

Thermal and X-Ray Studies of 1,6-Bis-[4-(trans-4-n-propylcyclohexyl)phenyl]-hexane and 3,5-Bis-[4-(trans-4-n-propylcyclohexyl)phenyl]-1,2,4-thiadiazol

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The liquid crystalline phases of the title compounds have been investigated by differential scanning calorimetry, optical microscopy and X-ray diffraction methods. Transition temperatures and transition enthalpies of these compounds have been determined. The diffraction photographs in the nematic phase of the first compound showed diffraction patterns corresponding to two coexisting mass density fluctuations with commensurate wavelengths, whereas a single diffraction pattern was observed in the nematic phase of the second compound. The thermal and X-ray data showed that the first compound has a quasi-smectic layer structure.

Introduction

Recently, the authors reported that the replacement of a phenyl group by a carboxylate group in the disubstituted cyclohexylbiphenyls remarkably affects their mesomorphic properties [1]. The correlation between the mesomorphic properties and the molecular structure of liquid crystals is not yet completely clear, although many efforts [2–4] have been made.

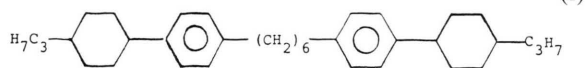
De Jeu and Eidenschink [5] have recently studied the mesomorphic properties of nonpolar compounds named *p*-substituted cyclohexyl-biphenyl-cyclohexanes (CBC) [6].

This work represents a study of the effect of insertion of a bridging group between the two phenyl rings of H_7C_3 -C₆H₄-C₆H₄-C₃H₇ (CBC 33) on its mesomorphic properties and packing.

Experimental

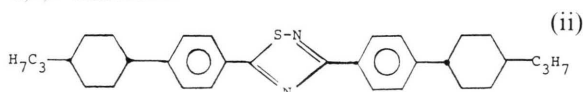
The following compounds have been studied:

1,6-bis-[4-(trans-4-n-propylcyclohexyl)phenyl]-hexane



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3,5-bis-[4-(trans-4-n-propylcyclohexyl)phenyl]-1,2,4-thiadiazol



These compounds were synthesized at the laboratories of E. Merck, Darmstadt. The transition temperatures and enthalpy changes were determined using a Du Pont differential scanning calorimeter. The thermal analysis showed that the purity of the compounds was better than 99%. The characterization of the liquid crystalline phases was established by texture observations as well as X-ray diffraction. The samples were put in 0.7 mm Lindemann glass capillaries. CuK_{α} radiation was used. Flat-plate photographs were taken in the liquid crystalline phases subsequent to cooling of the samples from the isotropic phase in an electromagnet of about 1 Tesla.

Results and Discussion

Thermal Data

Figure 1 shows some DSC thermograms of compound (i) over the temperature range 340 K to 410 K obtained during heating and cooling cycles with the rate 2 K/min. The first heating cycle (Run 1) shows two endothermic transitions, whereas

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four exothermic peaks are observed during the first cooling cycle (Run 2). The different phases and transition temperatures of compound (i), based on DSC and optical microscopy data, can be represented as follows:

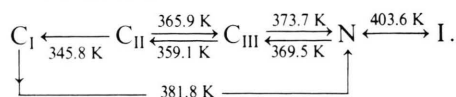
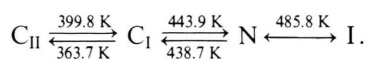


Table I summarizes the transition temperatures and transition enthalpies of compound (i). It is significant that the clearing enthalpy of compound (i) is high compared to normal nematic phases. This high value is caused mainly by a quasi-smectic local ordering. Such high N–I transition enthalpies were reported for di-alkylazoxybenzenes [7]. We can not yet explain the small C_{III} –N transition enthalpy. Presumably this depends on non complete crystallization by the cooling process.

Figure 2 shows some DSC thermograms of compound (ii) over the temperature range 300–500 K, with heating and cooling rates of 2 K/min. Three endothermic transitions are observed during the first heating cycle (Run 1). The first cooling cycle (Run 2) shows three exothermic peaks corresponding to the endothermic transitions of Run 1. The third heating cycle (Run 5) is obtained by cooling the sample to 170 K (Run 4) and reheating immediately. Run 5 shows five endothermic transitions. The different phases and transition temperatures of compound (ii), based on DSC and optical texture data in the temperature range 300–500 K, can be represented as follows:



The transition temperatures and transition enthalpies of compound (ii) are also given in Table I. Attempts to measure the transition enthalpies of the C_{IV} – C_{III} and C_{III} – C_{II} phase transitions were not successful. All transition enthalpies of compound (ii) are of normal order of magnitude.

The mesomorphic properties of the compounds studied are compared to those of CBC 33 [6] in Table I. The comparison shows that the insertion of a hexane bridge or a thiadiazol bridge between the two aromatic rings of CBC 33 destroys the layered structure exhibiting only a nematic phase. On the other hand, the thermodynamic stability of compounds (i) and (ii) is markedly decreased compared to that of CBC 33.

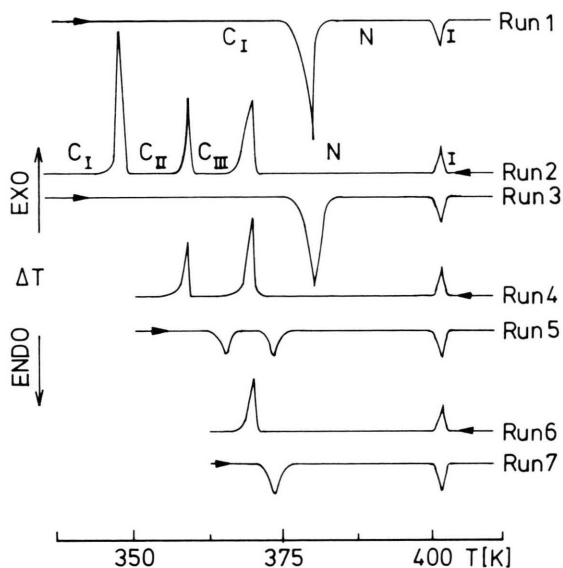


Fig. 1. DSC thermograms of 1,6-bis-[4-(trans-4-n-propyl-cyclohexyl)phenyl]-hexane.

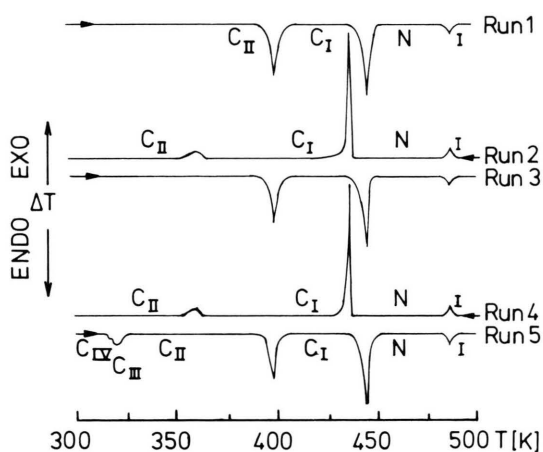


Fig. 2. DSC thermograms of 3,5-bis-[4-(trans-4-n-propyl-cyclohexyl)phenyl]-1,2,4-thiadiazol.

X-Ray Diffraction Data

The diffraction photographs in the nematic phase of compound (i) showed diffraction patterns corresponding to two coexisting mass density fluctuations with commensurate wavelengths, such that the wave vector $q_2 = 2q_1$ ($q = 4\pi \sin \theta / \lambda$ [8], where θ is the diffraction angle and λ is the wavelength of the radiation used). These results show that compound

Table 1. Phase transitions and transition enthalpies of the compounds studied. The data for CBC 33 see [6].

Compound	Transition	Temperature [K]	Enthalpy [kJ/mol]
(i)	C _I -N	381.8	28 ± 1
	C _{II} -C _{III}	365.9	2.2 ± 0.5
	C _{III} -N	373.7	3.5 ± 0.7
	N-I	403.6	4.9 ± 0.5
(ii)	C _{II} -C _I	399.8	8.5 ± 0.4
	C _I -N	443.9	15.3 ± 0.6
	N-I	485.8	0.3 ± 0.1
CBC 33	C _{II} -C _I	400	0.1
	C _I -S _B	428	12
	S _B -S _A	483	5.2
	S _A -N	493	~ 0
	N-I	598	1.2

(i) has a quasi-smectic layer and support the thermal data. Table 2 gives the fluctuation wavelengths of compound (i) and the corresponding calculated molecular length. The calculated molecular length l is obtained by using the X-ray data for trans-4-n-propyl-(4'-cyanophenyl)-cyclohexane (PCH3) [9]. (C2-H161 distance ~ 12 Å including the covalent radius of hydrogen), using the atomic numbering given in [9] and the well known bond lengths and angles for the (CH₂)₆ group (~ 8.6 Å) supposing that the molecules are in the fully extended form.

In the nematic phase of compound (ii), normal structural behaviour was observed as evidenced by

Table 2. Fluctuation wavelengths ($2\pi/q$), intermolecular distances (D) and calculated molecular lengths (l).

Compound	T [K]	$2\pi/q_1$ [Å]	$2\pi/q_2$ [Å]	l [Å]	D [Å]
(i)	385 (N)	31.3 ± 0.5	15.7 ± 0.5	32.6	5.6 ± 0.1
(ii)	445 (N)	26.7 ± 0.5	-	30.6	5.5 ± 0.1

a single diffraction pattern. The fluctuation wavelength of compound (ii) is also given in Table 2 as compared to the calculated molecular length.

Furthermore, Table 2 shows that the average distance between neighbouring molecules " D " ($2D \sin \theta = 1.117 \lambda$ [10]) in the nematic phase of the compounds studied is of the same order of magnitude as found in other cases [1, 11].

Other investigations are in progress to explain the anomalous results of compound (i).

Acknowledgements

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