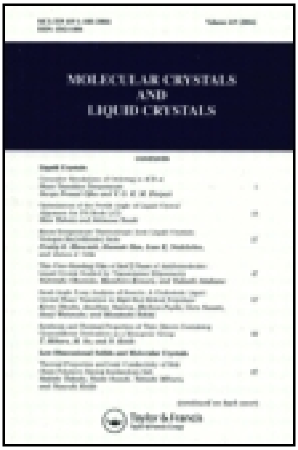

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Takeyasu Tasaka, Hiroaki Okamoto, Yuki Morita, Kazuo Kasatani & Shunsuke Takenaka (2004): The Effect of Lateral Long Hydrocarbon Chain on Mesomorphic Properties, Molecular Crystals and Liquid Crystals, 411:1, 111-117

To link to this article: http://dx.doi.org/10.1080/15421400490434883

Mol. Cryst. Liq. Cryst., Vol. 411, pp. 111/[1153]–117/[1159], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490434883

THE EFFECT OF LATERAL LONG HYDROCARBON CHAIN ON MESOMORPHIC PROPERTIES

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A homologous series of 4-(4-C_nH_{2n+1}O-phenoxycarbonyl)-phenyl 3-C_mH_{2m+1}O-4-cyanobenzoates and the bromo derivatives were synthesized ($m = 2 \sim 14$, $n = 2 \sim 8$). The LC properties are notably affected by m rather than n. The members with large m preferentially exhibit a smectic C phase. The layer structures of smectic A and C phases and the phase transition behavior were examined by a small angle X-ray diffraction method, and the results are discussed in terms of their molecular structures.

Keywords: conformational analysis; liquid crystals; smectic C; thermal properties; X-ray analysis

INTRODUCTION

Linearity of a molecular shape is one of important factors for exhibiting liquid crystal (LC) properties. Many LC materials hitherto reported have been designed and prepared according to the concept. However, recent works have shown that molecules having a bent or a broad shape sometimes exhibit LC phases. A typical example is "banana" shape molecules exhibiting smectic phases, and these sometimes accompany with interesting ferroelectric phenomena [1,2]. The formation of these smectic phases has been discussed in terms of favorable packing of the bent shape molecules. Considering thus, many materials belong to the boundary between the bent and linear shapes are also expected to exhibit LC phases. According to this concept, we have developed some LC materials having a long alkoxy group at a lateral position of the LC core [3,6].

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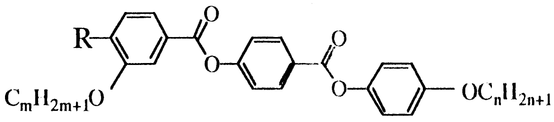
In this paper, we describe the LC properties of some members of compounds **2** and **3**, where an alkoxy group is introduced at the adjacent position of the terminal substituent.



Compounds **1** R = H
2 R = Br
3 R = CN

EXPERIMENTALS

Some homologs of **1** – **3** were prepared by a conventional method appeared in our earlier paper [7].

Transition temperature and latent heat were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900).

X-ray diffraction measurement was performed using a Rigaku-denki RINT 2200 diffractometer, where CuKα ($\lambda = 1.541$Å) was used as an X-ray source. The reflection angle (2θ) was calibrated by the comparison of both right and left angles. The temperature was controlled using a Rigaku PTC-20A thermo-controller. The samples filled in a quartz capillary ($\phi = 1$ mm) were oriented by a constant magnetic field (480 G).

RESULTS AND DISCUSSION

The transition temperatures for **2** and **3** are summarized in Table 1. Compounds **1**, 4-(4-alkoxyphenoxycarbonyl)phenyl 2-alkoxy-benzoates (m = 8 or 14, n = 8), do not exhibit any mesophase even in rapid cooling process [5]. For compounds **2**, a bromine atom at the 4 position causes the formation of N, Sm A, and C phases. The N phase disappears by elongating the alkoxy chain at the 3 position. The Sm A and C phases are exhibited even in long alkoxy homologs (m = 14). These results indicate that **2** intrinsically have the mesomorphic sequence of an Sm C-Sm A-N-I type.

Compounds **3** having a cyano group exhibit the N phase, when m is small. The N-I transition temperature gradually becomes low with elongating the carbon chain (m = 4 ~ 6) at the 3 position. The homologs with a large m (m = 8 ~ 14) preferentially exhibit the Sm C phase. These results

TABLE 1 Transition Temperatures (T/°C) for **2** and **3**

	R	m	n	C		Sm C		Sm A		N		I
2	Br	2	5	•	111	–		(•	91	•	100)	•
			6	•	96	–		•	101	•	111	•
			7	•	100	–		•	107	•	108	•
		5	5	•	96	(•	70	•	83	•	84)	•
			6	•	78	•	80	•	91	•	92	•
			7	•	77	•	78	•	91	–		•
		8	1	•	101	–		–		–		•
			5	•	69	•	71	•	92	•		•
			6	•	63	•	82	•	96	•		•
			7	•	76	•	86	•	96	•		•
		14	5	•	75	(•	57)	•	89	•		•
			6	•	79	(•	72)	•	96	•		•
			7	•	74	•	77	•	97	•		•
3	CN	4	4	•	125	–		–		(•	120)	•
			5	•	113	–		–		•	117	•
			6	•	118	(•	102)	–		•	121	•
			8	•	105	•	110	–		•	122	•
		5	4	•	116	–		–		(•	115)	•
			5	•	112	(•	104)	–		•	114	•
			6	•	105	•	109	–		•	118	•
			8	•	92	•	116	–		•	120	•
		6	4	•	112	•	112	–		•	117	•
			5	•	108	•	109	–		•	116	•
			6	•	106	•	116	–		•	120	•
			8	•	100	•	119	–		•	120	•
		8	4	•	113	•	109	–		•	117	•
			5	•	109	•	118	–		–		•
			6	•	108	•	122	–		–		•
			8	•	103	•	127	–		–		•
		12	4	•	104	•	118	–		–		•
			5	•	102	•	120	–		–		•
			6	•	101	•	125	–		–		•
			8	•	99	•	129	–		–		•
		14	4	•	100	•	118	–		–		•
			5	•	102	•	122	–		–		•
			6	•	100	•	126	–		–		•
			8	•	98	•	129	–		–		•

Parentheses indicate a monotropic transition. Sm C, Sm A, N, I indicate smectic C, A, nematic, and isotropic phases, respectively.

indicate that the lateral alkoxy group is favorable to the formation of the Sm C phase.

Miscibility of smectic phases between **2** and **3** and the conventional linear LC molecules was examined, and the results are shown in Figure 1.

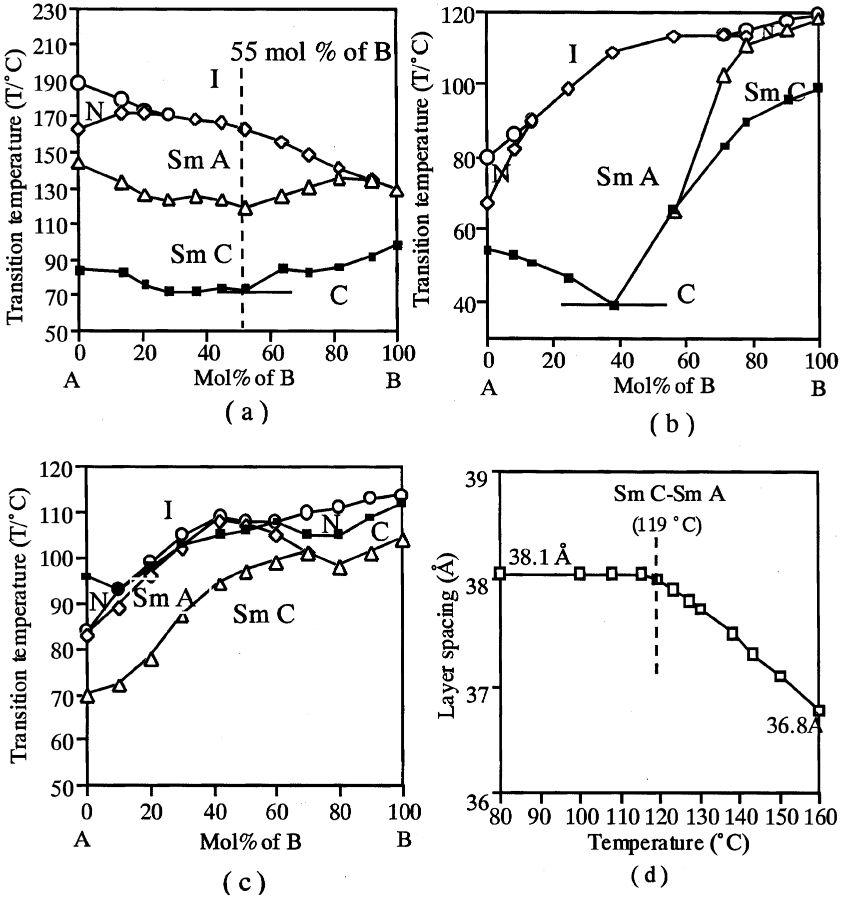


FIGURE 1 Binary phase diagrams for the mixtures:(a) 4-(4-octyloxyphenoxycarbonyl)phenyl 4-octyloxybenzoate (A) and 3 (m = 14, n = 8) (B), (b) 4-cyano-4′-octyloxybiphenyl (A) and 3 (m = 6, n = 8)(B), (c) 2 (m = 5, n = 5) (A), and 3 (m = 5, n = 5) (B). (d) Plot of layer spacing vs. temperature for the mixture of 4-(4-octyloxyphenoxycarbonyl)phenyl 4-octyloxybenzoate (45 mol/%) and 3 (m = 14, n = 8, 55 mol%) in Figure 1a.

In Figure 1a the Sm A and C phases of 2 are miscible with those of 4-(4-octyloxyphenoxycarbonyl)phenyl 4-octyloxy-benzoate [7], while the Sm A-N (I) and Sm C-A transitions show a weak non-linear behavior. In Figure 1b the Sm A-N transition shows a notable enhancement, similar to polar-nonpolar LC mixtures [8]. On the other hand, the Sm C-A (N) transition shows a steep depression with increasing the molar concentration of the reference compound. In Figure 1c both Sm C phases are miscible each other, where the transition temperature shows a little upward swelling. These results indicate that the Sm C for **1**, **2**, and **3** are continuously miscible each other in their binary mixtures.

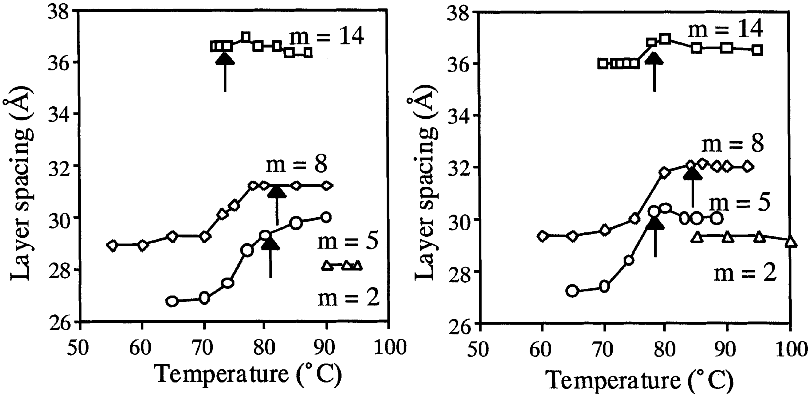
The layer structure was further examined by a small angle X-ray diffraction method. The profiles for **2** and **3** show two reflection maxima in the region of $2\theta = 2.0$ and 2.5° as a sharp and intense peak and near $2\theta = 20^\circ$ as a broad one. From the former peak, the layer spacing was calculated and are plotted against temperature in Figure 2.

For compounds **2**, the layer spacing gradually becomes short on the cooling process, when m is small, for example, m = 5 and 8. When m is large (m = 14), however, the layer spacing remains almost constant and is independent of the phase transition, where the plot shows a weak swelling in the vicinity of the transition point. A similar phase transition behavior has been observed in a ferroelectric LC material [9]. Similarly, the layer spacing for the Sm C phase of **3** is almost independent of temperature. The characteristic feature is observed in the layer spacing for the mixture of 4-(4-octyloxyphenoxycarbonyl)phenyl 4-octyloxybenzoate (48 mol/%) and **3** (m = 14 n = 8) in Figure 1d. In the figure, interestingly, the layer spacing increases ca. 1.3 Å in the Sm A region, while it remains constant throughout the Sm C phase.

The X-ray results are summarized in Table 2.

As mentioned above, the difference of the layer spacing between the Sm C and A phases becomes small with increasing m.

In order to correlate the layer structure with the molecular shape, the molecular length was estimated by a semi-empirical molecular orbital



(a) (b)

FIGURE 2 Plots of layer spacing vs. temperature for **2**: (a) n = 6, and (b) n = 7. Arrows indicate the Sm C-A transition point.

TABLE 2 The Layer Spacing (Å) for **2** and **3**

Compounds **2**				Compounds **3**		
m	n	Sm C	Sm A	m	n	Sm C
2	5		27.2	5	5	
	6		28.2		6	26.8
	7		29.2		8	28.5
5	5		28.6	8	5	28.3
	6	27.1	29.3		6	29.0
	7	27.3	30.1		8	30.7
8	5	29.3	31.0	12	5	32.5
	6	29.3	31.2		6	32.6
	7	30.0	32.0		8	33.5
14	5		35.7	14	5	34.2
	6	36.6	36.6		6	34.8
	7	36.0	36.3		8	35.7

method (MOPAC97). The entire molecular length is strongly dependent on the relative conformation of both terminal alkoxy groups. Although the relative conformation of two ester groups may affect on the physical properties, the entire molecular shape or length is affected a little.

Therefore, we supposed that two ester groups have an s-trans conformation so as to keep the best linearity of the LC core, and the alkoxy groups form a zigzag conformation. Under the supposition, four extreme conformations for the tetradecyloxy homolog of **2** are illustrated in Figure 3.

The energy difference between models A and B or C and D is almost zero, (Strictly speaking, the difference is calculated to be 1.2 kJ/mol) so that it is assumed that both conformers are equally distributed not only in gas phase but also isotropic and LC ones. On the other hand, the energy differences between models A and C or B and D are calculated to be 17.8 and 14.9 kJ/mol for **2** and **3**, respectively. The energy differences are enough large to incline the equilibrium to models A and B.

From Table 2, the observed layer spacing of **3** ($m = 14$, $n = 8$) is 35.7 Å in the Sm C phase, and these of **2** are 36.3 and 36.0 Å in the Sm A and C ones, respectively. These values are far shorter from the molecular lengths expected from models A and B in Figure 3.

On the other hand, the layer spacing of 2 ($m = 2$, $n = 5$) in the Sm A phase (27.2 Å) closes to the molecular length of ca. 26 Å for model A. The layer spacing of **3** ($m = 5$, $n = 6$) in the Sm C phase (26.8 Å) is shorter a little than the calculated molecular length of ca. 32 Å for model A.

These results indicate that for **2** and **3**, the layer spacing closes to the calculated molecular lengths for model A, when m is small, and to B for large m.

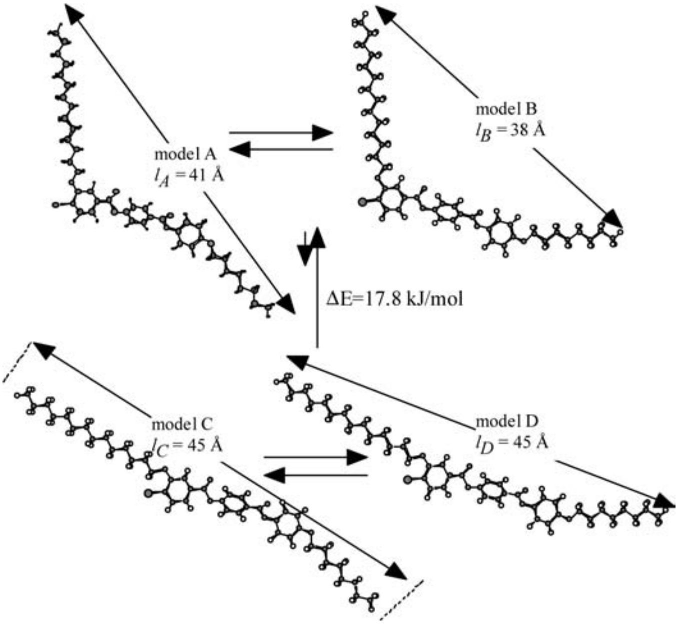


FIGURE 3 Extreme conformational models of **2** (m = 14, n = 7).

Even though, the layer spacing for large m members is far shorter than the calculated molecular length. We assume, therefore, that a characteristic packing of molecules like "banana" ones presents in these compounds.

Further examination is now underway.

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