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Liquid Crystals

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LIQUID CRYSTALS, 2001, VOL. 28, NO. 7, 1025–1034

Liquid crystalline properties of dissymmetric molecules
VI. The effect of alkyl chain length on molecular arrangement in the smectic A phase in three-aromatic-ring systems with two ester groups†

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The effect of alkyl and alkoxy chain lengths on the layer structures of smectic A and C phases has been examined by X-ray diffraction measurements on three isomeric systems: 4-alkoxyphenyl and 4-*n*-alkylphenyl 4-[(4-octyloxyphenyl)carbonyloxy]benzoates (**1**); 4-octyloxyphenyl 4-[4-(octyloxyphenyl)carbonyloxy]benzoates (**2**); 4-octyloxyphenyl, 4-alkoxyphenyl and 4-*n*-alkylphenyl terephthalates (**3**); and *p*-phenylene 4-octyloxybenzoates, 4-alkoxybenzoate and 4-*n*-alkylbenzoate (**4**). Although all the derivatives exhibit smectic A and/or C phases having a monolayer arrangement of the molecules, the layer spacings are considerably affected by alternation of the ester linkages. The layer spacings for the homologues of **1** are a little shorter than the calculated molecular lengths, while those for **2** agree with the calculated molecular lengths. The layer spacings for **3** show a notable even–odd alternation in the higher homologues. The results are discussed in terms of a subtle change in the molecular structures due to replacement of the ester groups.

1. Introduction

An ester group is a most important linkage in the constituents of a liquid crystalline core. The presence of the ester group results in an increase in flexibility of the core, and its electron-withdrawing nature increases the core polarity. In addition, the ester group is intrinsically dissymmetric, and the two substituents attached at the ester group are not equivalent from a physical point of view. Exchange of the substituents therefore results in a subtle change in the molecular structure, sometimes giving rise to a notable change in liquid crystalline properties.

For example, 4-butoxyphenyl 4-octyloxybenzoate (R_1 = octyloxy, R_2 = butoxy in figure 1) has the phase sequence of a smectic C(SmC)–smectic A(SmA)–nematic(N)–isotropic(I) type, while 4-octyloxyphenyl 4-butoxybenzoate (R_1 = butoxy, R_2 = octyloxy in figure 1) has an N–I type phase sequence [1], indicating that the exchange of the terminal alkoxyl groups is solely responsible for the change in smectic properties. Similarly, 4-methoxyphenyl 4′-octyloxybiphenyl-4-ylcarboxylate (R_1 = 4-octyloxyphenyl, R_2 = methoxyphenyl) has the phase sequence of an SmB–SmA–N–I type, while 4-octyloxyphenyl 4′-methoxybiphenyl-4-ylcarboxylate has a N–I phase sequence [2].

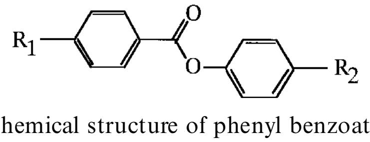

Figure 1. Chemical structure of phenyl benzoate derivatives.

A common factor for these systems is that both substituents attached at the ester linkage are rather different in both electrostatic and geometric properties. Azomethine, azoxy and thioester linkages are also intrinsically dissymmetric, so that a similar dissymmetric effect on liquid crystalline properties has been observed [1, 3].

It has long been known that many liquid crystals having an ester linkage tend to exhibit SmC and SmA phases in addition to the N phase. In general, the smectic properties of the ester compounds have been interpreted in terms of intermolecular polar interactions around the ester group involving dimer formation [4, 5]. As is evident from above examples, the formation and thermal

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†For part V see Ref. [8].

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stability of the smectic phases are strongly dependent on the relative orientation of the long alkyl group with respect to the ester linkage. Therefore, such a polar interaction model is insufficient to interpret the liquid crystalline properties for these systems.

In earlier papers, we described the thermal properties of the following four isomeric ester compounds [6, 7].

Compounds **1** show SmA and SmC phases in the lowest homologues, but isomers **2** show a SmC only phase in the higher homologues [6]. The tendency is similar to the substituted phenyl benzoates. These results also indicate that the position of the long octyloxy group relative to the orientation of two ester groups is very important in determining the smectic properties. Although compounds **3** and **4** have a symmetric core, their smectic properties are notably different from each other. These results indicate that there are some additional factors that must be taken into consideration in the formation of the smectic phases.

In this paper, we will describe further examination of the smectic properties for these systems by means of small angle X-ray diffraction (XRD). The homologues of compounds **4** exhibit only an SmC phase with a low SmC–N transition temperature [8] and are not discussed further in detail.

2. Experimental

2.1. *Materials*

The homologous series **1**–**3** were prepared by the conventional method described in our earlier paper [8].

2.2. *Methods*

Transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC instrument; indium (99.9%) was used as a calibration standard (m.p. 156.6°C, ΔH 28.4 $J\,g^{-1}$). The DSC thermogram was operated at a heating or cooling rate of $5°C\,min^{-1}$. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900); temperatures were calibrated with benzoic acid (m.p. 122.4°C).

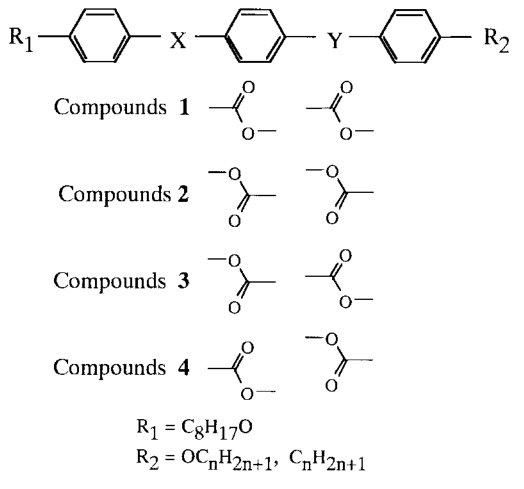


Figure 2. Chemical structures of compounds **1**–**4**.

XRD experiments for the smectic phases were performed using a Rigaku-denki RINT 2200 diffractometer; CuK_α ($\lambda = 1.541$ Å) was used as the X-ray source. The reflection angle was calibrated by a comparison of both right- and left-hand angles. The temperature was controlled using a Rigaku PTC-20A thermo-controller. The samples filled in quartz capillaries ($\phi = 1$ 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 scanning of the nematic and smectic reciprocal lattice mode along q ($q = 2p/d$ is the reciprocal space vector), i.e. in the direction parallel to the director **n**. The samples were heated to the isotropic temperature, and measurement was carried out during cooling.

The molecular orbital parameters referenced in this paper were obtained by a semi-empirical molecular orbital calculation, MOPAC (ver. 6.0), where minimization of the total energy was achieved by an AM1 method.

3. Results and discussion

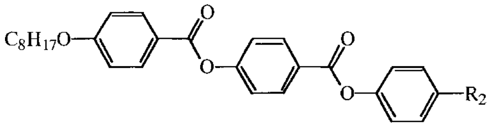
3.1. *Phase transitions*

The SmA and SmC phases of the derivatives were characterized by polarizing optical microscopy and DSC measurements [8]. The transition temperatures for the homologous series **1**, **2**, and **3** are summarized in tables 1–3.

The thermal properties of some derivatives in the tables have been already reported [1]. As can be seen, the formation of SmA and SmC phases, and their thermal stabilities, are strongly influenced not only by the relative orientation of the two ester groups but also by the chain lengths of both terminal alkoxy and/or alkyl chains. For example, the hydrogen derivative and the methoxy homologue of series **1** have the phase sequence of an SmA–N–I type, while the methoxy homologue of series **2** does not exhibit the SmA phase, indicating that in the liquid crystal cores of **1** and **2**, the terminal octyloxy group at the R_1 position is very important in determining the smectic properties of the core. This characteristic tendency agrees with the liquid crystalline properties of the 4-alkoxyphenyl 4-alkoxybenzoates (figure 1).

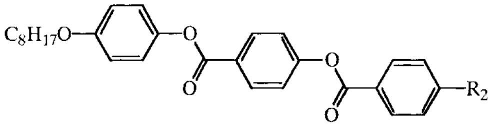
The liquid crystalline cores of compounds **3** and **4** are symmetric, so that the molecules are expected to have a similar molecular arrangement in the SmA phase. Nevertheless most of the compounds **3** exhibit SmA and SmC phases commencing from the lower homologues (C_3 onward), in contrast to the highly nematogenic

Table 1. Transition temperatures, X-ray and MO results for compounds **1**. Parenthesis indicate a monotropic transition. The molecular lengths were calculated by an AM1 method (MOPAC) for rotamer **a** in figure 5.



	Transition temperatures T/°C									Layers spacing d_{SmA}/Å	Molecular length l/Å	$\Delta(d-l)$/Å
R_2	Cr		SmC		SmA		N		I			
H	•	118	—		•	119	•	140	•	28.7	28.5	0.2
OCH_3	•	107	—		•	122	•	226	•	30.3	30.6	− 0.3
OC_2H_5	•	110	—		•	130	•	213	•	31.0	31.6	− 0.6
OC_3H_7	•	100	•	106	•	144	•	206	•	32.7	33.0	− 0.3
OC_4H_9	•	95	•	133	•	150	•	205	•	33.7	34.0	− 0.3
OC_5H_{11}	•	93	•	136	•	156	•	200	•	34.6	35.3	− 0.7
OC_6H_{13}	•	91	•	144	•	158	•	197	•	35.7	36.4	− 0.7
OC_7H_{15}	•	87	•	143	•	162	•	193	•	37.1	37.7	− 0.6
OC_8H_{17}	•	84	•	142	•	163	•	188	•	38.2	38.8	− 0.6
CH_3	•	109	—		•	134	•	195	•			
C_2H_5	•	97	—		•	138	•	192	•	30.3	30.7	− 0.4
C_3H_7	•	89(	•	79)	•	144	•	192	•	32.0	31.6	0.4
C_4H_9	•	90	•	98	•	149	•	184	•	32.9	32.9	0
C_5H_{11}	•	85	•	101	•	152	•	185	•	34.0	33.9	0.1
C_6H_{13}	•	84	•	103	•	156	•	179	•	35.3	35.2	0.1
C_7H_{15}	•	81	•	98	•	158	•	178	•	36.6	36.3	0.3
C_8H_{17}	•	84	•	88	•	160	•	174	•	37.7	37.4	0.3

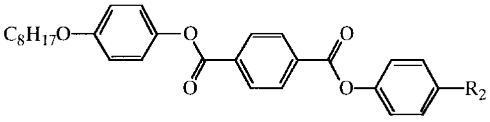
Table 2. Transition temperatures, X-ray and MO results for compounds *2*. Parentheses indicate a monotropic transition.



	Transition temperatures T/°C									Layer spacing d_{SmA}/Å	Molecular length l/Å	$\Delta(d-l)$/Å
R_2	Cr		SmC		SmA		N		I			
H	•	118	—		—		•	135	•			
OCH_3	•	101	—		—		•	214	•		30.1	
OC_2H_5	•	115	—		—		•	223	•		31.4	
OC_3H_7	•	103	—		—		•	209	•		32.6	
OC_4H_9	•	99(	•	65)	—		•	207	•		33.9	
OC_5H_{11}	•	97	•	101	—		•	201	•	(35.1)	35.1	0
OC_6H_{13}	•	96	•	132	•	144	•	198	•	36.4	36.4	0
OC_7H_{15}	•	89	•	142	•	155	•	193	•	37.3	37.6	− 0.3
OC_8H_{17}	•	84	•	142	•	163	•	188	•	38.2	38.8	− 0.6
					—		•		•			
CH_3	•	112	—		—		•	189	•		28.8	
C_2H_5	•	110	—		—		•	187	•		29.9	
C_3H_7	•	89	—		—		•	189	•		30.9	
C_4H_9	•	89	—		—		•	182	•		32.0	
C_5H_{11}	•	91(	•	72)	—		•	182	•		33.0	
C_6H_{13}	•	89	•	95	—		•	180	•	34.0[a]	34.2	− 0.2
C_7H_{15}	•	91	•	115	—		•	177	•	34.9[a]	35.1	− 0.2
C_8H_{17}	•	93	•	127	—		•	175	•	35.9[a]	37.0	− 0.1

[a] The value was taken from the maximum position around the SmC–N transition.

Table 3. Transition temperatures, X-ray and MO results for compounds **3**. Parenthesis indicate a monotropic transition. The molecular lengths were calculated by an AM1 method (MOPAC) for rotamer **a** in figure 5.



	Transition temperatures T/°C											
R_2	Cr		SmC		SmA		N		I	Layer spacing d_{SmA}/Å	Molecular length l/Å	$\Delta(d-l)$/Å
H	•	154	—		—	(	•	140)	•			
OCH_3	•	167	—		—		•	218	•			
OC_2H_5	•	175	—		—		•	222	•			
OC_3H_7	•	165	—		•	175	•	208	•	32.8	32.9	− 0.1
OC_4H_9	•	155	•	172	•	182	•	208	•	33.9	34.1	− 0.2
OC_5H_{11}	•	142	•	176	•	183	•	200	•	34.1	35.4	− 0.3
OC_6H_{13}	•	145	•	177	•	183	•	200	•	35.2	36.6	− 1.4
OC_7H_{15}	•	142	•	178	•	183	•	194	•	35.4	37.8	− 2.4
OC_8H_{17}	•	144	•	180	•	183	•	191	•	36.9	39.0	− 2.1
CH_3	•	140	—		—		•	187	•			
C_2H_5	•	154	—		—		•	195	•			
C_3H_7	•	148	—		•	152	•	193	•	31.4	31.7	− 0.3
C_4H_9	•	133	•	142	•	157	•	184	•	32.9	33.1	− 0.2
C_5H_{11}	•	133	•	150	•	160	•	182	•	33.9	34.2	− 0.3
C_6H_{13}	•	129	•	152	•	163	•	179	•	34.4	35.5	− 1.1
C_7H_{15}	•	134	•	154	•	164	•	177	•	35.8	36.6	− 0.8
C_8H_{17}	•	138	•	158	•	167	•	175	•	36.2	37.9	− 1.7

compounds **4**. The contrast in smectic properties should be interpreted in terms of a subtle difference between both core moieties due to the exchange of the ester groups [6].

3.2. *X-ray diffraction*

Following these results, the effect of the alkyl chain length on the layer structures of the SmA and SmC phases was examined by XRD. The X-ray profiles for SmA and SmC phases show a sharp reflection around $2\theta = 3°$ arising from the d_{001} direction, and a broad reflection around $2\theta = 20°$ arising from the d_{100} direction. In this paper, we report only on the behaviour of the d_{001} peak. The layer spacings converted from the d_{001} peaks of compounds **1**, **2** and **3** are plotted against temperature in figures 3 and 4.

The layer spacings for the alkoxy homologues of **1** show a notable temperature dependency without exhibiting any plateau region throughout the SmA and SmC regions. The remarkable change in layer spacing is attributable to a continuous change in the tilt angle of the average molecular axis to the layer plane. Apparently, the intervals of the plots for the homologues are not equivalent in the SmC phase. For example, the plots for the octyloxy and heptyloxy homologues contact at 113°C; those for the hexyloxy and pentyloxy homologues intersect at 135°C. These facts indicate that the tilt angles of the even homologues are larger than those of odd homologues at these temperatures. Simply supposing that the SmC phase has a monolayer arrangement, and the layer spacing (d) in the SmC phase is given by a function of the tilt angle ($d \cos \theta$), the tilt angles at $T_{SmC\text{-}SmA} - 20°C$ were estimated to be 26.5°, 22.8°, 22.9°, 20.3°, and 20.0° for octyloxy, heptyloxy, hexyloxy, pentyloxy, and butoxy homologues, respectively. From these values, we assume that the tilt angle tends to increase on ascending the homologues series, and shows the even–odd alternation, where the tilt angles for the even homologues are larger than those for the odd homologues.

The alkyl homologues of **1** exhibit a wide range SmA phase, so that the temperature dependency of the layer spacings in figure 3 (*b*) is weak; the layer spacings for all the homologues tend to increase with decreasing temperature, that is, 0.2 Å/50°C, and 0.3 Å/50°C for octyl and propyl homologues, respectively. A notable fact is that the layer spacings show a small upward rise (*c*. 0.2 Å) around the SmC–SmA transition temperature. A similar upward rise is observed in other compounds, as shown in figure 3. Probably, the SmC–SmA transition is accompanied by a certain molecular rearrangement affecting the layer spacing.

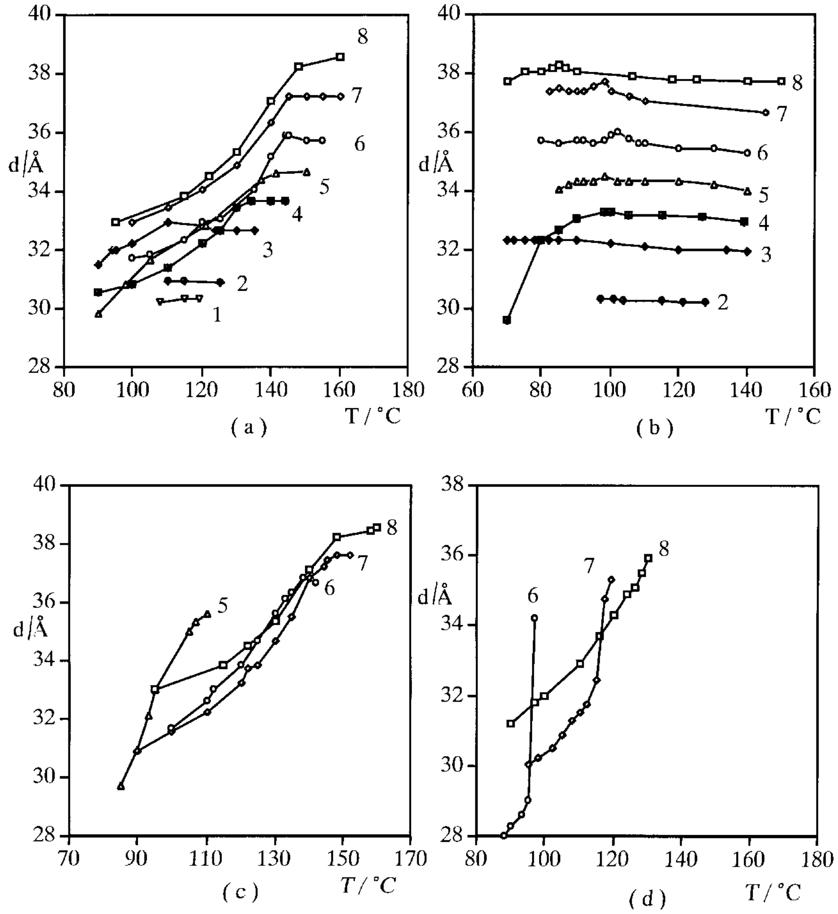


Figure 3. Plots of the layer spacings vs. temperature for: (*a*) octyloxy(8), heptyloxy(7), hexyloxy(6), pentyloxy(5), butoxy(4), propoxy(3), ethoxy(2), and methoxy(1) homologues of **1**; (*b*) octyl(8), heptyl(7), hexyl(6), pentyl(5), butyl(4), propyl(3), and ethyl(2) homologues of **1**; (*c*) octyloxy(8), heptyloxy(7), hexyloxy(6), and pentyloxy(5) homologues of **2**; (*d*) octyl(8), heptyl(7), and hexyl(6) homologues of **2**.

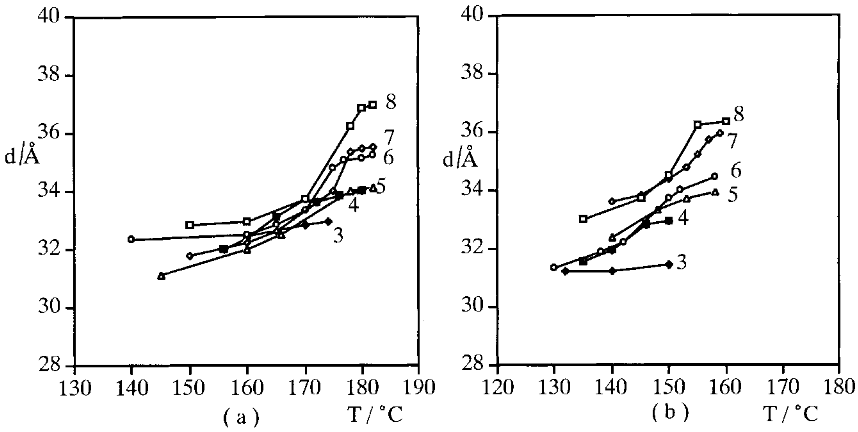


Figure 4. Plots of the layer spacings vs. temperature for: (*a*) octyloxy(8), heptyloxy(7), hexyloxy(6), pentyloxy(5), butoxy(4), and propoxy(3) homologues of **3**; (*b*) octyl(8), heptyl(7), hexyl(6), pentyl(5), butyl(4), and propyl(3) homologues of **3**.

For the alkoxy homologues of **2**, the C_6–C_4 homologues have the enantiotropic phase sequence of a SmC–SmA–N–I type, so that the plots for the layer spacing show similar features to those for the alkoxy homologues of **1**. A simple calculation gave values of 26.2°, 25.7°, and 26.0° for the tilt angles of the octyloxy, heptyloxy, and hexyloxy homologues at $T_{\mathrm{SmC\text{-}SmA}} - 20°\mathrm{C}$, respectively.

On the other hand, the hexyl, heptyl, and octyl homologues of **2** have the enantiotropic phase sequence of a SmC–N–I type, so that the layer spacings steeply decrease with decreasing temperature and have no plateau region, as shown in figure 3 (*d*). For these homologues, however, the maximum layer spacings around the SmC–N transition almost agree with the calculated molecular lengths, indicating that these homologues have a layer structure with an orthogonal arrangement like an SmA phase at the boundary of the SmC–N transition, while the apparent SmA phase cannot be observed by either DSC or microscopy. A similar transient formation of the SmA phase has been postulated in the smectic B–isotropic transition [9].

The alkoxy homologues of **3** have the phase sequence of a SmC–SmA–N–I type, except for the methoxy, ethoxy, and propoxy derivatives. The layer spacing decreases with decreasing temperature, due to increasing SmC properties. The simple calculation gave the values of 26.9°, 24.9°, 23.4°, 21.6° and 21.2° for the tilt angles of the octyloxy, heptyloxy, hexyloxy, pentyloxy, and butoxy homologues at $T_{\mathrm{SmC\text{-}SmA}} - 20°\mathrm{C}$, respectively. The tilt angles show a similar even–odd alternation to those for the alkoxy homologues of **1**. The layer spacing for the propoxy homologue, exhibiting no SmC phase, decreases with decreasing temperature, 0.4 Å/35°C, being opposite to the alkyl homologues of **1** shown in figure 3 (*b*).

The plots for the alkyl homologues of **3** also show the even–odd alternation in the SmC phase, where the intersection occurs in the plots of octyl and heptyl homologues, and hexyl and pentyl homologues, around 147°C. The simple calculation gave values of 24.2°, 22.0°, 23.7°, 23.5° and 19.6° for the tilt angles of the octyl, heptyl, hexyl, pentyl, and butyl homologues at $T_{\mathrm{SmC\text{-}SmA}} - 20°\mathrm{C}$, respectively. From these results, it is concluded that the alkoxy and alkyl derivatives of **3** have similar smectic properties, while the transition temperatures for the former are higher by *c.* 20°C than those for the latter.

We have already reported that the even–odd alternation of the tilt angle is also observed in the SmC–SmA(or N) transition temperature [8]. For alkoxy and alkyl homologues of **4**, only an SmC phase with low thermal stability is formed, so that further examination was not carried out.

The maximum values of the reflection peak around the SmA–N or the SmC–N transition are summarized in tables 1–3; layer spacings are plotted against the carbon numbers of the alkoxy and alkyl chains in figures 5 and 6.

3.3. *Molecular orbital calculations*

The molecular lengths were evaluated from the most stable conformation estimated by a semi-empirical molecular orbital calculation (AM1 method, MOPAC, ver. 6.0), where the van der Waals radii of neither terminal hydrogen atoms were involved. All the compounds should have some rotational isomers being almost equivalent in energy, whilst the entire molecular shape affecting the molecular length is fairly different. Figure 7, for example, shows structures of some representative rotamers for the octyloxy homologue of **1** (**2**). In the model, we supposed that the alkyl chain forms a *trans*-conformation on average in the liquid crystalline phases due to the rotational barrier of 13.8 kJ mol^{-1}, giving a zigzag conformation.

Rotamer **a** keeps the most linear shape among the rotamers, having the lowest rotational barrier. Rotamers **b** and **c** obtained by rotating 180° around the alkoxy chains are 0.01 and 0.00 kJ mol^{-1} less stable than rotamer **a**, respectively. Similarly, rotamer **d** obtained by rotating 180° around the ester group is 0.2 kJ mol^{-1} less stable than rotamer **a**. Considering the energy difference, all the rotamers should be present in an equivalent probability in the gas phase. It would be reasonable to assume that the observed layer spacing in the SmC and SmA phases is a mathematical average of every rotamer; that is, $d = \Sigma\, l_{\mathrm{rotamer}\, n} \times [\mathrm{rotamer}\ n]/n$, where $l_{\mathrm{rotamer}\, n}$ and [rotamer n] indicate the longitudinal length and molar concentration of rotamer n ($\Sigma\, n = 1$), respectively. As shown in figure 3 (*b*), the layer spacings of the derivatives having no tilted phases are almost independent of temperature, and agree with the longitudinal lengths for the most linear conformation (rotamer **a**). These results indicate that the population of the conformers with the bent shape, that is unfavourable for liquid crystalline properties, is lower in the SmA phase. Therefore, we assume that in anisotropic situations such as the N and SmA phases, the molecules tend to become linear as far as possible, like rotamer **a**, so that the longitudinal length in the liquid crystalline states can be substituted by that of the most stable and linear conformation for the present compounds; the results are summarized in the tables.

For the alkoxy homologues of **1**, the plot for the longitudinal molecular lengths calculated from rotamer **a** vs. *n*, figure 5 (*a*), shows a straight line with a weak even-odd alternation. The observed layer spacings of the SmA phase increase along the calculated molecular length, as shown in figure 5 (*a*). Interestingly, however, the layer spacings are always 0.5 Å shorter than the calculated molecular lengths. The disparity should be caused by the bent shape of the core of **1**, as shown below. On the other hand, the layer spacings for the alkyl homologues of **1** roughly agree with the calculated molecular lengths, as shown in figure 5 (*b*). A noteworthy fact is that the maximal layer spacings around SmC–SmA transition—dashed line in figure 5 (*b*)—are *c.* 1 Å longer than the

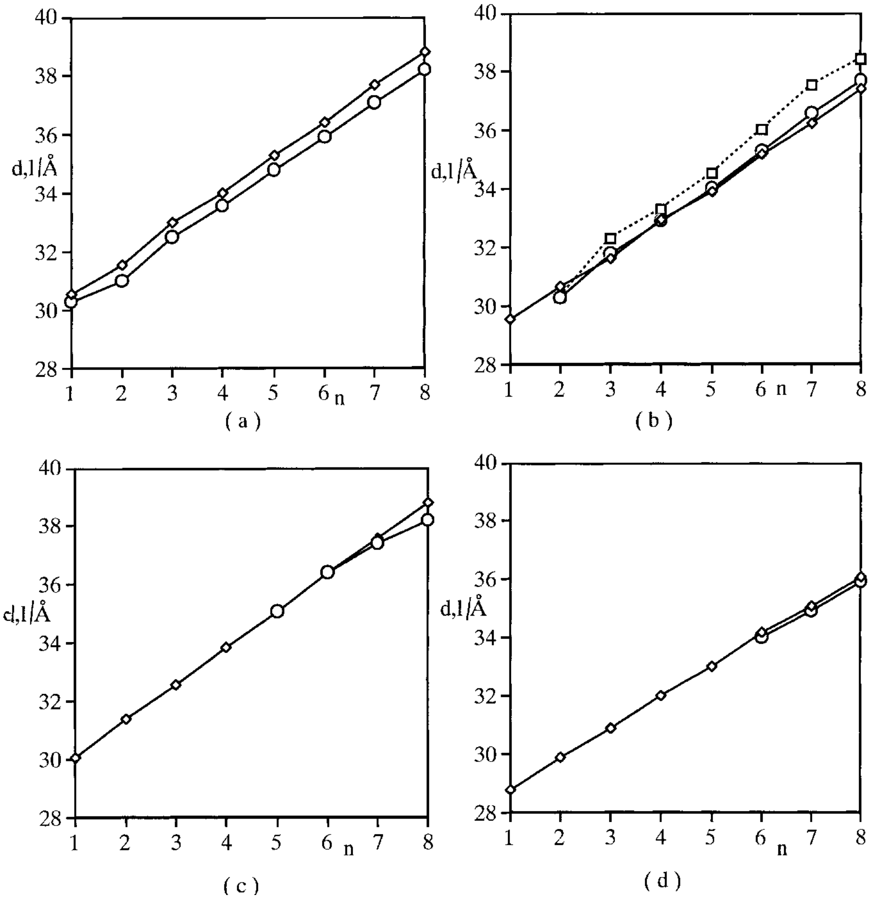


Figure 5. Plots of maximum layer spacings (○) and calculated molecular lengths (◇) vs. carbon number (*n*) for: (*a*) the alkoxy homologues of **1**; (*b*) the alkyl homologues of **1**; (*c*) the alkoxy homologues of **2**; (*d*) the alkyl homologues of **2**. The dashed line in (*b*) indicate the maximum layer spacings around the SmC–SmA transition. ◇ indicates the calculated molecular lengths for rotamer **a**.

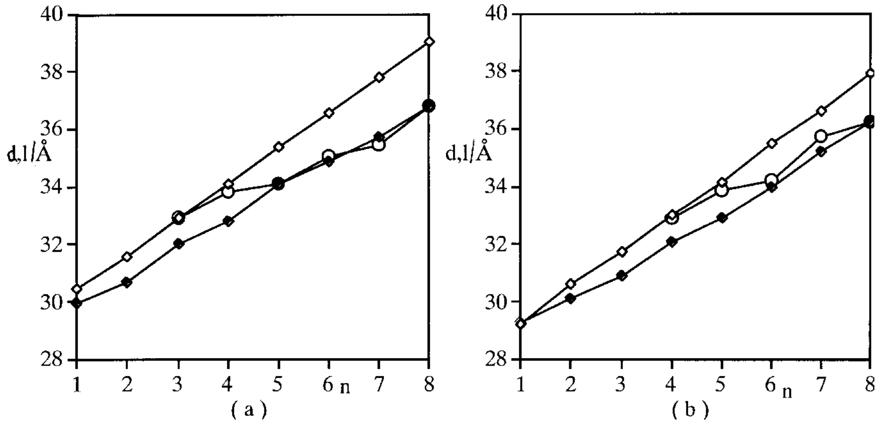


Figure 6. Plots of maximum layer spacings (○) and calculated molecular lengths (◇ and ◆) vs. carbon number (*n*) for: (*a*) the alkoxy homologues of **3**; (*b*) the alkyl homologues of **3**. ◇ and ◆ indicate the calculated molecular length for rotamers **e** and **f**, respectively.

calculated molecular lengths. One possibility is that the SmC–SmA transition is accompanied by a certain molecular rearrangement within the smectic layer.

As shown in figure 5(*c*), the layer spacings for the butoxy, pentyloxy, and hexyloxy homologues of **2** are in good agreement with the longitudinal lengths calculated

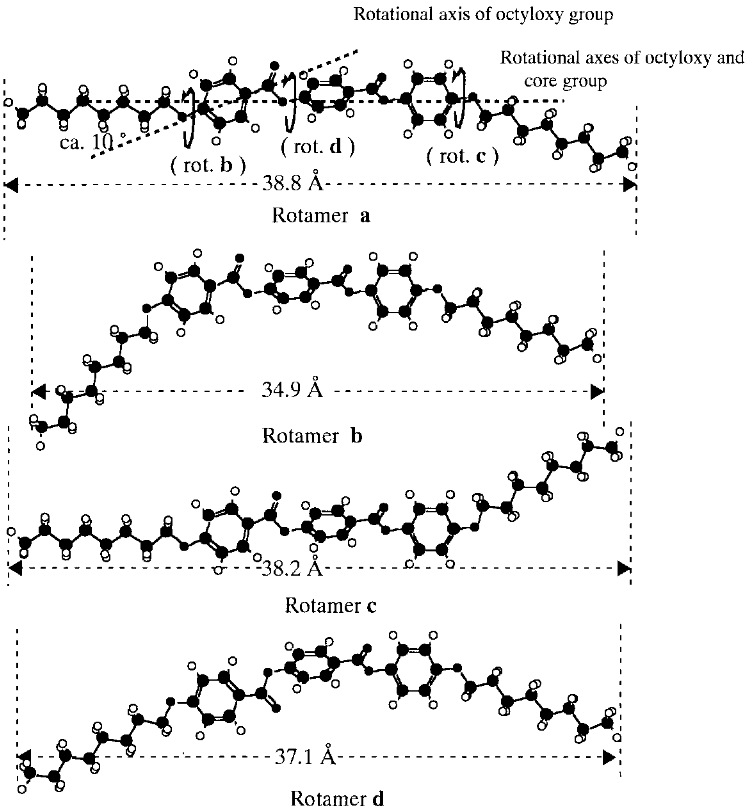


Figure 7. Molecular geometries of rotamers **a**–**d** for the octyloxy homologues of **1** (**2**).

from rotamer **a**, but those for the heptyloxy and octyloxy homologues are shorter than the calculated molecular lengths. The layer spacings for the alkyl homologues of **2** are also in good agreement with the longitudinal lengths calculated from rotamer **a**, as shown in figure 5 (*d*), similar to those for the alkyl homologues of **1**. From these results, we conclude that the alkoxy and alkyl homologues of **1** and **2** form a monolayer arrangement in the SmA phase, and the layer spacings essentially agree with the calculated molecular lengths from rotamer **a**.

Furthermore, molecules in an anisotropic situation such as the SmA phase favour the most linear conformation, so that the layer spacings almost agree with the calculated molecular lengths, see for example figures 5 (*b*), 5 (*c*), and 5 (*d*).

An exceptional case is provided by the alkoxy homologues of **1**, where the layer spacings are *c*. 0.5 Å shorter than the calculated molecular lengths for rotamer **a** in figure 5 (*a*). Interestingly, the layer spacings for the heptyloxy homologue of **2** is also 0.3 Å shorter than the calculated molecular length, as shown in figure 5 (*c*). No doubt the disparity between the layer spacings and calculated molecular lengths arises from the intrinsic nature of phenyl 4-(4-octyloxybenzoyloxy)benzoate, the core of **1**. As mentioned in our earlier paper [6], phenyl 4-(4-octyloxybenzoyloxy)benzoate intrinsically has a bent shape due to the parallel orientation of two ester groups within the molecule, where the small phenyl–CO–O bond angle (112.9°), compared with the CO–O–phenyl bond angle (120.2°) and phenyl–O–alkyl bond angle (115.9°), is responsible for the bent shape. This indicates that the rotational axis of the alkoxy group at the R_1 position has an angle of *c*. 10° to the average rotational axis of the phenyl 4-benzoyloxybenzoate core, supposing that the rotational axis of the core passes through the centres of both terminal aromatic rings.

As shown in figure 7, the rotation of the $C_8H_{17}O$–phenyl bond at the R_1 position results in a notable change in the entire molecular shape (rotamers **a** and **b**), compared with that in the R_2 position (rotamers **a** and **c**). Therefore, the disparity of the layer spacings in figure 5 (*a*) might be attributable to the contribution of rotamer **b**, where the bend of the entire molecular shape becomes notable from the heptyloxy homologue of **2**, as shown in figure 5 (*c*). In addition, the bent shape of the core of **1** is solely responsible for the formation of the SmA phase, and the alkoxy and alkyl groups at the R_2 position enhance the SmA thermal stability, and monotonously increase the layer spacing, as shown in figures 5 (*a*) and 5 (*b*).

The plots for alkoxy and alkyl homologues of **3** in figures 6 (*a*) and 6 (*b*) show a notably different feature from those for **1** and **2**. In the figure the molecular lengths for rotamers **e** and **f**, corresponding to **a** and **b** in figure 7, respectively, are also plotted.

The layer spacings agree with the calculated molecular lengths for rotamer **e** corresponding to **a** in figure 7, as the alkyl chain is short, i.e. the ethoxy, propoxy, and butoxy homologues. However, the layer spacings become shorter than the calculated molecular lengths on ascending the homologous, series and rather extend along the molecular lengths for rotamer **f** corresponding to **b** in figure 7. Interestingly, the layer spacings show an apparent even–odd alternation in the higher homologues, while the even–odd alternation is not recognizable in the $T_{\mathrm{SmA\text{-}N}}$, as shown in table 3. Generally, the even–odd alternation for the $T_{\mathrm{N\text{-}I}}$ is observed only in the lower homologues, for example as shown in tables 1 and 3. Therefore, the even–odd alternation observed in the layer spacings for the higher homologues should be caused by the specific packing of the terminals of the alkoxy or the alkyl group around the surface of the smectic layer.

As shown in figure 8, both rotational axes of the alkoxy and core groups are arranged parallel to the average rotational axis passing through the centres of both terminal aromatic rings, so that the entire molecular shape might be linear. In particular, rotamer **e** should keep good linearity and be favourable for liquid crystalline properties. On the other hand, rotamer **f** has a bent shape and is unfavourable for liquid crystalline properties. As shown in figure 6, in practice the layer spacings of the SmA phase for the propoxy, butoxy, butyl, and pentyl homologues are in good agreement with the molecular lengths for rotamer **e**. These results indicate that the molecules form a monolayer arrangement, where rotamer **e** is preferable. On the other hand, the layer spacings for the higher homologues approach and extend along the molecular lengths for rotamer **f**. As we can see from figure 6, however, the even–odd alternation for the calculated molecular lengths of both alkyl and alkoxy homologues is noticeable in the lower homologues. Therefore, the trend of the layer spacings is not interpreted in terms of continuous change from rotamer **e** to **f** on ascending the homologues series. In order to explain the abnormal even–odd alternation and shortening of the layer spacings for compounds **3**, we suppose that the terminal of both alkyl groups bend to the smectic layer plane, as shown in figure 9.

Thereby, we assume that the terephthalate cores retain a tight packing of nearest neighbours, due to the rigidity, linearity and planarity of the terephthalate moiety. In such circumstances, the rotational freedom of both terminal hydrocarbon chains is more or less restricted, giving the bent shape of both terminal alkyl groups. The rigidity, planarity, and linearity around the terephthalate core, in addition, may cause the marked smectic properties of compounds **3**. The large latent heats of 0.2–0.4 and 1–2 kJ mol^{-1} for the SmC–SmA and SmA–N transitions, respectively, may be the result of the tight packing [6]. For series **1** and **2**, the latent heats for the SmC–SmA and SmA–N transitions are 0 and 0–1 kJ mol^{-1}, respectively [8]. In this connection, the alkoxy chain for the octyloxy homologues of **3** has been reported to have a linear structure in the crystalline state [10].

On the other hand, 1,4-dibenzoyloxybenzene, the core of series **4** compounds, should be flexible and non-planar due to the low rotational barrier of 0.0 kJ mol^{-1} around both phenyl–CO–O–phenyl bonds. In addition, the entire molecular shape should be linear due to cancellation of the bending around the ester groups. These geometrical factors might reduce the smectic properties of compounds **4**.

4. Conclusion

The thermal stability of the smectic A phase is affected by (a) the relative orientation of two ester groups within the core and (b) the terminal alkoxy and/or alkyl chain

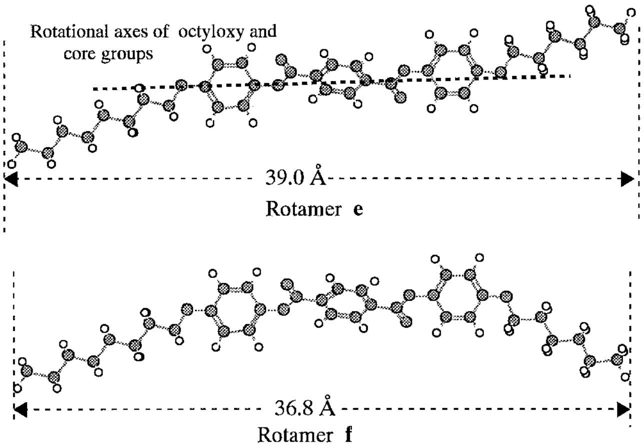


Figure 8. Molecular geometries of rotamers, **e** and **f** for the octyloxy homologue of **3**.

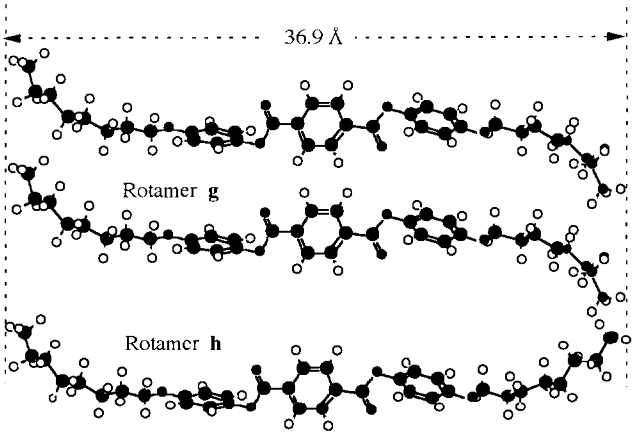


Figure 9. Possible molecular arrangement of the octyloxy homologues of **3** in the SmA phase.

lengths. For layer formation of the ester compounds, a subtle change in molecular parameters such as rigidity, planarity, and linearity, due to alternation of the ester groups, is of primary importance in determining the smectic properties. We wish to emphasize that the notable smectic properties of the phenyl benzoate system with compounds **1** arise from the bent shape due to the long alkoxy group in the benzoate portion. The rigidity, planarity, and linearity of the core portion are responsible for the difference in the smectic properties between series **3** and **4** compounds.

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