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A new smectic phase between S_E and S_B in 4,4'-dipentylbiphenyl

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A new smectic phase between S_E and S_B in 4,4′-dipentylbiphenyl

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A new smectic phase existing between S_E and S_B in the non-polar compound 4,4′-dipentylbiphenyl was observed (DPB). It has been termed smectic E′ [1]. Enthalpies and phase transition temperatures for DPB were measured and characteristic textures of all three smectic phases are presented.

1. Introduction

The polymorphism of 4,4′-dipentylbiphenyl has previously been investigated. In this work [2], the following phase transitions temperatures were cited: C 12 S_E 47 S_B 52 I; these results were confirmed by X-ray investigations [3]. In other work [4], higher temperatures for the phase transitions were disclosed: C 26 S 47·6 S 52·2 I, but the smectic phases were not identified.

Using samples of high purity, between the smectic phases E and B, there has now been found an additional phase which has been termed smectic E′. The existence of two kinds of smectic E phase in polar compounds from the homologous series of 4-alkyl,4″-cyano-*p*-terphenyls has lately been suggested [1]. This new smectic E′ phase was found between phases E and A_d. It is interesting that a similar phase may also exist in the non-polar 4-4′-dipentylbiphenyl. In the case of this compound, the temperature range of existence of the E′ phase is more convenient from an experimental point of view, allowing detailed investigation of this phase.

2. Experimental

4,4′-Dipentylbiphenyl was prepared according to a known method of synthesis for such compounds. The scheme is shown below in figure 1. The compound was purified chromatographically using a silica gel column; hexane was used as eluant.

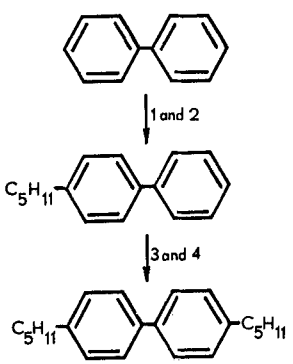

Figure 1. Synthesis scheme (1 and 3, $C_4H_9COCl/AlCl_3/CH_2Cl_2$, 0°C; 2 and 4; $H_2/Pd/C$).

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Then the compound was crystallized three times from a mixture of methanol–THF (5:1). Purity was determined as 99·3 per cent by gas chromatography. The following conditions for analysis were used: chromatograph HP 5890 Series II with capillary column Ultra 2–25 m × 0·32 mm × 0·52 μm, helium as carrier gas, injector temperature 350°, column temperature 260°, injected volume 0·2 μl of 50 per cent chloroform solution (split 1:40) The chromatogram obtained is shown in figure 2. Purity established by DSC according to the procedure given by SETARAM [5] and was 99·5 per cent. Phase transitions temperatures were measured and the textures of the phases observed using a programmable Linkam heating stage 'THM 600' equipped with a polarizing microscope 'Biolar PI'. Enthalpies and temperatures of phase transitions were also determined by use of a scanning calorimeter SETARAM DSC92. Investigations were carried out using a N_2 atmosphere of purity 99·9 per cent.

3. Results

3.1. *DSC measurements*

A DPB sample of 30 mg weight, heating rate 0·5°C min^{-1}, exhibited four phase transitions at the following temperatures (°C):

$$C\ 25{\cdot}1\ S_E\ 46{\cdot}1\ S_{E'}\ 47{\cdot}1\ S_B\ 52{\cdot}3\ I.$$

The enthalpies of these phase transitions (J mol^{-1}) are the following:

$$C\ 7100\ S_E\ 250\ S_{E'}\ 2030\ S_B\ 9560\ I.$$

DSC diagrams are presented in figures 3 (*a*) and (*b*).

A full separation of the thermal events for the phase transitions E–E′ and E′–B was not possible because of the small difference between the phase transition temperatures (1°C), although the maxima for both phase transitions are well

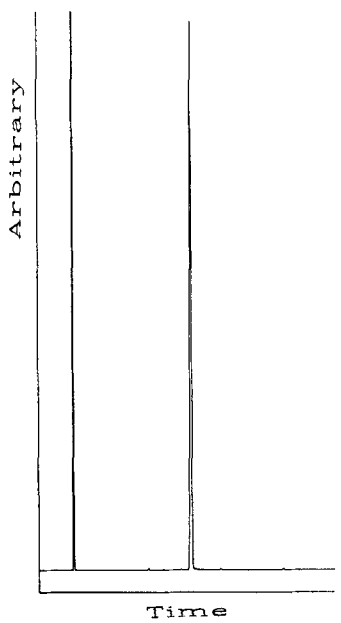
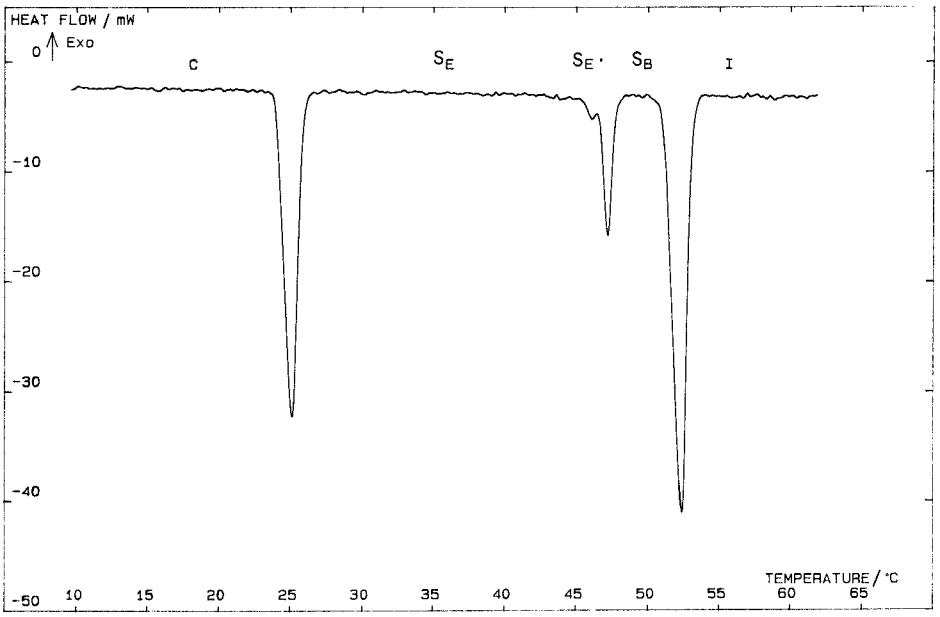
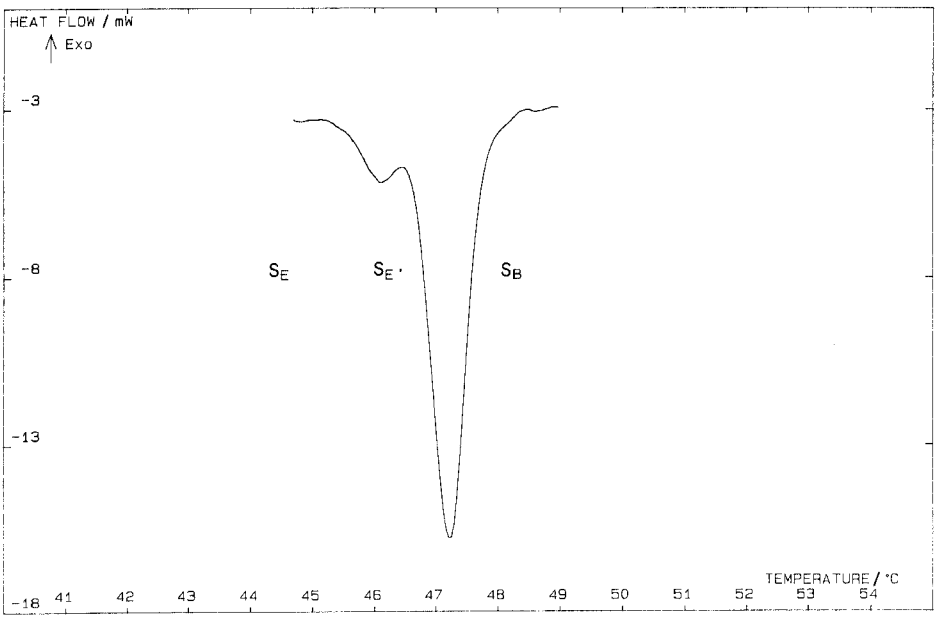


Figure 2. Gas chromatogram for 4,4′-dipentylbiphenyl.



(*a*)



(*b*)

Figure 3. DSC diagrams for 4,4'-dipentylbiphenyl: (*a*) full (*b*) in the temperature range of phase transition E–E'–B.

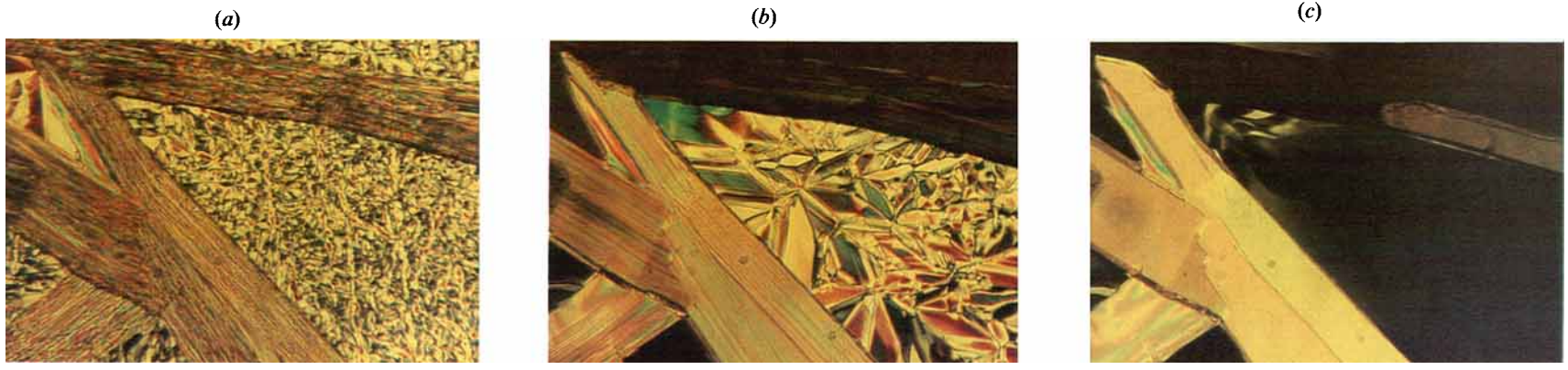


Figure 4. Textures of the smectic phases of 4,4′-dipentylbiphenyl obtained on heating (0·2°C min^{-1}): (*a*) smectic E at 45·5°C, (*b*) smectic E′ at 46·5°C, (*c*) smectic B at 47·2°C.

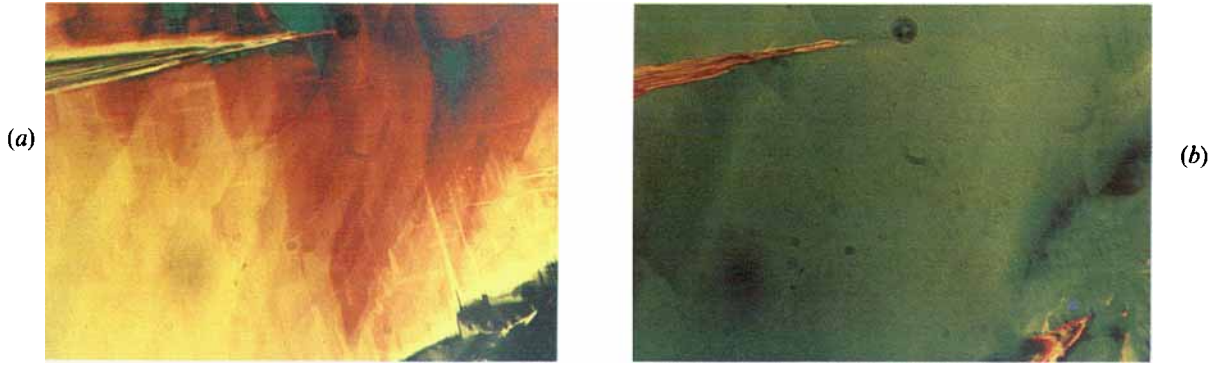


Figure 5. Textures of the smectic phases of 4,4′-dipentylbiphenyl obtained on cooling (0·2°C min^{-1}): a pseudohomeotropic (optically dark) sample of the smectic B phase: (*a*) smectic E′ at 46·6°C, (*b*) smectic E at 45·7°C.

defined. The presence of two peaks at 46·1°C and 47·1°C (see figure 3 (*b*)) shows that three smectic phases exist above the melting point.

In the cooling process, the phase transition E–E′ could not be observed by DSC because the S_B phase supercools about 1°C and the strong thermal effect of the $S_{E'}$–S_B transition overlaps the small thermal effect of the $S_{E'}$–S_E transition.

3.2. *Phase identification*

The smectic phases were identified by using polarizing microscopy. Test samples were placed in the form of the isotropic liquid (after melting) between two carefully cleaned microscopic plates (cleaned with boiling HNO_3). Textures were observed on heating and cooling cycles (0·2°C min^{-1}).

Previous results of X-ray investigations showed that the high temperature smectic phase was a S_B phase and the low temperatures phase was S_E [4]. No other phase between them was observed. In this work, the intermediate phase observed has a characteristic texture which is different from E and B. The textures observed on the heating cycle are shown in figure 4 (*a*)–(*c*). Figure 4 (*a*) was taken at 45·5°C; it presents the texture of the smectic E phase with strongly broken doubly refracting lancets. Between the lancets there are mosaic areas. Figure 4 (*b*) was taken at 46·5°C; it presents the texture of the smectic E′ phase. The lancets are smoother and the boundaries between them are more distinct; the mosaic texture is built up from larger fragments. Figure 4 (*c*) was taken at 47·2° and shows the S_B phase. The lancets are very smooth and the mosaic texture becomes pseudoisotropic. The strongly double refracting mosaic effect disappears. For a better distinction of the difference between the E and E′ phases, a pseudohomoeotropic texture of the smectic B phase was prepared at 47·2°C. When this optically dark sample was cooled to the phase transition S_B to $S_{E'}$, a strongly coloured marbled texture appeared (figure 5 (*a*) at 46·6°C).

Continued cooling to the phase transition $S_{E'}$ to S_E give some movement of the sample and the colour changes but without significant change in the marbled texture. Such behaviour suggests that during the phase transition, the molecules only change their position in the smectic layer in relation to the optic axis.

These results on texture changes and DSC measurements give evidence of the existence of a new phase between the E and B phases. What the structure of this phase is and what the differences are in relation to the E phase is not yet clear. Further precise X-ray investigations are required.

It was noted by a referee, that although this new E phase and that observed [1] for 4-alkyl-4″-cyano-*p*-terphenyls have both been given the code smectic E′, there is no evidence as yet to show that the phases are of the same type and structure, and indeed the textures of the E′ phase for the polar materials are quite different from those described here for 4,4′-dipentylbiphenyl.

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