Printed in Holland

Liquid Crystal Transitions of *p*-Sexiphenyl

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(*Received July 14, 1978; in final form October 20, 1978*)

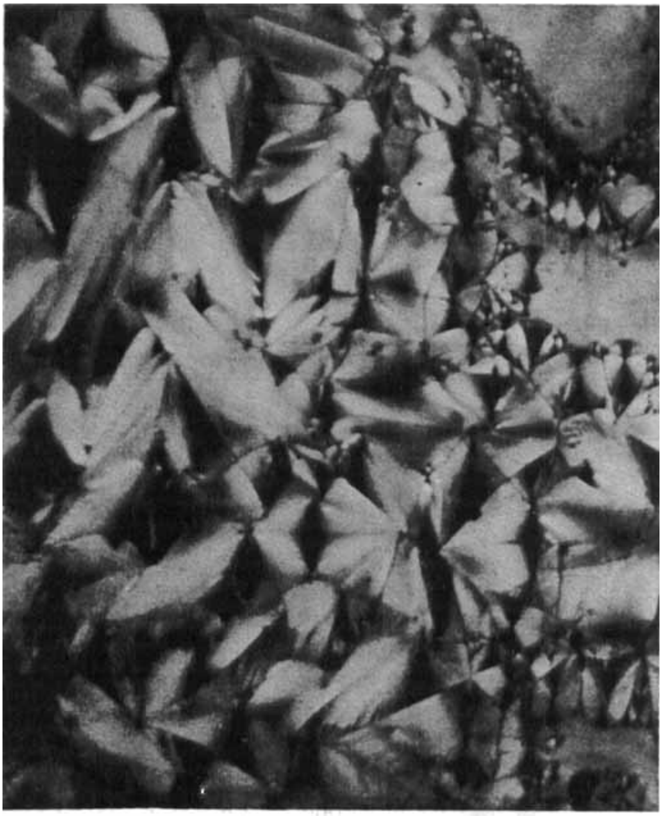
I INTRODUCTION

Vorlander,[1] studying the melting behavior of various polyphenyl compounds, reported that both *p*-quinquephenyl and *p*-sexiphenyl exhibited liquid crystalline behavior. Based on these early qualitative observations and subsequent melting point determinations,[2] specific mesophase transitions were designated for each compound in the extensive compilations by Demus.[3] Transformation temperatures for solid-to-nematic and nematic-to-isotropic states were assigned for *p*-quinquephenyl. On the other hand, two liquid crystal transitions, solid-to-smectic and smectic-to-nematic, were assigned to *p*-sexiphenyl. Since there is no direct evidence to confirm the nature of these phases and since the occurrence of a smectic transition for *p*-sexiphenyl is inconsistent with recent liquid crystal theory,[4] we have reexamined the melting behavior of *p*-sexiphenyl with the aid of hot-stage polarized light microscopy and differential scanning calorimetry (DSC). The results provide definitive proof for the nature of the liquid crystalline states of *p*-sexiphenyl.

II EXPERIMENTAL PROCEDURE

A Synthesis of *p*-sexiphenyl

p-Sexiphenyl was synthesized by the reaction of *p*-terphenyl (Aldrich Chemical) with $AlCl_3$ and $CuCl_2$.[5] A quantity of six grams of anhydrous $AlCl_3$ and 6 grams of $CuCl_2$ was added to a solution of 10 grams of *p*-terphenyl dissolved in 60 ml of 1,2,4-trichlorobenzene. The mixture was



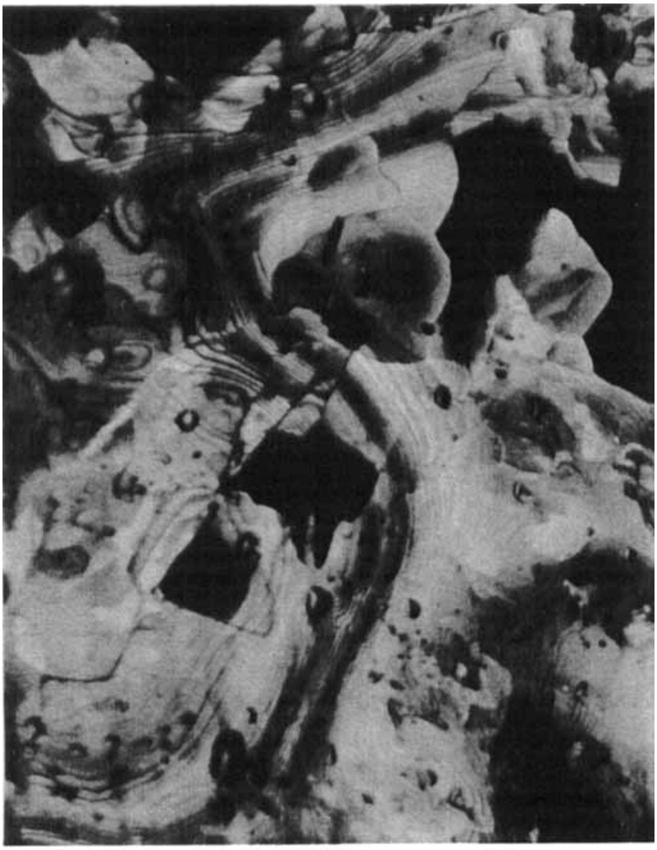
(a)

FIGURE 1 Hot-stage polarized light photomicrographs of smectic mesophase from *p*-sexiphenyl at 435°C (100 × magnification). (a) Focal conic texture. (b) Step droplets.

heated to 80°C and stirred for one hour. The reaction mixture was hydrolyzed with 1 *N* HCl. The solid product was washed with concentrated HCl and water. The unreacted *p*-terphenyl was removed from the product by a Soxhlet extraction with benzene. The benzene insoluble portion was vacuum sublimed to give 2.7 grams of white crystalline *p*-sexiphenyl.

B Hot stage polarized light microscopy

The melting behavior was examined by using a Leitz Ortholux microscope equipped with a polarizer and a Köfler micro hot stage which had been modified to allow purging of the sample chamber with inert gas. The sample was placed between cover slips on the hot stage, heated at a rate of 2°C minute through the melting range under a N_2 atmosphere, and observed in



(b)

FIGURE 1 *(Continued)*

the reflection mode. Photomicrographs were taken with the aid of a Polaroid camera attachment.

The heating rate was controlled with a Hewlett-Packard temperature programmer controller. The temperature was measured with an iron constantan thermocouple inserted into the body of the hot stage and attached to an Omega Model 250 Temperature Indicator.

C Different scanning calorimetry

The DSC measurement was performed by using a DuPont Model 990 Thermal Analyzer with a DSC attachment. The heating rate was 5°C per minute, and the sample was maintained in an N_2 atmosphere. The data

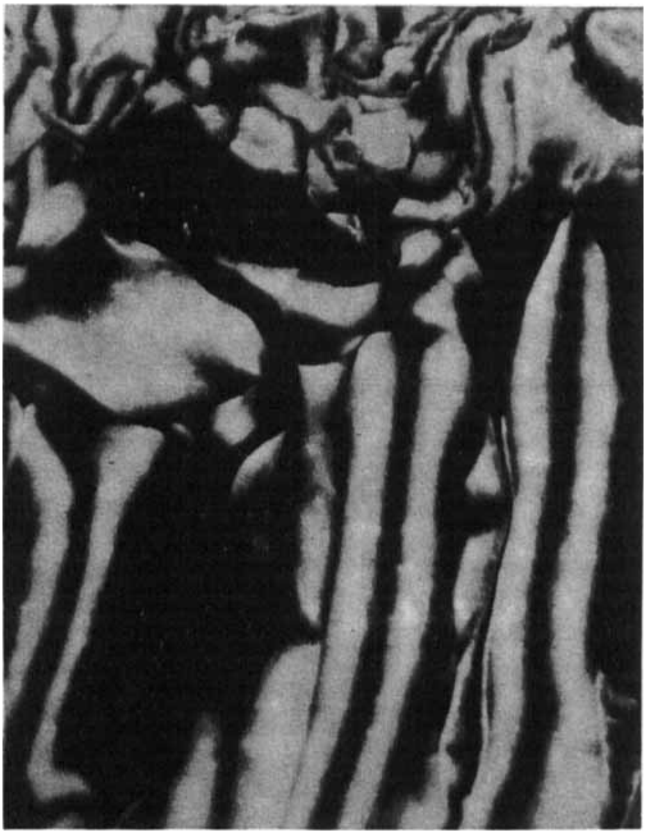


FIGURE 2 Hot-stage polarized light photomicrographs of nematic mesophase from *p*-sexiphenyl at 470°C (100 × magnification).

were analyzed with the aid of a PDP 11/40 computer; standard procedures[6] were followed.

III RESULTS AND DISCUSSION

Two distinct liquid crystal transitions were observed when *p*-sexiphenyl was heated on the microscope hot stage. The first melting transition of the crystalline solid was observed at 435°C, in agreement with melting data in the literature.[2,7] Polarized light photomicrographs depicting the appearance of the mesophase, which forms at 435°C, are shown in Figure 1. The two types of optical textures, focal conic (Figure 1a) and step droplets (Figure 1b), confirm the smectic nature of the mesophase. In fact, the occurrence of these textures is consistent with a smectic A mesophase.[8]

Upon further heating, a second transition to a nematic state occurred at 470°C. Figure 2 presents a photomicrograph depicting the thread-like nematic mesophase observed at 470°C. The nematic state persisted to 500°C, the upper temperature limit of the hot stage. At this temperature, irreversible decomposition reactions began to occur.

The DSC curve measured for *p*-sexiphenyl is shown in Figure 3. The transition temperatures measured from the DSC curve were at 434°C and 464°C. The enthalpy values were determined as 16.9 cal/gm (7.7 Kcal/mole) for the solid-to-smectic transition and 2.43 cal/gm (1.1 Kcal/mole) for the smectic-to-nematic transition. The magnitudes of these enthalpy changes indicate that they are both first-order transitions. The ΔH value of 1.1 Kcal/mole for the second transition is consistent with heat changes that have been reported for other smectic A mesophases.[9]

The observation of a smectic A mesophase for *p*-sexiphenyl is of particular interest in light of current liquid crystal theory. All theoretical treatments of smectic mesophases have to date been based on the theory of McMillan.[4] This theory assumes that the occurrence of a smectic phase in a rodlike molecule results from a strong molecular interaction at a conjugated aromatic central portion of the molecule with the flexible aliphatic ends of the molecule acting to take up space and to increase the interplanar spacing.

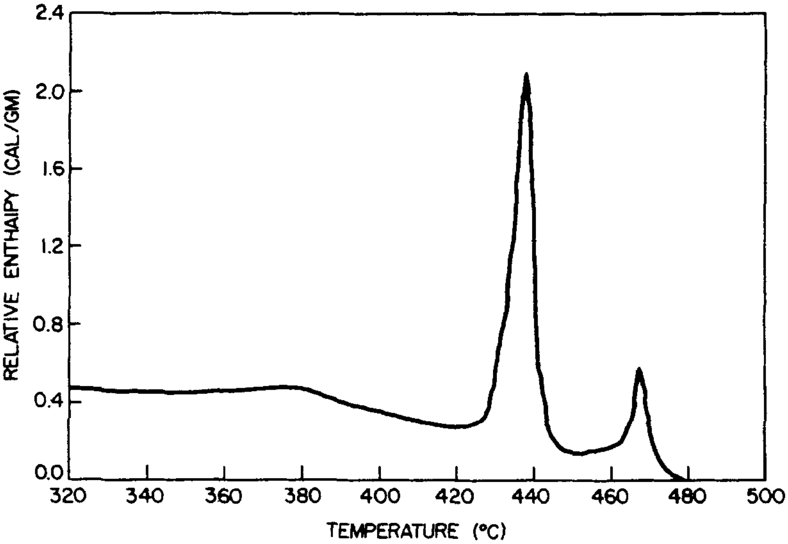


FIGURE 3 Melting behavior of *p*-sexiphenyl by differential scanning calorimetry. (Solid-to-smectic transition at 434°C, smectic-to-nematic at 464°C.)

This structural model has been shown to apply to many known examples of smectic liquid crystals. The fully aromatic hydrocarbon *p*-sexiphenyl, however, is not composed of two dissimilar molecular segments and consists soley of nonplanar phenyl rings. The similarity of the UV absorption spectrum of *p*-sexiphenyl and benzene[10] indicates that very little conjugation occurs between the adjacent phenyl groups in *p*-sexiphenyl. The *p*-sexiphenyl molecule is therefore a particularly striking example of a smectic mesophase which does not conform to the McMillan theory.

The formation of a smectic phase from *p*-sexiphenyl can therefore not be attributed to intermolecular interactions between adjacent planar segments. These results suggest that the McMillan theory is not applicable to all smectic systems and that other effects, such as steric interactions, may perhaps be important in smectic liquid crystal ordering.

Acknowledgement

The authors wish to express their appreciation to Professor A. Saupe for the benefit of valuable discussions and to Dr. S. L. Hager for obtaining the DSC data.

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