

Thermal Properties and Molecular Arrangement of Smectic Phase for 4-Alkoxy-3-nitrobenzoic Acids

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The homologous series of 4-alkoxy-3-nitrobenzoic acids exhibit a smectic A phase which commences from the nonyloxy homologue, and the layer spacing is ca. 1.4 times longer than the molecular length calculated by MOPAC2000. From the X-ray results and MO calculation, the layer structure and molecular packing in the smectic A phase are postulated.

Key words: LC properties, smectic A phase, X-ray diffraction, layer structure

1. INTRODUCTION

4-Alkoxybenzoic acids have been known to be one of the most simplest materials exhibiting liquid crystal (LC) properties, where a hydrogen bond is supposed to play an important role for the LC phenomena, and the formation of nematic (N) and smectic C (SmC) phases is a characteristic in the derivatives. Because of the simple molecular structure, the LC properties are notably affected by the geometrical nature of the substituent at the 3-position.

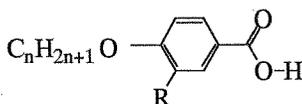


Fig. 1, Molecular structure. Compounds **1** (R=NO₂), **2** (R=H), **3** (R=F, n=12), **4** (R=Cl, n=12), **5** (R=Br, n=12), **6** (R=OCH₃, n=12), **7** (R=CN, n=12).

A homologous series of **2** (R=H) exhibits the N phase and the SmC one as well, when *n* is suitably long. Compounds **3** (R=F) and **4** (R=Cl) are also known to exhibit a similar phase transition behavior, though the clearing points become low by the order of **2** > **3** > **4**, and **5** does not reveal any LC phase. The tendency has been interpreted in terms of the increased lateral width due to the substituent.¹

Recently, we reported that the higher homologues of **1** (R=NO₂) possess LC properties, while the nitro group would be bulkier than halogens. A noteworthy fact is that the homologous members do not exhibit the SmC phase but a smectic A (SmA) one.

In this paper, we will further examine the LC behavior

of **1**, and propose a possible layer structure model based on the X-ray results and molecular orbital consideration.

2. EXPERIMENTAL

All the materials were prepared by the Williamson synthesis of the corresponding 4-hydroxy-3-R-benzoic acids and 1-alkylbromides.

The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC. The DSC thermogram was operated at a heating or a cooling rate of 5 °C/min. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900).

X-ray diffraction experiments for the smectic phases were performed using a Rigaku-denki RINT 2200 diffractometer, where CuKα (λ = 1.541 Å) was used as the X-ray source. The reflection angle was calibrated by a 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 (φ = 1 mm) were oriented by a constant magnetic field (480 G). The samples were placed along the goniometer axis so that the counter movement in the recording plane allowed us to scan the nematic and smectic reciprocal lattice mode, i.e. in the direction parallel to the director *n*. The samples were heated to the isotropic temperature, and measurement was carried out during the cooling process.

The molecular orbital parameters were obtained by a semi-empirical molecular orbital method, MOPAC2000, where minimization of the total energy was achieved by an AM1 method.

3. RESULTS

The transition temperatures for 2~7 are summarized in Table I.

Table I. Transition temperatures of 2~7.

Compounds	Transition temperatures (°C)				
	R	C	SmC	N	I
2	H ^{*1}	• 95	• 129	• 137	•
3	F ^{*1}	• 109	• 113	• 115	•
4	Cl ^{*1}	• 102	(• 84)	• 88	•
5	Br ^{*1}	• 108	-	-	•
6	OCH ₃	• 109	-	-	•
7	CN	• 108	-	-	•

C, SmC, N, and I indicate crystal, smectic C, nematic, and isotropic phases, respectively. Parenthesis indicates a monotropic transition. *1 Ref. 1.

Compounds 2~5 have been reported to exhibit both N and SmC phases, and the clearing point becomes low by the order of 2 > 3 > 4, and 5 is non-mesogenic.¹ For the comparative work, 6 and 7 were also prepared in this work. However, these do not exhibit any mesophase even in a rapid cooling process, and the clearing points extrapolated from the binary phase diagrams were very low, as described in the later part. This tendency should be interpreted in terms of the increased molecular breadth due to the bulky substituents. Transition temperatures for the homologous series of 1 are summarized in Table II.

Table II. Transition temperatures of 1

n	Transition temperatures (°C)			Latent heats (kJ/mol)	
	C	Sm A	I	$\Delta H_{\text{SmA-I}}$	
6	• 140	-	•		
7	• 124	-	•		
8	• 116	-	•		
9	• 94	(• 83)	•	2.0	
10	• 98	(• 88)	•	1.2	
11	• 91	(• 90)	•	2.2	
12	• 92	• 94	•	2.3	
13	• 89	• 95	•	1.9	
14	• 96	• 97	•	2.7	
15	• 95	• 97	•	1.9	
16	• 98	• 98	•	2.5	

Parentheses indicate a monotropic transition.

Interestingly, the higher homologues of 1 exhibit a smectic phase assigned to the A modification in the later part, while the lateral nitro group would notably increase the molecular breadth. The smectic phase commences

from the nonyloxy homologue, and the smectic-isotropic (I) transition temperature rises a little on ascending the homologues and becomes plateau at ca. 100 °C. The transition temperatures are plotted against carbon number in Fig. 2.

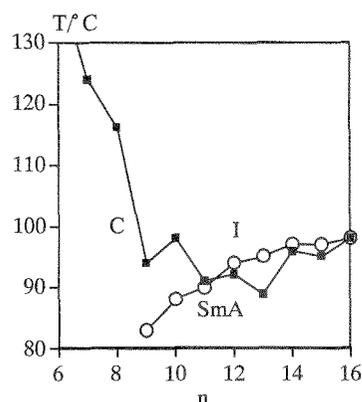


Fig. 2. Plots of transition temperatures vs. carbon number (n). ■; melting point, ○; SmA-I. Transitions below melting point were observed on the cooling process.

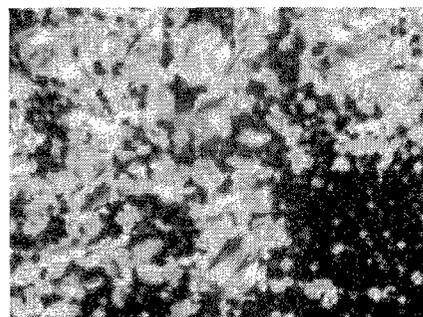


Fig. 3. Micrograph of the SmA phase for the hexadecyloxy homologue of 1 (90 °C, 100 X).

The micrograph of the smectic phase is shown in Fig. 3. The smectic phase tends to form a homeotropic alignment even on a glass surface covered with a polyimide film (Toshiba SP-810). It is apparent from the micrograph that the smectic phase has a fan texture under the homogeneous alignment and an isotropic one under the homeotropic one, suggesting that the smectic phase has an optical uni-axial nature.

The smectic phase was further characterized by some binary phase diagrams, and the results are shown in Fig. 4.

In Fig. 4(a) the smectic phase is miscible with the so-called "polar SmA" phase of 8OCB, where the smectic-I transition temperature shows a weak upward convexity.

In Fig. 4(b) the smectic phase is continuously miscible

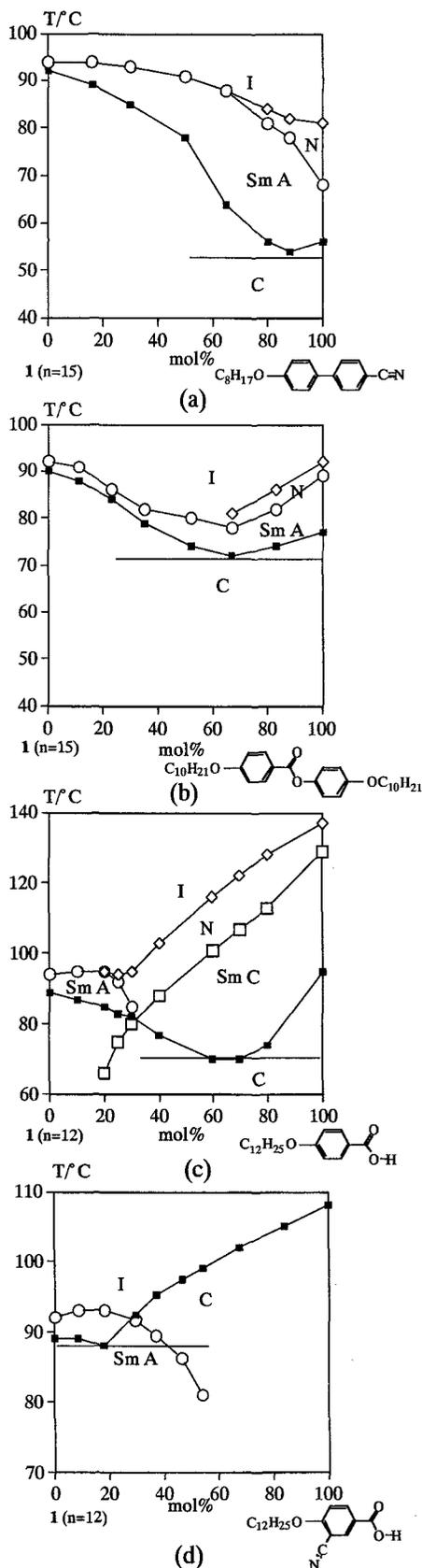


Fig. 4. Binary phase diagrams for the mixtures of (a) **1** ($n=12$) (on left) and 4-octyloxy-4'-cyanobiphenyl (8OCB) (on right), (b) **1** ($n=12$) and 4-decyloxyphenyl 4-decyloxybenzoate, (c) **1** ($n=15$) and **2** ($n=12$), and (d) **1** ($n=15$) and **7**.

with the so-called “non-polar SmA” phase of the reference compound, while the smectic-I transition temperature shows a downward convexity with a minimum at 78 °C. Fig. 4(c) shows the binary phase diagram for the mixture of **1** ($n=15$) and **2** ($n=12$). **2** ($n=12$) is known to exhibit N and SmC phases. In the diagram the N-I transition temperature shows a linear correlation against the molar concentration of both components in the range between 25 and 100 mol% of **2**, and the N-I transition temperature of **1** ($n=15$) is estimated by extrapolation of the straight line, giving 80 °C. The SmC-N transition temperature also shows a straight line in the range between 30 and 100 mol% of **2**, and the SmC phase goes below the smectic phase of **1**. The SmC-smectic transition temperature of **1** ($n=15$) is extrapolated from the straight line, giving 59 °C. These results suggest that the smectic phase of **1** is classified into the A modification (SmA). For the comparative work, the thermal properties for the mixture of **1** ($n=12$) and **7** ($n=12$) were examined, and the results are shown in Fig. 4(d). The SmA-I transition temperature steeply decreases in the range between 0 and 60 mol% of **7**, and the N phase is not observed in the whole range. A similar phase transition behavior was observed for the mixture of **1** ($n=15$) and **6** ($n=12$). It is apparent from these results that the lateral substituent notably decreases LC properties, and the evolution of the SmA phase for **1** is a characteristic for the 3-nitrobenzoic acid compounds.

The SmA phase was further characterized by a small angle X-ray diffraction measurement. The X-ray profiles are shown in Fig. 5

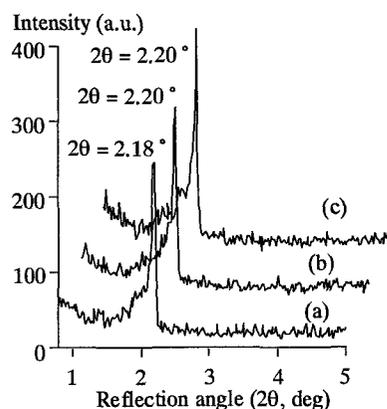


Fig. 5. X-ray profiles of the hexadecyloxy homologue of **1**: at (a) 88 °C, (b) 92 °C, and (c) 96 °C.

The SmA phase shows two kinds of reflection maxima; that is, one is observed as a sharp reflection at $2\theta=2.20^\circ$, and the other in the range between 18 and 22° as a weak and broad one. As shown in Fig. 5, the maximum position of the reflection peak is almost independent of

For even members

$$d = 0.755n\{\sin(55.65-\theta)+\sin(55.65+\theta)\}$$

For odd members

$$d = 0.755\{(n-1)\sin(55.65-\theta)+(n+1)\sin(55.65+\theta)\}$$

The calculated d values are plotted against the hydrocarbon number in Fig. 8(b). We have to be in mind that θ in the equations is not the conventional angle of the LC molecule in the SmC phase, but that of the hydrocarbon chain to the Sm layer. Three important conclusions can be drawn from the figure. First, the layer spacing increases $1.25 \text{ \AA}/\text{CH}_2$, when the average angle of the hydrocarbon chain to the Sm layer is 90° . Second, the linear correlation between the layer spacing and the hydrocarbon number should be lost, if the hydrocarbon chain twists or shrinks. Third, the layer spacing in the Sm phase is expected to show an even-odd alternation in the wide range of θ , and the tendency should be apparent, when the tilt angle is close to 55° . Fig. 9 represents the correlation between the average slope obtained from Fig. 8 and the tilt angle, θ .

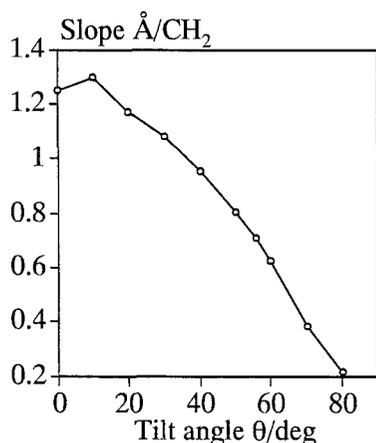


Fig. 9. Plot of slope ($\text{\AA}/\text{CH}_2$) vs. tilt angle (θ/deg). refer to Fig. 8.

By substituting the observed slope in Fig. 9, we can determine the tilt angle, θ_{obs} , of the hydrocarbon chain to the Sm layer.

The plot of the layer spacing in Fig. 6 gives a slope of $1.49 \text{ \AA}/\text{CH}_2$, and interestingly shows a weak even-odd alternation, as expected from Fig. 8(b). The layer spacings in Fig. 6 are always longer than the calculated molecular lengths, indicating that **1** form dimers in the SmA phase. Therefore, the practical molecular length in the SmA phase should be twice of the calculated one, and the practical slope for **1** is a half of the observed one, $1.49 \text{ \AA}/\text{CH}_2$. Putting the slope of $0.75 \text{ \AA}/\text{CH}_2$ in Fig. 9

gives the tilt angle of ca. 52° . This means that the hydrocarbon chain of **1** has an angle of 52° to the smectic layer. Taking these results into consideration, two molecules of **1** ($n=12$) are arranged within the smectic layer of $d_{\text{obs}} = 35.5 \text{ \AA}$ obtained from the X-ray measurement in Fig. 10(a).

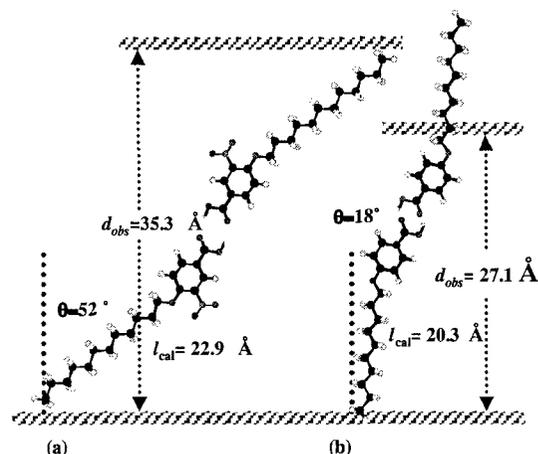


Fig. 10. Possible layer structures of: (a) **1** ($n=12$) and (b) **2** ($n=12$).

In the model, interestingly, two carboxyl groups closely arrange enough to form the hydrogen bond. In this connection, the layer spacings for $n=10, 11$, and 12 homologues of **2** were also determined, giving $27.1, 29.6$, and 32 \AA , respectively.⁹ Thereby, the calculated molecular lengths for $n=10, 11, 12$ homologues are $20.3, 21.6$, and 22.8 \AA , respectively. Putting these values to Figs. 8 and 9, the tilt angle of the hydrocarbon chain to the SmC layer was calculated to be 18° . The tilt angle may be close to the reference value.^{2,4} Supposing that 4-alkoxybenzoic acids form dimers due to the hydrogen bond similar to the solid phase^{5,6}, and the long hydrocarbon chain has the angle of 18° to the SmC layer, the dimer molecule may be put in the smectic layer, as shown in Fig. 9(b). Apparently, the longitudinal length is too long for the dimer molecules to take in the SmC layer. Therefore, the molecular arrangement in the SmC phase for **2** is now in consideration.⁹

Conclusively, the higher homologues of 4-alkoxy-3-nitrobenzoic acid exhibit the SmA phase, and the average tilt angle of the long hydrocarbon chain to the smectic layer is ca. 50° . In the smectic layer the carboxy groups are assumed to form the hydrogen bond, giving the dimers. For the evolution of the SmA phase, there is no doubt that the electrostatic and geometrical factors of the lateral nitro group are important and specific. The method for the determination of the tilt angle of the hydrocarbon chain should be a novel and convenient tool

temperature in the range. The reflection maxima are plotted against the carbon number in Fig. 6.

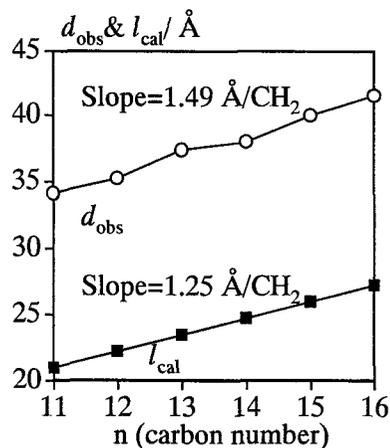


Fig. 6. Plots of layer spacing (d_{obs} , ○) and calculated molecular length (l_{cal} , ■) vs. n (carbon number) for 1.

4. DISCUSSION

In order to clarify the molecular arrangement in the SmA phase, the molecular shape of 1 was examined by a semi-empirical molecular orbital calculation (MOPAC 2000), where the total energy was minimized by an AM1 method, and the C-C-C bond angle and C-C bond length are 111.6° and 1.514 \AA , respectively. The most stable conformation for the hexadecyloxy homologue of 1 is shown in Fig. 7.

The MO calculation suggests that a zigzag conformation for the hydrocarbon chain is the most stable, and the hydrocarbon chain extends toward the opposite site to the nitro group due to a repulsive interaction between the hydrocarbon chain and the adjacent nitro group.

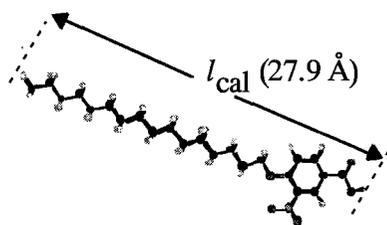
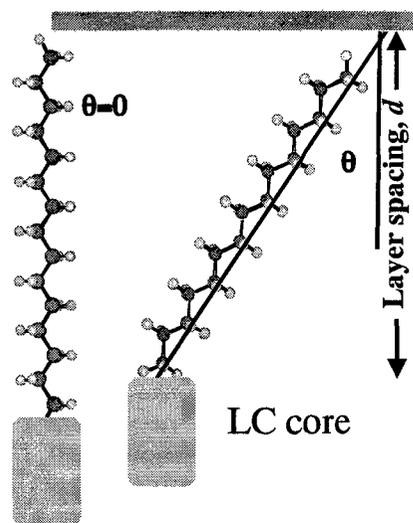


Fig. 7. Molecular shape of the hexadecyloxy homologue of 1

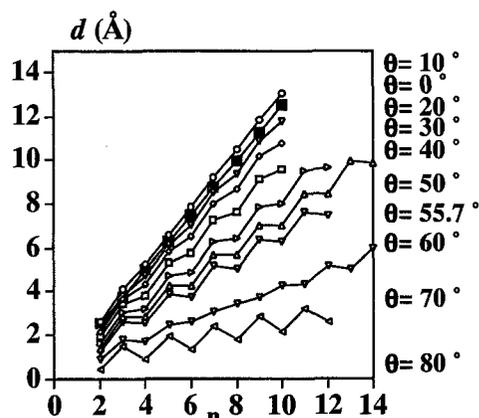
The longitudinal length (l_{cal}) of the molecule was calculated from the conformer. In Fig. 6 the l_{cal} values are plotted as a function of the hydrocarbon number (n), where the slope for the plot of l_{cal} vs. n is 1.25 \AA/CH_2 . The layer spacing (d_{obs}) obtained by the X-ray measurement is also plotted in Fig. 6. There is no doubt that the d_{obs} has a linear correlation against the hydrocarbon number, and the plot accompanies with a weak even-odd

alternation. The plot gives a slope of 1.49 \AA/CH_2 .

Here, we consider the physical meaning of the slope in the d_{obs} - n plot with a simple model shown in Fig. 8.



(a)



(b)

Fig. 8. Relationship between layer spacing ($d/\text{Å}$) and tilt angle (θ) of hydrocarbon chain to the Sm layer. The tilt angle, θ , is the angle between the average line of the hydrocarbon chain and the perpendicular axis of the smectic layer indicated by the heavy lines in (a). In practice, the terminal of the hydrocarbon chain is connected with LC core.

We suppose that the long hydrocarbon chain always extends linearly with a zigzag conformation in LC states such as N, SmA, and SmC phases, and the C-C-C angle and C-C length used in the calculation are 111.6° and 1.514 \AA , respectively. If the average axis of the hydrocarbon chain arranges perpendicular to the smectic layer, the model structure can be illustrated as shown in Fig. 8(a). In such conditions, the layer spacing will increase 1.25 \AA/CH_2 . If the average axis has a tilt angle, θ , to the smectic layer, d should be given as a function of the hydrocarbon chain number, n , and tilt angle, θ :

for the analysis of molecular arrangement in smectic layer and widely applicable in SmA and C phases of conventional LC materials having terminal hydrocarbon chains.

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