Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Reinvestigation of Mesomorp1iic Properties of 4,4′-Dialkylbiphenyl. New Orthogonal Phases

K. Czupryński [a] , J. Przedmojski [b] , R. Dąbrowski [a] & M. Brodzik [a]

[a] Military University of Technology, Institute of Chemistry, 01-489, Warsaw, Poland

[b] Warsaw University of Technology, 01-662, Warsaw, Poland

Version of record first published: 04 Oct 2006

To cite this article: K. Czupryński, J. Przedmojski, R. Dąbrowski & M. Brodzik (1997): Reinvestigation of Mesomorp1iic Properties of 4,4′-Dialkylbiphenyl. New Orthogonal Phases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 503-508

To link to this article: http://dx.doi.org/10.1080/10587259708042034

Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 503–508
Reprints available directly from the publisher
Photocopying permitted by license only

REINVESTIGATION OF MESOMORPHIC PROPERTIES OF 4,4'-DIALKYL-BIPHENYL. NEW ORTHOGONAL PHASES

KRZYSZTOF CZUPRYŃSKI, JAN PRZEDMOJSKI*, ROMAN DĄBROWSKI, MARZENA BRODZIK

Military University of Technology, Institute of Chemistry, 01-489 Warsaw, Poland

* Warsaw University of Technology, 01-662 Warsaw, Poland

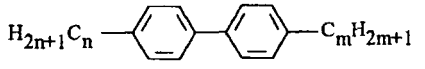
Abstract The phase situation in a few members of 4,4'-dialkylbiphenyl homologous series were investigated. Different orthogonal smectic E phases existing in the temperature range below the smectic B_{cryst} phase were observed. The simultaneous existence of three different smectic E phases in 4-pentyl 4'-hexylbiphenyl by thermomicroscopic, DSC and rentgenographic methods was confirmed. The miscibility studies were used to assign these phases to other smectic phases existing in other members of this homologous series.

INTRODUCTION

The new orthogonal smectic phase existing between E and B_{cryst} (L) phases in 4,4'-dipentylbiphenyl was observed.[1] In 4,4'-dihexylbiphenyl and 4,4'-diheptylbiphenyl the existence of two different smectic phases: E and E' was determined.[2] The small enthalpy of the phase transition S_E-$S_{E'}$ (0.25 kJ mol^{-1}) in 4,4'-dipentylbiphenyl and much bigger (10.5 kJ mol^{-1}) in 4,4'-dihexylbiphenyl imply that both phases E and E' may be different in both compounds. To examine and compare the phases with each other the further compounds of this homologous series,[1,2] among them 4-pentyl 4'-hexylbiphenyl (Cr ? S_E 42 S_B 53.5 I)[3] were synthesized.

EXPERIMENTAL

The investigated compounds had the following structure:



symmetrically substituted: n=m=5 (**C5-C5**); n=m=6 (**C6-C6**); n=m=7 (**C7-C7**);
unsymmetrically substituted: n=5, m=6 (**C5-C6**); n=6, m=7 (**C6-C7**).

These compounds were synthesized according to the known method[1] and were carefully purified. The purity determined by gas chromatography was not less than 99.5 %.

Phase transition temperatures were measured and the textures of the phases were 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 %.

X-ray measurements were performed using Guinier photographic method as well as a diffractometer with scintillation counter. In the case of Guinier transmission method the $CoK_{\alpha 1}$ radiation was focused by a curved quartz monochromator and the temperature was controlled with an accuracy of ±0.25 K. The sample holder of 0.4 mm thick consists of holes of 0.8 mm in diameter.

Diffractometric smectic phase measurements were carried out using the reflecting method from flat sample aligned by surface (glass). The $CuK_{\alpha 1}$ radiation was obtained by a flat Ge (III) monochromator. The 2θ scan curves were obtained step by step every 0.05° at desired constant temperature. The temperature was controlled by a regulator with an accuracy of ±0.01 K. The d values as well as elementary cells were calculated from diffraction data using special computer program.

The miscibility of compounds was tested by preparation isobaric phase diagrams of two component mixtures using single concentration technique.

RESULTS AND DISCUSSION

The results of thermomicroscopic, X-ray and DSC measurements for compounds **C5-C5**, **C6-C6**, **C7-C7** were presented in Refs. 1 and 2. Thermomicroscopic reinvestigations of compound **C5-C6** have shown that in temperature range below the smectic B_{cryst} phase

three different smectic E phases exist. Similarly as it was reported in Ref. 3 the crystallization of this compound was not reached. The results of thermomicroscopic measurements were confirmed by DSC technique (see Figure 1). The phase transitions were observed in the following temperatures (°C):

Cr ? E" 11.7 E 41.7 E' 42.6 Bcryst 53.7 I

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

Cr ? E" 342 E 200 E' 1620 B_{cryst} 9990 I

From the X-ray diffraction patterns the conclusion can be drawn that in these four smectic phases the long axes of molecules remain perpendicular to the smectic layers. The smectic layer spacing grows up from 22.53 A at 11 °C to 23.28 A at 45 °C, as seen in Figure 2. Since the smectic reflections were absent on X-ray photographs of free-standing film the perpendicularity of long axis was also confirmed, Figure 3. X-ray photographs of both Guinier and free-standing film present also high degree of crystallinity of the liquid crystal sample. Therefore all four phases were indexed in orthorombic system (E" phase (11°C) a=8.39 b=5.68 c=22.53, E phase (20°C) a=8.47 b=5.43 c=22.69, E' phase (42°C) a=8.77 b=5.88 c=23.04, B_{cryst} (L) phase (45°C) a=8.77 b=5.22 c=23.28). Three phases are of the smectic E type and the phase above 43 °C is smectic B crystal phase (L phase). In the range of temperatures from ~37 to 42 °C continuous changes in geometry and intensity of reflections are visible, Figure 2. The phase E which proceeds phase B is difficult to detect, mainly due to the thermal hysteresis. To obtain additional information about these phases the polarizing transmission microscope observation were performed using the free standing film of the liquid crystalline sample. Microscopic observations confirmed existence of three different E phases.

In Figure 4 the fragments of isobaric phase diagrams of binary mixtures consisting of **C5-C6** which exhibits three E phases and another compound which exhibits two different smectic E phases[2] (**C5-C5**, or **C6-C6**, or **C7-C7** or **C6-C7**) are presented. The smectic E' phase as well as the E phase of compound **C5-C6** mix in the whole concentration range with adequate phases of compound **C5-C5**, and the smectic E" phase of compound **C5-C6** destabilizes (see Figure 4a).

In mixtures of compound **C5-C6** with other compounds (**C6-C6**, **C7-C7**, **C6-C7**) the situation is similar (see Figure 4b,c,d). In the whole concentration range the smectic

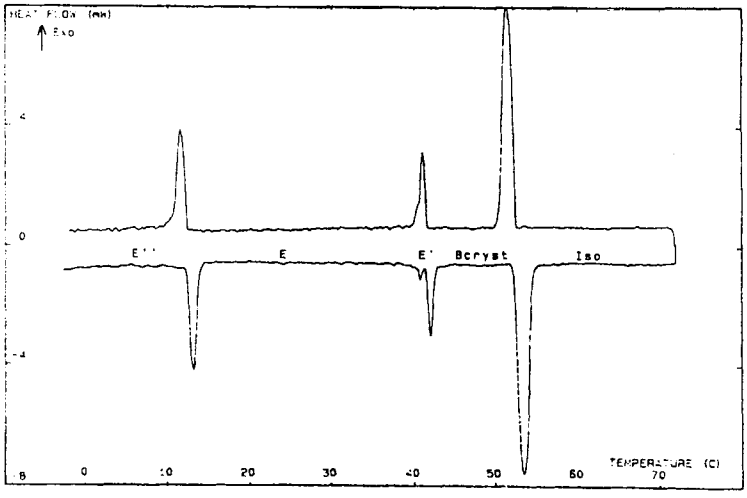


FIGURE 1 DSC diagram for compound **C5-C6**.

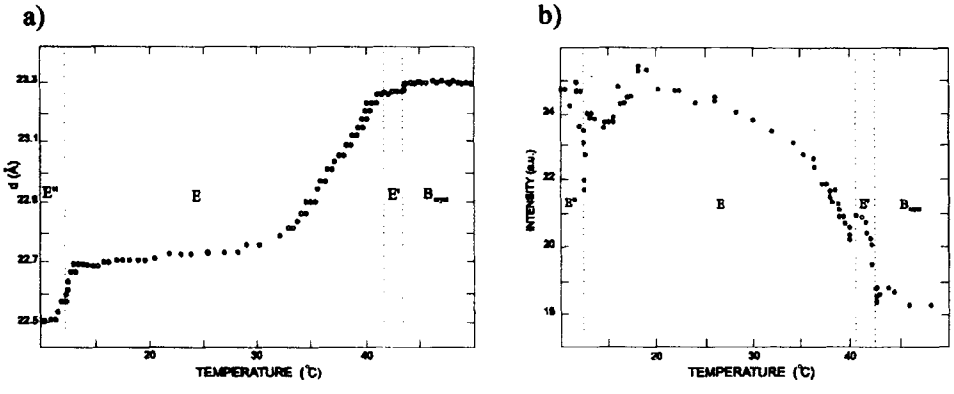


FIGURE 2 Dependence of small angle layer spacing (a) and intensity (b) versus temperature for **C5-C6**.

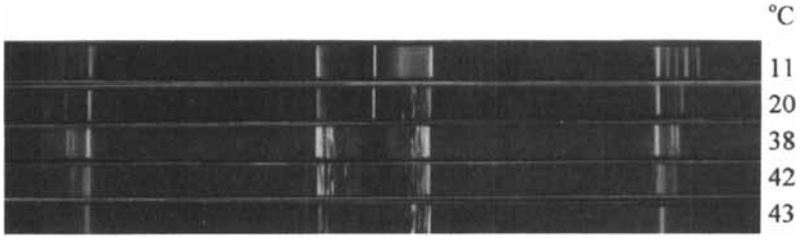


FIGURE 3 X-ray Guinier photographs of liquid crystalline phases of compound **C5-C6**.

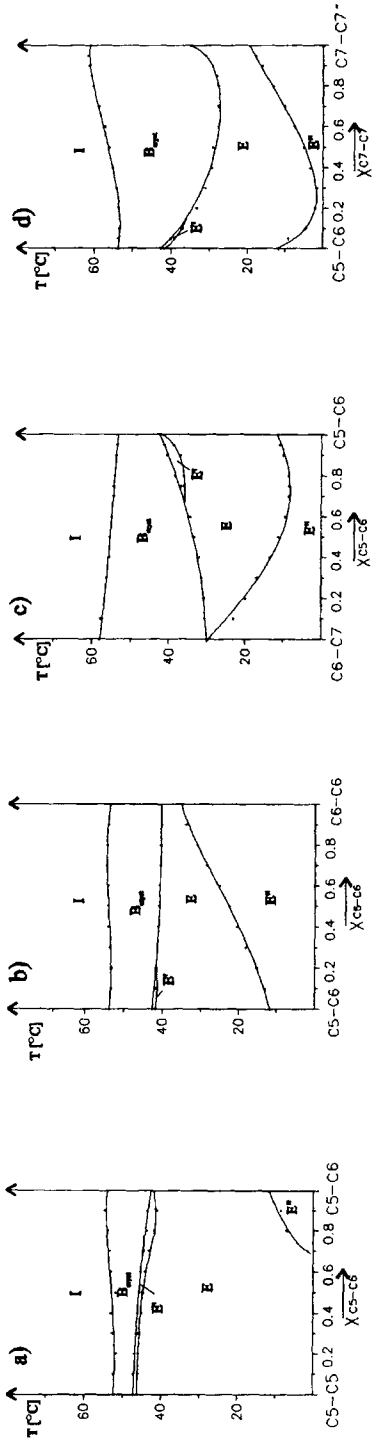


FIGURE 4 Phase diagrams of mixtures: C5-C5 - C5-C6 (a); C5-C6 - C6-C6 (b); C6-C7 - C5-C6 (c); C5-C6 - C7-C7 (d).

FIGURE 5 Phase diagrams of mixtures: C6-C6 - C5-C5 (a); C5-C5 - C7-C7 (b); C6-C6 - C7-C7 (c); C7-C7 - C6-C7 (d).

phases E and E" are mixed and high temperature E' phase destabilizes.

Thus in compounds **C5-C6** and **C5-C5** similar are phases E' and E, and in compounds **C5-C6** and **C6-C6**, **C6-C7** and **C7-C7** similar are phases E and E".

In the mixtures of compound **C5-C5** with compounds **C6-C6** or **C7-C7** (Figure 5a,b) the common phase is only the smectic E phase, the smectic phases E' and E' destabilize. The phase diagrams shown in Figure 5c,d indicate that the all smectic phases in compounds **C6-C6**, **C7-C7** and **C6-C7** are similar.

On the base of X-ray, thermomicroscopic, DSC and miscibility studies it is possible to conclude that in the tested compounds belonging to the homologous series 4,4'-dialkylbiphenyls three different smectic E phases (E", E, E') exist as it is shown in Table I.

TABLE I The phase transition temperatures and the phase sequence in a few members of 4,4'-dialkylbiphenyl homologous series.

Compound	Temperatures (°C)									
C5-C5	Cr	25.1	-		E	46.1	E'	47.1	Bcryst 52.3	Iso
C5-C6	Cr	?	E"	11.7	E	41.7	E'	42.6	Bcryst 53.7	Iso
C6-C6	Cr	34.0	E"	35.0	E	40.0	-		Bcryst 53.4	Iso
C6-C7	Cr	?	E"	29.7	E	30.2	-		Bcryst 58.1	Iso
C7-C7	Cr	?	E"	19.5	E	35.1	-		Bcryst 61.0	Iso

This work was supported by the Polish Committee for Scientific Research under grant No 2 P303 01907.

M.Brodzik is a holder of a scholarship of Foundation for Polish Science.

REFERENCES

1. K. Czupryński, Liq.Cryst., 16, 399 (1994).
2. K. Czupryński, J. Przedmojski, and J. Baran, Mol.Cryst.Liq.Cryst., 260, 435 (1995).
3. V. Vill, Landolt-Börnstein, Liquid Crystals, edited by J. Thiem (Springer Verlag, 1992), Chap. 7a.