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A NEW SMECTIC PHASE IN 4,4'-DIALKYLBIPHENYL

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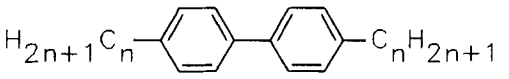
Abstract The phase transitions in a few members of homologous series of 4,4'-dialkylbiphenyls were reinvestigated. The new orthogonal smectic phase existing between the smectic E and the smectic $S_{Bcryst.}$ phase was found in these compounds. The existence of a different smectic E phase in the same compounds was confirmed by thermomicroscopic, roentgenographic and DSC studies. Measured and calculated lattice spacings in E, E' and B phases are given.

INTRODUCTION

A new orthogonal phase existing between smectic E and smectic $B_{cryst.}$ (L) phases was found in 4,4'-dipentylbiphenyl. Its existence was established using thermomicroscopic and microcalorimetric (DSC) method [1]. It was suspected, that the same phase may be present in other members of homologous series of 4,4'-dialkylbiphenyls. In this work we report more compounds with this phase and the results of X-ray investigations and the structural differences between E, E' and $B_{cryst.}$ (L) phases are discussed.

EXPERIMENTAL

Compounds belonging to homologous series:



with n=5 (**C5-C5**), n=6 (**C6-C6**), n=7 (**C7-C7**) were tested.

They were prepared according to the common known method [1] and were carefully purified. Purity was determined to be 99.3 per cent by gas chromatography. 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 DSC 92". Investigations were carried out using a N_2 atmosphere of purity 99.9 per cent.

X-ray diffraction studies were carried out using various methods. Liquid crystalline samples either free standing films, or applied to a single glass surface. Diffraction patterns were recorded using the flat-plate Laue method and a free-standing thin film sample, the Guinier photographic method using thick free-standing film and the diffractometer reflecting method with scintillation counter and a sample with one free surface. X-rays were monochromated with a flat Ge crystal or a focusing quartz monochromator. Temperature control was better than ± 0.1°C. The X-ray techniques were previously described in the literature[2,3,4].

RESULTS AND DISCUSSION

In Table 1 phase transition temperatures and enthalpies of the investigated compounds C5-C5, C6-C6, C7-C7 are listed. In 4,4'-diheptylbiphenyl, the smectic E and E' phases in occur over the broadest temperature ranges. The S_E phase exists below -40°C, and compound kept at that constant temperature do not crystalize. The smallest enthalpy of phase transition $S_E \rightarrow S_{E'}$ was determined in compound C5-C5 and the largest enthalpy of

this transition was observed in compound C6-C6. The enthalpy of phase transition $S_{E'} \rightarrow S_{Bcryst.}$ (S_L) increases with increasing number of carbon atoms in the alkyl chains. Figures 1a, b show DSC traces for compounds C6-C6 and C7-C7. DSC for compound C5-C5 has been reported[1].

TABLE 1. Phase transition temperatures and enthalpies of compounds: C5-C5, C6-C6, C7-C7

n	Cr	S_E	$S_{E'}$	$S_{Bcryst.}$	I
			Temperature (°C) enthalpy (kJ/mol)		
5	* 25.1 7.10	* 46.1 0.25	* 47.1 2.03	* 52.3 9.60	*
6	* 34.0 20.0	* 35.0 10.5	* 40.0 2.6	* 53.4 10.7	*
7	* ?	* 19.5 7.0	* 35.1 9.0	* 61.0 13.0	*

X-ray analysis shows unusual structural changes and confirms phase transitions in the compound under study.

In Figs. 2, 3 and 4 layer spacings (a) and intensity of X-ray scattering (b) are presented. Phase transitions are distinctly visible and their assignments are in good agreement with those obtained with DSC measurements.

All three compounds have smectic phases: E, E' and $B_{cryst.}$, as determined by Guinier photographs and the free-standing film method using X-ray diffraction. The most crystalline phases, smectic E and E', are found in compound C7-C7. Interplanar distances and calculated lattice parameters for the E, E' and B phases are given in Table 2.

More detailed studies of the structures of the E and E' phases in all three compounds are necessary to better understand the differences between them and nature of the phase transitions. For this purpose, the integrated intensities of the 001 reflections (Table 3) could be used. It is notable that compounds C5-C5 and C6-C6 have all four orders of reflections while in C7-C7 lacks second order reflections.

TABLE 2. Measured (m) and calculated (c) lattice spacings in the E, E' and B phases (in angstroms).

C5-C5			C6-C6			C7-C7		
d (m)	d (c)	hkl	d (m)	d (c)	hkl	d (m)	d (c)	hkl
E phase, 42.0°C a=8.70 b=5.31 c=21.8			E phase, 34.5°C a=9.80 b=5.38 c=23.9			E phase, 15°C a=8.88 b=5.4 c=25.6		
21.8	21.8	001	23.9	23.9	001	25.6	25.6	001
10.9	10.9	002	11.6	11.9	002	8.60	8.53	003
7.27	7.27	003	8.02	7.97	003	6.43	6.40	004
5.45	5.45	004	6.04	5.98	004	4.616	4.614	110
4.625	4.619	104	4.598	4.598	101	4.570	4.63	013
4.535	4.535	110	4.425	4.425	200	4.519	4.511	111
4.352	4.352	200	4.298	4.291	210	4.440	4.440	200
4.306	4.289	013	4.078	3.999	014	4.200	4.195	202
4.082	4.042	202	3.429	3.418	210	4.18	4.127	014
3.411	3.401	204	3.379	3.83	211	4.049	4.059	113
3.350	3.557	210	3.280	3.286	212	3.378	3.399	211
						3.312	3.313	201
						3.191	3.182	213
E' phase, 46.8°C a=8.70 b=5.40 c=22.1			E' phase, 39.0°C a=8.79 b=5.38 c=24.1			E' phase, 30.0°C a=8.62 b=5.47 c=25.0		
22.1	22.1	001	24.1	24.1	001	25.8	25.8	001
11.0	11.0	002	12.0	12.0	002	8.70	8.60	003
4.591	4.591	110	4.589	4.589	110	6.48	6.45	004
4.520	4.495	110	4.513	4.508	111	4.618	4.620	110
4.352	4.352	200	4.395	4.395	200	4.529	4.548	111
3.400	3.389	210	4.316	4.324	201	4.350	4.349	112
3.348	3.350	211				4.310	4.310	200
						4.152	4.173	014
						4.042	4.070	113
						3.891	3.853	203
						3.375	3.387	210
						3.342	3.357	211
						3.255	3.275	212
						3.112	3.151	213
B phase, 50.0°C a=5.22 b=9.04 c=22.1			B phase, 45.0°C a=5.21 b=9.02 c=24.1			B phase, 36.0°C a=5.18 b=8.97 c=26.6		
22.1		001	24.1		001	26.6		001
4.528		110,020	12.0		002	4.488		110,020
			4.511		110,020			

TABLE 3. Measured integral intensities of 001 reflections for C5-C5 and C7-C7 in the smectic E, E' and B

C5-C5			C7-C7		
Temperature (°C)	Order	Intensity	Temperature (°C)	Order	Intensity
30	1	5257	31	1	1842
	2	59		2	-
	3	36		3	677
	4	252		4	51
47.0	1	25437	34	1	1784
	2	346		2	-
	3	92		3	78
	4	64		4	62
47.2	1	27383	37.8	1	2428
	2	382		2	-
	3	86		3	51
	4	48		4	56
48.2	1	26368			
	2	329			
	3	67			
	4	31			

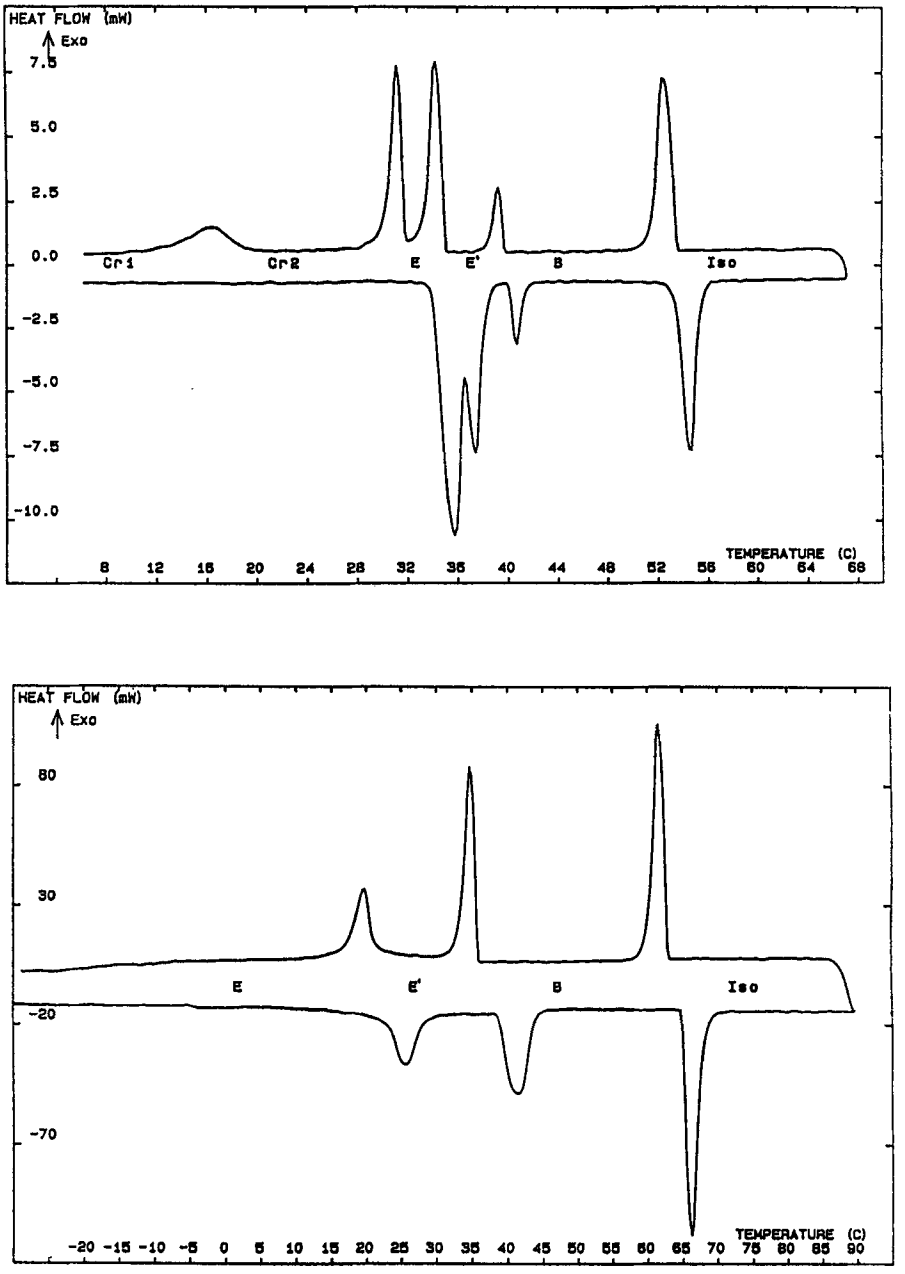


FIGURE 1 DSC diagrams for compounds: (a) C6-C6, (b) C7-C7

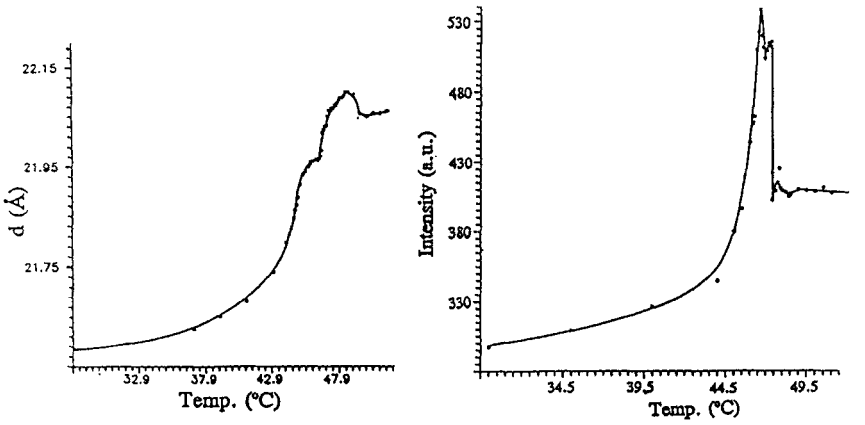


FIGURE 2 Dependence of small angle layer spacing (a) and intensity (b) versus temperature for C_5-C_5

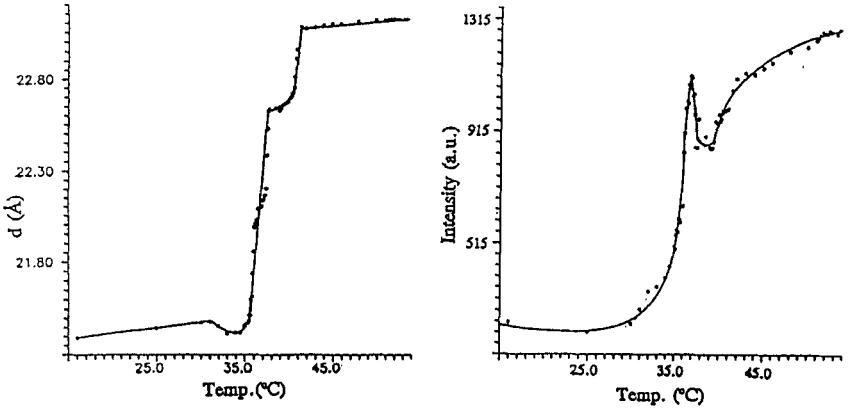


FIGURE 3 Dependence of small angle layer spacing (a) and intensity (b) versus temperature for C_6-C_6

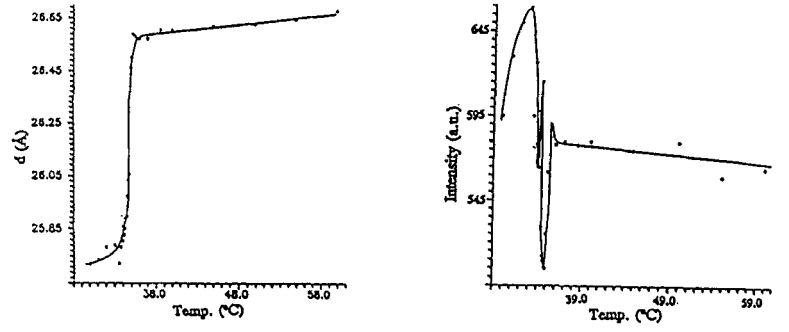


FIGURE 4 Dependence of small angle layer spacing (a) and intensity (b) versus temperature for C_7-C_7

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