Study of the Liquid Crystalline Phases in Some Compounds of 4-Trans-(4-Alkyl)Cyclo-Hexylphenyl-Alkylcarboxylate

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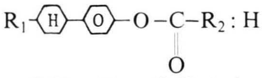
Three mesogenic compounds of the general formula  $R_1\text{-(H)-(O)-O-C(=O)-}R_2$: H33 ($R_1 = C_3H_7$, $R_2 = C_3H_7$), H34 ($R_1 = C_3H_7$, $R_2 = C_4H_9$) and H75 ($R_1 = C_7H_{15}$, $R_2 = C_5H_{11}$) have been investigated by differential scanning calorimetry, thermal optical microscopy and X-ray diffraction methods. Enthalpy changes of the different phase transitions for these compounds have been determined. H33 exhibits smectic B and nematic phases, whereas H34 and H75 exhibit only smectic B phases. The thickness of the smectic layers and the average intermolecular distance have been evaluated, as well as the corresponding molecular parameters in the nematic phase.

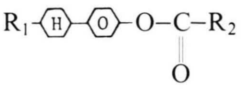
Introduction

Several series of molecules with cyclohexylphenyl core have been synthesized [1 – 5]; some of these compounds exhibit several mesophases. Recently, Osman [6] has discussed the importance of considering the effect of substituents, in connection with the nature of the rigid core in stabilizing the mesophase or favouring a certain one. De Jeu and Eidenschink [7] have pointed out that, quite generally, nonpolar molecules form orthogonal smectic B phases.

Recently, Müller and Haase [8] have studied the mesomorphic properties of a series of disubstituted cyclohexylbiphenyls. Interesting was the question of how the mesomorphic properties of this class of substances are influenced by replacing the phenyl group attached to the alkyl group in the disubstituted cyclohexylbiphenyls by a carboxylate group.

Experimental

The compounds studied are three members of a series of compounds with the chemical formula [4]



$$R_1\text{-(H)-(O)-O-C(=O)-}R_2$$

H33 ($R_1 = C_3H_7$, $R_2 = C_3H_7$), H34 ($R_1 = C_3H_7$, $R_2 = C_4H_9$) and H75 ($R_1 = C_7H_{15}$, $R_2 = C_5H_{11}$). These compounds were synthesized at the laboratories of E. Merck, Darmstadt, and were used as such without any further purification. The thermal analysis showed that the purity of the compounds studied was better than 99%. The transition temperatures and enthalpy changes were determined using a Du Pont differential scanning calorimeter. The transition temperatures were confirmed by a Leitz Orthoplan polarizing microscope, equipped with a Mettler FP52 hot stage.

The classification of the liquid crystalline phases was confirmed by texture observations. To establish these phases, X-ray diffraction studies were carried out. Photographs were made from oriented and nonoriented samples in 0.7 mm Lindemann glass tubes using CuK_α radiation. An electromagnet of about 1 Tesla was used to orient the samples.

Results and Discussions

Thermal and microscopy data

The transition temperatures and transition enthalpies of the studied compounds are summarized in Table I. The smectic B phase of H33 was identified by the mosaic texture, whereas the smectic B phases of H34 and H75 were identified by the lancets textures. The nematic phase of H33 was identified by the typical schlieren texture. Table I shows that H33, as the lower member,

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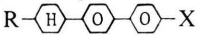
Table I. Transition temperatures and transition enthalpies of the compounds studied (C = crystalline, S = smectic, N = nematic, I = isotropic).

Compound	Transition	Temperature [°C]	Enthalpy [kJ/mol]
H33	$C-S_B$	11.0 ± 0.3	16.4 ± 0.8
	S_B-N	26.1 ± 0.3	4.9 ± 0.2
	$N-I$	30.3 ± 0.3	0.4 ± 0.1
H34	$C-S_B$	32.3 ± 0.3	22.1 ± 0.8
	S_B-I	42.7 ± 0.3	8.8 ± 0.4
H75	$C-S_B$	34.2 ± 0.3	29.2 ± 0.9
	S_B-I	64.5 ± 0.3	7.8 ± 0.3

Table II. The mesomorphic properties of compounds with the chemical structure  (BCHRX) [8] Symbols as in Table I).

R	X		Transition	Temperature [°C]	Enthalpy [kJ/mol]
C_3H_7	H	(BCH30)	$C-S_B$	72.2 ± 0.3	12.0 ± 0.7
			S_B-I	92.9 ± 0.5	8.3 ± 0.6
C_5H_{11}	H	(BCH50)	$C-S_B$	57.9 ± 0.3	12.0 ± 0.2
			S_B-N	81.6 ± 0.3	4.7 ± 0.2
			$N-I$	97.9 ± 0.5	0.4 ± 0.2
C_5H_{11}	C_2H_5	(BCH52)	$C-S_B$	34.8 ± 0.9	18.5 ± 0.6
			S_B-N	143.2 ± 0.3	6.8 ± 0.5
			$N-I$	157.6 ± 0.8	0.5 ± 0.2
C_5H_{11}	C_4H_9	(BCH54)	$C-S_B$	17.5 ± 0.5	–
			S_B-N	159.1 ± 0.4	7.9 ± 0.6
			$N-I$	170.6 ± 0.4	0.5 ± 0.2

exhibits smectic B and nematic phases whereas the next number exhibits only smectic B phase.

The mesomorphic properties of the compounds studied (see Table I) are compared to those of the disubstituted cyclohexylbiphenyls in Table II. The comparison shows that the replacement of a phenyl group by a carboxylate group decreases the stability of the mesophase as well as the mesophase ranges. This is because of the decrease of the polarizability. Moreover, the melting point of H33 is decreased remarkably.

Changes of enthalpy values (see Table I) show as usual that the enthalpy increases with increasing the length of the alkyl chain. The big difference between the enthalpies of the $C-S_B$ transitions of H33 and H34 may be due to an odd-even effect. Enthalpy changes of the compounds studied are compared with the data in Table II for the same type of transition. The S_B-N, S_B-I and $N-I$ transition enthalpies are of the same order of magnitude for both series. $C-S_B$ transition enthalpies of the studied compounds are slightly higher than the analogous data of the dialkyl substituted cyclohexylbiphenyls. This can be shown by comparing H34 (Table I) and BCH52 (Table II).

X-ray diffraction data

To establish the evidence of the liquid crystalline phases, X-ray diffraction photographs were taken. These show for the oriented smectic B phases of H33 and H34 sharp inner reflections, which are caused by the smectic layer arrangement, and outer bars (slightly diffused) which are caused by the interaction between neighbouring parallel molecules. The intensity of the outer bars was so weak that we could not identify whether the smectic B phase is a hexatic or a crystal one. Photographs of nonoriented samples of H33 and H34 show hexagon, and this means homeotropic orientation. Therefore we think that the strength of the magnetic field did not suffice for the orientation of the samples. The photographs of the oriented sample of H75, however, show hexagon as in the case of BCH30 [9], but we did not succeed in taking good photographs. On the other hand the photographs of the nonoriented smectic B phase of H75 show sharper inner and outer rings.

For the smectic B phases of the compounds studied, the "d" values (the thickness of the smectic layers) in Table III are calculated with Bragg's equation ($2d\sin\theta = n\lambda$, where θ is the diffraction angle, n is the order of the diffraction maximum used and λ is the wavelength of the radiation, 1.5418 Å for our measurements). The calculated lengths l_{calc} of the molecules are based on the data of the solid crystalline state of trans-4-*n*-octyl-(4′-cyanophenyl)-cyclohexane [10] and on the covalent radii N = 0.55 Å and H = 0.30 Å. These values are given in Table III. The difference $x = l_{calc} - d$ increases in relation to the length of the alkyl chain. This may be attributed to the increase of the probability for thermal fluctuations as well as for different conformations with increasing the alkyl chain. This difference (x) is also attributed to the effects of orientational disorder.

In the hexagonal smectic B phase the average distance between neighbouring molecules "D" is

Table III. X-ray parameters of the compounds studied (d: layer thickness or fluctuation wavelength, l_{calc}: calculated molecular length, x: $l_{\text{calc}} - d$, D: intermolecular distance) (Symbols as in Table I).

Compound	Temperature [°C]	d [Å]	l_{calc} [Å]	x [Å]	D [Å]
H33	21.0 (S_B)	19.1 ± 0.5	20.0	0.9	5.5 ± 0.1
	28.0 (N)	17.4 ± 0.5	20.0	2.6	5.3 ± 0.1
H34	37.0 (S_B)	20.2 ± 0.5	21.2	1.0	5.4 ± 0.1
H75	39.0 (S_B)	26.0 ± 0.5	27.6	1.6	5.4 ± 0.1

calculated with the formula $2D \sin\theta = 1.1547\,\lambda$ as given by de Vries [11]. The D values are tabulated in Table III too. Similar D values (~ 5.4 Å) have been found for the disubstituted cyclohexylbiphenyls [9].

The mass density fluctuations that exist in the nematic phase are periodic and can be characterized by a wavelength $d = \lambda / 2 \sin\theta$. The fluctuation wavelength in the nematic phase of H33 is also given in Table III. This wavelength is shorter than the calculated molecular length. We attribute this to the effects of orientational disorder and thermal fluctuations. The difference between the d values in the smectic B and nematic phases of H33 is normal and reflects the difference between orientational disorder and thermal fluctuations in the two phases. The intermolecular distance in the nematic phase is deduced with the formula $2D \sin\theta = 1.117\,\lambda$ [12]. This D value is reported in Table III too, and is identical with that found for the trans-4-*n*-octyl-(4′-cyanophenyl)-cyclohexane [10].

Acknowledgements

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