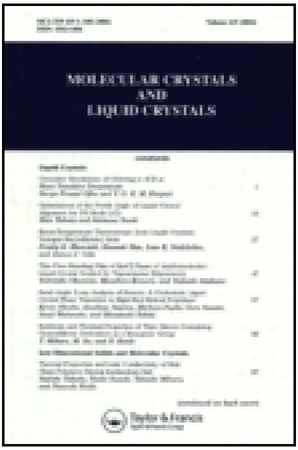

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Liquid Crystalline Properties of Dissymmetric Molecules Part 5: the Effects of Alkyl Chain Length and Linkages on Thermal Properties of Smectic A and C Phases in Three Aromatic Ring Systems

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Liquid Crystalline Properties of Dissymmetric Molecules Part 5: the Effects of Alkyl Chain Length and Linkages on Thermal Properties of Smectic A and C Phases in Three Aromatic Ring Systems

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This paper describes the effect of alkyl and alkoxy chain lengths on the thermal properties of four isomeric systems; 4-R-phenyl 4-(4-octyloxybenzoyloxy)benzoates (1), 4-octyloxyphenyl 4-(4-R-benzoyloxy)benzoates (2), 4-(4-R-benzoyloxy)phenyl 4-octyloxybenzoates (3), and 4-R-phenyl 4-octyloxyphenyl terephthalates (4) (R=alkoxy, alkyl). The smectic properties for 1 and 2 are fairly different when both terminal alkyl and alkoxyl groups are short, while both have the same liquid crystalline core. The homologs of 3 exhibit only a smectic C phase even in the higher homologs. The homologs of 4 preferentially exhibit smectic A and C phases from the earlier homologs. The difference in the smectic properties will be discussed in terms of their molecular characteristics.

Keywords: liquid crystals; ester compounds; thermal properties; smectic properties; chain length effect

INTRODUCTION

In the theoretical treatment of liquid crystals molecules are regarded as a linear rod-like or a lath-shape, and the symmetry is one of the important factors in order to simplify the theoretical process.[1] In practice, however, most liquid crystalline mole-

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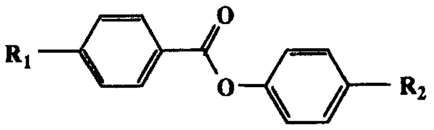
cules are rather dissymmetric, and the physical properties arising from the dissymmetric part play an important role in determining the liquid crystalline properties.

The liquid crystalline properties for 4-alkoxyphenyl 4-alkoxybenzoate systems are one of the typical examples.[2]



R_1	R_2	C		S_C		S_A		N		I
$C_8H_{17}O$	C_4H_9O		58		59		60		89	
C_4H_9O	$C_8H_{17}O$		65						89	

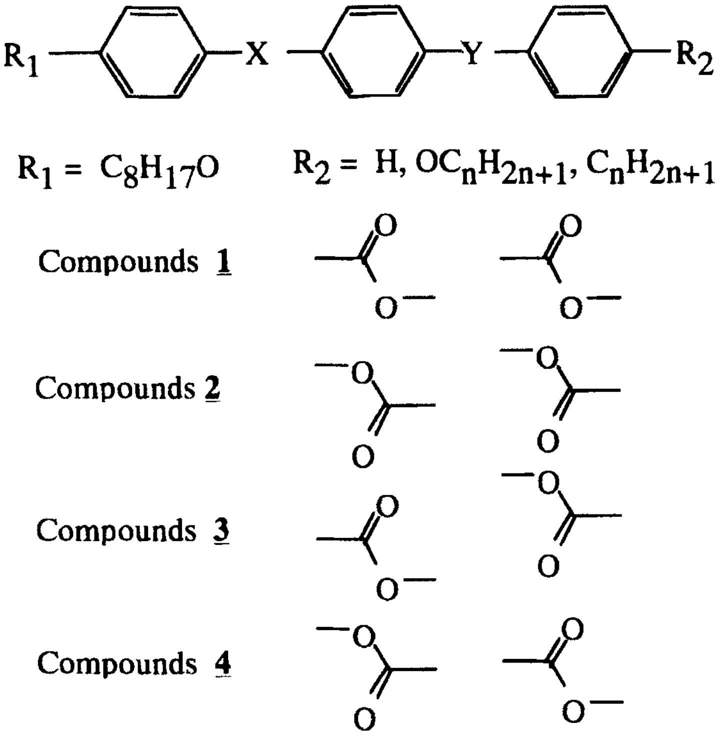
from ref. 1

4-Butoxyphenyl 4-octyloxybenzoate has the mesomorphic sequence of a smectic C(S_C)-smectic A(S_A)-nematic(N)-isotropic(I) type. In contrast, 4-octyloxyphenyl 4-butoxybenzoate, the isomer, has the simple sequence of an N-I type. These results indicate that for the formation of the S_A phase the role of the alkoxyl group at the R_1 position is different from that at the R_2 position. A similar trend has been known in the isomeric polar liquid crystals such as 4-cyanophenyl 4-alkoxybenzoates[3] and 4-alkoxyphenyl 4-cyanobenzoates,[4] where the former favors the S_A phase with a partially bilayer arrangement of molecules, and 4-nitrophenyl 4-alkoxybenzoates[5] and 4-alkoxyphenyl 4-nitrobenzoates,[6] where the former also tends to form the S_A phase. For the difference in the smectic properties, although the polar interactions between the polar terminal groups and/or the ester group have been emphasized, there is no doubt that the long alkoxyl groups at R_1 and R_2 positions are also very important in displaying the characteristic mesomorphism. A similar phenomenon is known in 4-methoxyphenyl 4-octyloxybiphenyl-4′-carboxylate (R_1= 4-$C_8H_{17}O$-C_6H_4, R_2 = 4-CH_3O) and 4-octyloxyphenyl 4-methoxybiphenyl-4′-carboxylate (R_1= 4-CH_3O, R_2= 4-$C_8H_{17}O$-C_6H_4), where the former has the phase sequence of an S_A-N-I type, and the latter exhibits only an N phase.[7]

It is known that many liquid crystals having an ester linkage tend to exhibit S_C and S_A phases as well as the N one, where the smectic properties have been interpreted in terms of intermolecular polar interactions around the ester groups and/or the dimer formation.[8,9] As is evident from above examples, however, the formation and thermal stability of the smectic phases are apparently concerned with the relative orientation of the long alkyl group or bulk substituent with respect to the dissymmetric ester linkage. Therefore, such a simple intermolecular interaction model is insufficient to interpret the liquid crystalline properties mentioned above. Rather, these examples suggest the importance of a subtle change in both molecular structures due to inversion of the ester linkage, or both substituents at the terminal positions.

A similar tendency is also observed in many dissymmetric liquid crystal systems such as 4,4′-disubstituted benzylideneaniline systems, while the tendency is less apparent than the ester compounds.[2,10]

In an earlier paper, we described the thermal properties of four isomeric ester compounds; 4-phenyl 4-(4-alkoxybenzoyloxy)benzoates (1, $R_1 = C_nH_{2n+1}O$, $R_2 = H$), 4-alkoxyphenyl 4-benzoyloxybenzoates (2, $R_1 = H$, $R_2 = C_nH_{2n+1}O$), 4-(4-alkoxybenzoyloxy)phenyl benzoates (3, $R_1 = C_nH_{2n+1}O$, $R_2 = H$), 4-alkoxyphenyl phenyl terephthalates (4, $R_1 = C_nH_{2n+1}O$, $R_2 = H$).[11]



Interestingly, the homologs of 4-phenyl 4-(4-alkoxybenzoyloxy)benzoates (1) tend to exhibit the S_A phase from the earlier homologs, while the homologs of 4-alkoxyphenyl 4-benzoyloxybenzoates (2) having the same core are difficult in the formation. The tendency is similar to the 4-alkoxyphenyl 4-alkoxybenzoates. Furthermore, 4-(4-alkoxybenzoyloxy)phenyl benzoates (3) and 4-alkoxyphenyl phenyl terephthalates (4) show notable different smectic properties to each other, while both have a symmetric liquid crystalline core.

These results indicate that for the formation of the smectic phases, some important factors arising from the dissymmetry around the ester linkages must be taken into consideration.

In this paper, we will describe the effect of an alkoxyl or an alkyl group attached at the terminal phenyl group (R_2) on the liquid crystalline properties. The liquid crystalline cores of compounds 1 and 2 are intrinsically dissymmetric, so that the terminal alkoxyl and alkyl groups at both R_1 and R_2 positions are always not equivalent. Although the liquid crystalline cores of 3 and 4 are intrinsically symmetric and both terminal positions are equivalent, substitution of terminal alkoxy and alkyl chains causes dissymmetry of the entire molecular shape.

EXPERIMENTAL

Materials

The homologs of 1 – 4 were prepared by the conventional method described in our earlier paper,[12] and the purity of the materials was confirmed by elementary analysis, HPLC, ^{1}HNMR spectroscopy, and DSC thermogram using a "DSCPURITY" program (Seiko-denshi Co.).

Method

The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp 156.6 °C, 28.4 J/g). 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). The molecular parameters used in this document were obtained by a semi-empirical molecular orbital calculation for a single molecule, using the AM1 method (MOPAC, ver. 6.0).

RESULTS AND DISCUSSION

The smectic A and C (S_A and S_C) were assigned by consideration of microscopic analysis. The S_A phase shows focal conic fan and isotropic textures under homogeneous and homeotropic alignments, respectively. The S_C phase shows broken focal conic fan and schlieren textures under homogeneous and homeotropic alignments, respectively. There is no fundamental difference in the textures all over the compounds.

McMillan has introduced a parameter, R (the ratio of the smectic A-nematic ($T_{SA\text{-}N}$) to nematic-isotropic ($T_{N\text{-}I}$) transition temperatures), which is in some way proportional to the smectic interaction strength.[13] The theory predicts that the entropy of the S_A-N transition becomes zero when R = 0.88, and the transition becomes more and more the second order nature when R< 0.88. It is known that the transition entropy of the S_A-N transition for many liquid crystals can be roughly correlated with R.[1] In this paper, we used the R value as the criterion of the S_A thermal stability.

The thermodynamic properties for the homologs of **1** – **4** are summarized in Tables I – IV, where some homologs have been already reported.[2]

TABLE I Transition temperatures and latent heats for **1**

R_2	Transition temperatures (T/°C)									Latent heats (kJ/mol)			$T_{SA\text{-}N}/T_{N\text{-}I}$
	C		S_C		S_A		N		I	$\Delta H_{SC\text{-}SA}$	$\Delta H_{SA\text{-}N}$	$\Delta H_{N\text{-}I}$	
H	·	114	–		·	126	·	140	·		1.6	0.8	0.95
OCH_3	·	107	–		·	129	·	215	·		0.0	0.6	0.82
OC_2H_5	·	110	–		·	130	·	219	·		0.2	1.3	0.82
OC_3H_7	·	98	·	100	·	144	·	205	·	0.0	0.2	1.3	0.87
OC_4H_9	·	97	·	132	·	149	·	206	·	0.0	0.3	1.3	0.88
OC_5H_{11}	·	103	·	133	·	156	·	200	·	0.0	0.3	1.7	0.91
OC_6H_{13}	·	98	·	143	·	158	·	197	·	0.0	0.3	1.5	0.92
OC_7H_{15}	·	87	.	144	.	162	.	193	.	0.0	0.3	1.7	0.94
OC_8H_{17}	·	84	·	145	·	163	·	188	·	0.0	1.0	1.8	0.95
CH_3	·	109	–		·	134	·	195	·		0.4	1.3	0.87
C_2H_5	·	97	–		·	138	·	192	·		0.5	1.2	0.89
C_3H_7	·	89(	·	79)	.	144	.	192	.	0.0	0.4	1.1	0.90
C_4H_9	·	90	·	98	·	149	·	184	·	0.0	0.4	0.9	0.92
C_5H_{11}	·	85	·	101	·	152	·	185	·	0.0	0.4	1.1	0.93
C_6H_{13}	·	84	·	103	·	156	·	179	·	0.0	0.5	1.2	0.95
C_7H_{15}	·	81	·	98	.	158	.	178	.	0.0	0.7	1.3	0.96
C_8H_{17}	·	84	·	88	·	160	·	174	·	0.0	0.8	1.5	0.97

C, S_C, S_A, N, and I indicate crystal, smectic C, smectic A, nematic, and isotropic phases, respectively. Parenthesis indicates a monotropic transition.

TABLE II Transition temperatures and latent heats for **2**

R_2	*Transition temperatures (T/°C)*									*Latent heats (kJ/mol)*			
	C		S_C		S_A		*N*		*I*	$\Delta H_{SC\text{-}SA}$ or $\Delta H_{SC\text{-}N}$	$\Delta H_{SA\text{-}N}$	$\Delta H_{N\text{-}I}$	$T_{SA\text{-}N}/T_{N\text{-}I}$
H	·	118	–		[·	45]	·	135	·			0.7	0.78
OCH_3	·	101	–		–		·	214	·			0.8	
OC_2H_5	·	115	–		–		·	223	·			0.2	
OC_3H_7	·	103	–		–		·	209	·			1.1	
OC_4H_9	·	99(	.	65)	–		.	207	.	0.0		1.0	
OC_5H_{11}	·	97	·	101	–		·	201	·	0.0		1.3	
OC_6H_{13}	·	96	.	132	.	144	.	198	.	0.0	0.0	1.5	0.89
OC_7H_{15}	·	89	.	142	.	155	.	193	.	0.0	0.0	1.6	0.92
OC_8H_{17}	·	84	.	145	.	163	.	188	.	0.0	1.0	1.8	0.95
CH_3	·	112	–		–		·	189	·			0.7	
C_2H_5	·	110	–		–		·	187	·			0.7	
C_3H_7	·	89	–		–		·	189	·			0.8	
C_4H_9	·	89	–		–		·	182	·			0.8	
C_5H_{11}	·	91(	·	72)	–		.	182	.	0.0		1.1	
C_6H_{13}	·	89	·	95	–		·	180	·	0.3		1.5	
C_7H_{15}	·	91	·	115	–		·	177	·	0.3		1.5	
C_8H_{17}	·	93	·	126	–		·	175	·	0.3		1.5	

Bracket indicates a virtual transition temperature extrapolated from a binary phase diagram for the mixtures of the hydrogen and butoxy homologs.

TABLE III Transition temperatures and latent heats for **3**

R_2	*Transition temperatures (T/°C)*								*Latent heats (kJ/mol)*	
	C		S_C		S_A	*N*		*I*	$\Delta H_{SC\text{-}N}$	$\Delta H_{N\text{-}I}$
H	·	117	–		–	·	141	·		1.0
OCH_3	·	124	–		–	·	224	·		1.2
OC_2H_5	·	125	–		–	·	228	·		1.2
OC_3H_7	·	130	–		–	·	217	·		1.3
OC_4H_9	·	124	–		–	·	215	·		1.5
OC_5H_{11}	·	115	–		–	·	205	·		1.6
OC_6H_{13}	·	108	.	109	–	.	200	.	2.0	1.6
OC_7H_{15}	·	112	.	119	–	.	197	.	2.7	1.8
OC_8H_{17}	·	122	·	126	–	·	194	·	3.2	2.1

R_2	Transition temperatures (T/°C)									Latent heats (kJ/mol)	
	C		S_C		S_A		N		I	$\Delta H_{SC\text{-}N}$	$\Delta H_{N\text{-}I}$
CH_3	·	102	–		–		·	199	·		1.1
C_2H_5	·	100	–		–		·	195	·		0.9
C_3H_7	·	98	–		–		·	199	·		1.2
C_4H_9	·	109	–		–		·	189	·		1.5
C_5H_{11}	·	110	–		–		·	190	·		1.6
C_6H_{13}	·	103	·	106	–		·	184	·	2.0	1.6
C_7H_{15}	·	100	·	115	–		·	182	·	2.3	1.7
C_8H_{17}	·	101	·	118	–		·	176	·	2.5	1.7

TABLE IV Transition temperatures and latent heats for **4**

R_2	Transition temperatures (T/°C)									Latent heats (kJ/mol)			
	C		S_C		S_A		N		I	$\Delta H_{SC\text{-}SA}$	$\Delta H_{SA\text{-}N}$	$\Delta H_{N\text{-}I}$	$T_{SA\text{-}N}/T_{N\text{-}I}$
H	·	154	–	(	[·	130]	·	140)	.			[a]1	[0.98]
OCH_3	·	167	–		–		·	218	·			0.6	
OC_2H_5	·	175	–		[·	165]	·	222	·			0.8	[0.88]
OC_3H_7	·	165[	·	163]	·	175	.	208	.		0.0	0.8	0.93
OC_4H_9	·	155	·	172	·	180	·	208	·	0.0	0.2	1.5	0.94
OC_5H_{11}	·	142	.	176	.	183	.	200	.	0.2	0.4	1.6	0.96
OC_6H_{13}	·	145	·	177	·	183	·	200	·	0.3	0.5	1.9	0.96
OC_7H_{15}	·	142	.	178	.	183	.	194	.	0.4	0.7	2.0	0.97
OC_8H_{17}	·	144	·	180	·	183	·	191	·	0.4	0.9	2.1	0.98
CH_3	·	140	–		–		·	187	·			0.8	
C_2H_5	·	154	–		[·	140]	·	195	·			1.0	[0.88]
C_3H_7	·	148	–		·	152	·	193	·		0.0	1.1	0.91
C_4H_9	·	133	·	142	·	157	·	184	·	0.0	0.3	1.0	0.94
C_5H_{11}	·	134	·	150	·	160	·	182	·	0.0	0.5	1.5	0.96
C_6H_{13}	·	129	·	152	·	163	·	179	·	0.1	0.6	1.7	0.96
C_7H_{15}	·	133	·	154	·	164	·	177	·	0.3	0.9	1.9	0.97
C_8H_{17}	·	132	·	156	·	164	·	175	·	0.4	1.1	2.0	0.98

Brackets and parenthesis indicate virtual and monotropic transitions, respectively.

a. N-I transition is not detected by DSC thermogram.

The melting points and the $T_{N\text{-}I}$ for the hydrogen derivatives and the average values for the homologs are summarized in Table V.

TABLE V Average transition temperatures (T/°C) and latent heats (kJ/mol)

Compounds	*H*			*Alkoxy*			*Alkyl*		
	T_{mp}	$T_{N\text{-}I}$	$\Delta H_{N\text{-}I}$	T_{mp}	$T_{N\text{-}I}$	$\Delta H_{N\text{-}I}$	T_{mp}	$T_{N\text{-}I}$	$\Delta H_{N\text{-}I}$
1	118	140	0.7	98	203	1.5	90	185	1.2
2	118	135	0.8	98	204	1.2	96	181	1.1
3	117	141	1.0	120	209	1.5	103	189	1.4
4	154	[140]		154	205	1.4	139	184	1.4

T_{mp} and $T_{N\text{-}I}$ indicate melting and nematic-isotropic transition temperatures, respectively. $\Delta H_{N\text{-}I}$ indicates the latent heat for the nematic-isotropic transition.

It would be reasonable to assume that physical characteristics of the liquid crystalline core are apt to reflect thermal properties of earlier homologs such as hydrogen and methoxy ones. The effective order for the melting point of the hydrogen derivatives is **4** > **1**= **2** = **3**. A similar trend is observed in the melting points of the alkoxy and alkyl derivatives. The rigidity of the terephthalate core should be responsible for the highest melting points of **4**.

For the hydrogen derivatives, the effective order for the $T_{N\text{-}I}$ is **1** = **2** = **4** > **3**, while the difference, however, is negligibly small in the thermodynamic point of view. For the alkoxy derivatives, on the other hand, the effective order for the $T_{N\text{-}I}$ is **3** > **1** = **2** = **4**. A similar trend is observed for the alkyl derivatives, **3** > **1** = **4** > **2**. Although the difference is quite small, the core of **3** seems to be the most effective for the N thermal stability. These results indicate that the alternation of the ester linkages affects the thermodynamic properties of the crystalline phase rather than those of the N phase.

The transition temperatures are plotted against the carbon numbers of the alkoxy and alkyl chains, in Figs. 1 and 2.

The $T_{N\text{-}I}$ values for the earlier homologs of some compounds show an apparent even-odd alternation, where the $T_{N\text{-}I}$ values for the alkoxy homologs having even carbon number are higher than the odd ones, and vice versa for the alkyl ones. The feature is common in the N-I transition for usual liquid crystals.[14] The even-odd alternation for the $T_{N\text{-}I}$ has been interpreted in terms of difference in the packing mode at the terminal methyl group or the relative orientation of the terminal methyl group with respect to the longitudinal axis of the liquid crystalline core. That is, the terminal methyl group of the alkoxy chain for the odd homologs increases the molecular breadth rather than the longitudinal length, while that for the even homologs increases the longitudinal length. As a result, the $T_{N\text{-}I}$ values for the even homologs are higher than those for the odd ones, just similar to the $T_{N\text{-}I}$ for **1**.

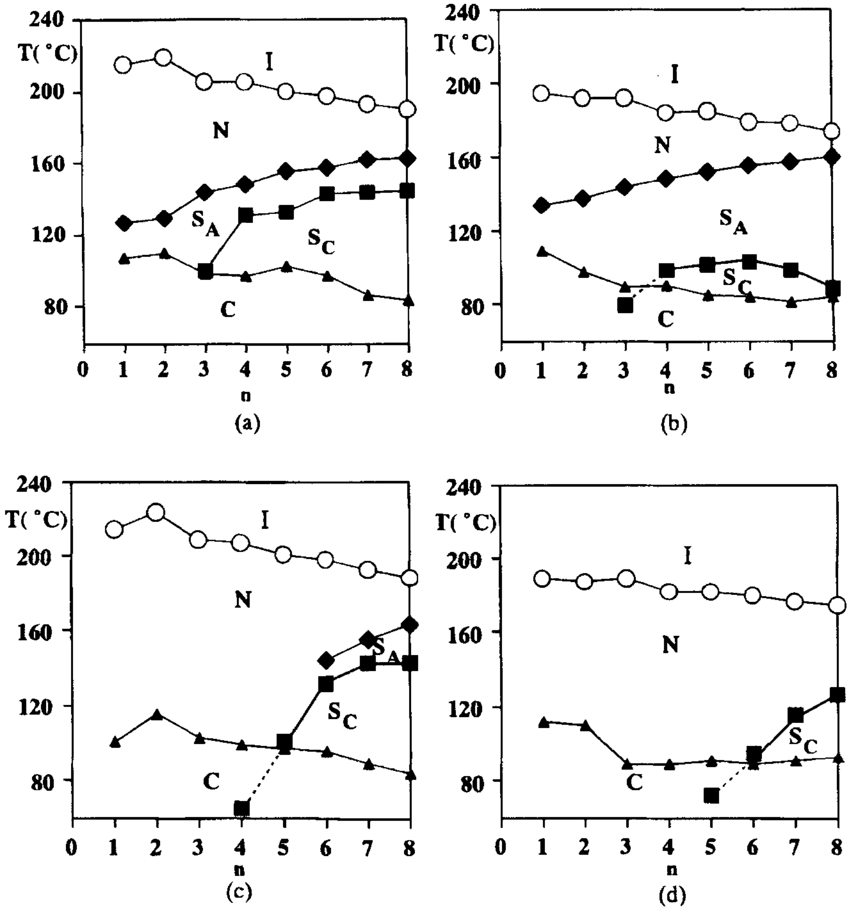


FIGURE 1 Plots of transition temperatures against alkoxy and alkyl chain lengths for (a) 1 (alkoxy), (b) 1 (alkyl), (c) 2 (alkoxy), and (d) 2 (alkyl). ○; N-I, ◆; S_A-N, ■; S_C-S_A(N) transition, and ▲; melting point. Dashed lines indicate a monotropic transition

As shown in Figures 1 and 2, the smectic properties are strongly affected by both relative orientation of the ester groups and variable alkoxy and alkyl chain lengths at the R_2 position.

Not only all the alkoxy and alkyl homologs of 1 but also the hydrogen derivative exhibit an enantiotropic S_A phase, and the $T_{SA\text{-}N}$ gradually increases on ascending the homologs. These results indicate that the core of 1 intrinsically favors the layer arrangement. Interestingly, the $T_{SA\text{-}N}$ values show an apparent even-odd alternation having an invert feature to the $T_{N\text{-}I}$, where the $T_{SA\text{-}N}$ values

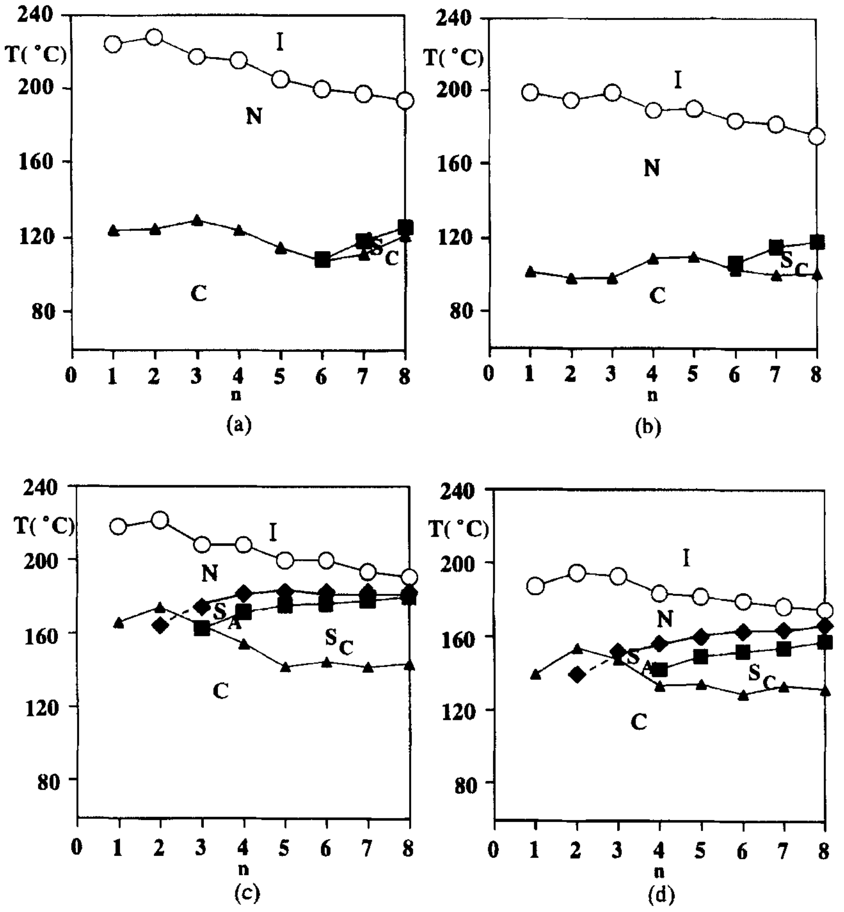


FIGURE 2 Plots of transition temperatures against alkoxy and alkyl chain lengths for (a) 3 (alkoxy), (b) 3 (alkyl), (c) 4 (alkoxy), and (d) 4 (alkyl). ○; N-I, ◆; S_A-N, ■; S_C-S_A(N) transition, and ▲; melting point. Dashed lines indicate a monotropic transition

for the odd homologs are apparently higher than those for the odd ones, as shown in Fig. 1a. The even-odd alternation is more apparent in the plots of the R values vs. n, as shown in Fig. 3.

As mentioned above, the inter-molecular interactions at the terminals of the alkyl chain cause the even-odd alternation for the $T_{N\text{-}I}$. It would be reasonable to assume that not only the lateral interactions within the layer but also the inter-layer ones around the layer surface are very important in determining the layer structure and thermal stability of the S_A phase, and therefore, the terminal

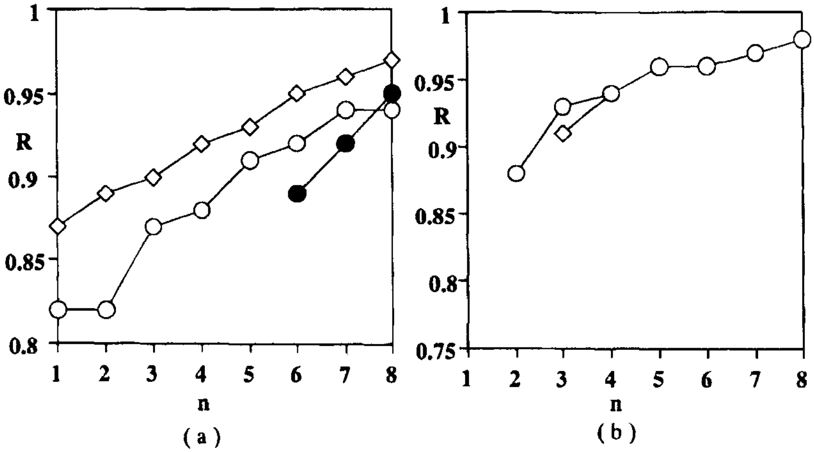


FIGURE 3 Plots of the R vs the carbon numbers (n) for **1**, **2**, and **4**. (a) ◊; alkyl derivatives of **1**, ∘; alkoxy derivatives of **1**, •; alkoxy derivatives of **2**, (b) ∘; alkoxy derivatives of **4**, ◊; alkyl derivatives of **4**

interactions causing the even-odd alternation for the T_{SA-N} occur around the surface of the smectic layer. Although it is difficult to analyze in more detail, the difference in these action points might be concerned with the opposite feature of the even-odd alternation. The transition entropy (ΔS) for the S_A-N transition is plotted against R in Fig. 4.

For the alkoxy homologs of **1**, the ΔS values are almost constant (0.16 eu.) in the range between 0.94 and 0.82, except the hydrogen (0.6 eu.) and octyloxy homologs (1.0 eu.), and seem to become zero around 0.82, as shown in Fig. 4, indicating that most of the S_A-N transitions for the alkoxy homologs have a second-order nature accompanied by a little entropy. A noteworthy fact is that the extension of the terminal alkoxyl group at the R_2 position affects the S_A-N transition temperature and the transition entropy a little, indicating that the notable smectic properties arise from the intrinsic nature of phenyl 4-(4-octyloxybenzoyloxy)benzoate.

The alkoxy homologs of **1** also exhibit the S_C phase commencing from the propoxy one, where the latent heats for the S_C-S_A transition are not detected by DSC thermogram. Interestingly, the T_{SC-SA}values for higher homologs also show a remarkable even-odd alternation, where the T_{SC-SA} values for the even homologs are higher than the odd ones, opposite to the T_{SA-N} and similar to the T_{N-I}. These facts indicate that the inter-layer interactions at the terminals of the long alkyl chain are responsible for the even-odd alternation in the S_A and S_C phases, and are different from those in the N phase.

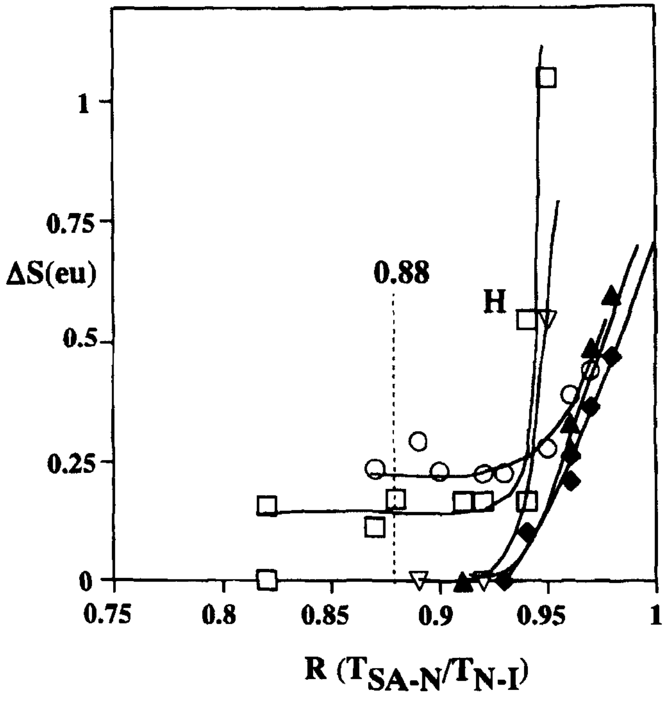


FIGURE 4 Plots of the transition entropies for the S_A-N transition vs. the R for **1**, **2**, and **4**. □; alkoxy derivatives of **1**, ○; alkyl derivatives of **1**, ▽; alkoxy derivatives of **2**, ♦; alkoxy derivatives of **4**, and ▲; alkyl derivatives of **4**. Transition entropies (ΔS) were calculated from the tables by ΔH/T

The similar even-odd alternation for T_{SA-N} and T_{SC-SA} has also been known in alkyl 4-alkoxybipenyl-4′-carboxylate,[15] where T_{SA-I} and T_{SC-SA} show an opposite feature.

Symmetric liquid crystal systems such as bis-(4-alkylphenylimino) terephthalaldehyde,[16] and bis-(4-alkoxyphenylimino)terephthalaldehyde[17] also show the different even-odd alternation. We assume that the even-odd alternation for the S_C-S_A and S_A-N transitions are influenced by the core structure and the counter-balance of both terminal alkyl chain numbers.

A similar trend is observed in the alkyl homologs of **1**. The S_A phase commences from the methyl homolog, and the T_{SA-N} is almost independent of the carbon number, as shown in Fig. 1b. In addition, the transition entropy is almost independent of the alkyl chain length, except the octyl homolog, similar to the alkoxy homologs of **1**. Although the even-odd alternation for the S_A-N transition is less apparent than the alkoxy homologs, the T_{SA-N} values for the odd homologs are higher than those for the even ones, inversely to the feature for the alkoxy derivatives. The less apparent even-odd alternation for the alkyl derivatives should be concerned with the fact that the rotational barrier for the alkyl-O-phenyl bond (6.8 kJ/mol) is larger than that for the alkyl-CH_2-phenyl bond (2.0 kJ/mol), so that the alkoxybenzene moiety is more rigid than the alkylbenzene one.

The plot of the R values vs. n for the alkyl homologs is shown in Fig. 3a. A noteworthy fact in the figure is that the R values, a criterion of the smectic interaction strength, for the alkyl homologs are larger than those for the alkoxy ones all over the homologs, and the difference appears to become large on descending the homologs, that is, the efficiency order for the R is H > CH_3 > OCH_3, and $OCH_3 < OC_2H_5 < OC_3H_7$, and so on. Probably, the difference in the effectiveness for the $T_{SA\text{-}N}$ between the methyl and methoxy groups is concerned with the difference in the electrostatic nature of these substituents. That is, these substituents have an electron-donating nature enhancing the electron density of the core portion, where the Hammett constants (σ_p^+) are –0.31 and –0.78 for methyl and methoxy groups, respectively.[18]

The alkyl homologs also exhibit the S_c phase commencing from the propyl one, where the latent heats for the S_C-S_A transition could not be detected all over the homologs. In Figure 1b, the plot of the $T_{SC\text{-}SA}$ values vs. n has a maximum at the hexyl homolog, where the even-odd alternation is observed in the lower homologs.

The hydrogen derivative of <u>2</u> does not exhibit the S_A phase, while the liquid crystalline core is the same as <u>1</u>. In addition, the virtual $T_{SA\text{-}N}$ extrapolated from the binary phase diagram is very low, ca. 45 °C. The S_A phase for the alkoxy homologs of <u>2</u> commences from the hexyloxy homolog, and the $T_{SA\text{-}N}$ gradually increases on ascending the homologs, as shown in Fig 1c, where the S_A-N transitions for the hexyloxy and heptyloxy homologs have no latent heat. For the plot, an important and interesting question is why the pentyloxy and the lower members do not show the S_A phase, while these homologs show the S_C phase. In order to clarify this question, the binary phase diagram for the mixture of the pentyloxy and octyloxy homologs was examined, and the results are shown in Fig. 5.

As shown in the figure, both homologs form a eutectic mixture in the solid phase, and are miscible in the N phase. Although the thermal stability of the layer structure ($T_{SA\text{-}N}$ and $T_{SC\text{-}N}$) also keeps a linear correlation against the molar concentration, the thermal stability of the tilt structure (the S_C-S_A and S_C-N transition temperatures) shows non-linear correlation against the molar concentration. These facts indicate that the layer structure of the pentyloxy homolog is kept only in the tilt arrangement. Therefore, the S_A phase commences from the hexyloxy homolog, and the lower homologs exhibit only an S_C phase, as shown in Fig. 1c.

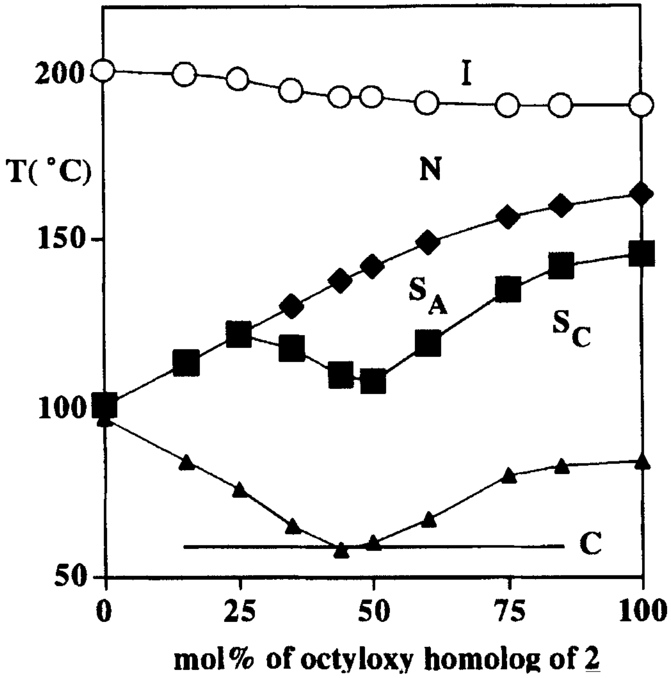


FIGURE 5 Phase diagram for the mixture of the pentyloxy (on left) and octyloxy (on right) of 2

As shown in Figure 4a, the R values for the alkoxy homologs of 2 steeply decrease on descending the homologs, indicating that the long chain at the R_1 position is very important in displaying the S_A phase.

The alkyl homologs of 2 exhibit only an S_C phase commencing from the pentyl one, where the latent heats for the S_C-N transition are very small. In addition, the T_{SC-SA} is very low compared with the alkyl homologs of 1. As is evident from comparison of Figs. 1a – 1d, in contrast to 1, the core of 2, 4-octyloxyphenyl 4-benzoyloxybenzoate is very unfavorable for the formation of the smectic layer. In order to clarify the cause of the notable difference in liquid crystalline properties between the homologs of 1 and 2 having the same liquid crystalline core, the molecular structures calculated by a semi-empirical molecular orbital method are shown in Fig. 6.

The model structures in Figure 6 are the most stable conformation calculated by the AM1 method for the single molecule, so that their conformations in bulk such as liquid crystalline states may be different. As shown in Figure 6, the core of 1 (2) intrinsically has a bent shape due to parallel orientation of two ester

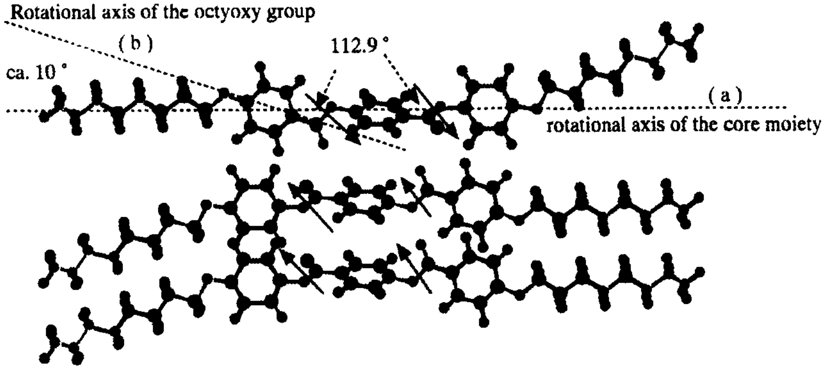


FIGURE 6 Molecular structures of the octyloxy homologs of **1** and **2**

groups, where the small bond-angle of the phenyl-CO-O bond of 112.9 ° compared with that of the CO-O-phenyl bond of 120.2 ° and phenyl-O-alkyl of 115.9 ° is responsible for the bent shape. In the figure, we suppose that the rotational axis of the core passes through the centers of both terminal phenyl rings. Then, the average rotational axis of the hydrocarbon chain attached at the terminal phenyl group (R_2) extends along the average longitudinal axis of the core, so that extension of the alkyl chain increases the linearity of the entire molecular shape. On the other hand, the average axis of the hydrocarbon chain attached at the terminal benzoyl group (R_1) has an angle of ca. 10 ° to the average longitudinal axis of the core, so that the long alkyl chains such as the octyl and octyloxy groups result in the bent of the entire molecular shape. Furthermore, the rotational barrier of 11.2 kJ/mol around the phenyl-COO bond interrupting the free rotation around the bond and the rotational barrier of 6.8 kJ/mol around the $C_8H_{17}O$-phenyl bond would enhance the planarity and rigidity of the 4-octyloxybenzoyloxy moiety. Therefore, we assume that the convenient packing of the bent molecules, the core of **1**, is responsible for high smectic properties. Therefore, the elongation of the alkoxy chain at the R_1 position enhances the smectic properties, as shown in Table I and Figs. 1c and 1d. On the other hand, the elongation of the alkoxy and alkyl groups at the R_2 position subsidiary enhances the smectic properties.

The liquid crystalline properties of ester compounds are frequently discussed in terms of the polar interactions such as dipole-dipole and dipole-induced dipole ones around the ester groups within antiparallel oriented molecules, as shown in Fig. 6a. In deed, the dipoles arising from the ester groups arrange antiparallel in some part of the bulk, and the interactions appear to facilitate the antiparallel arrangement of molecules. Our trouble, however, is that the molecules in the other part inevitably arrange parallel, where the polar interactions may be unfavorable for the layer arrangement. In addition, the polar interaction mechanism does not explain the mesomorphic characteristics of **1** and **2**, that is, the effect of the terminal chain lengths, as was mentioned above.

The hydrogen derivative of **3**, shows only an N phase, and substitution of a long alkoxyl or an alkyl group results in the formation of the S_C phase commencing from the hexyloxy homolog, while the $T_{SC\text{-}N}$ is lower than the $T_{SC\text{-}SA}$s for **1** and **2**. Interestingly, the latent heats for the S_C-N transition are larger by ca. 10 times than those for the the S_C-S_A transitions of the alkyl homologs of **1**.

In symmetric 1,4-di-(4-alkoxybenzoyloxy)benzenes, similarly, the homologs have been reported to show only S_C and N phases.[19] The difficulty of the layer structure having the orthogonal arrangement of molecules is assumed to be an intrinsic nature of the 1,4-dibenzoyloxybenzene core. As far as we know, the formation of the S_A phase for 1,4-di-(4-alkoxybenzoyloxy)benzene compounds is limited to the derivatives with nitro, trifluromethyl, and trifluoromethoxy groups as a terminal substituent.[20,21]

1,4-Dibenzoyloxybenzene is symmetric in structural point of view, so that the hydrocarbon chains substituted at both terminals will extend along the average rotational axis of the core, giving the linearity of the entire molecular shape all over the homologs, as shown in Fig. 6b. Defects for the liquid crystalline core would be that the rigidity around the central benzene ring is the lowest of four isomers due to the low rotational barrier of 1.9 kJ/mol around the phenyl-OOC bond, and the core must lack planarity due to steric repulsion between the central benzene ring and attached benzoate groups.

The homologs of **4** show S_A and S_C phases as well as the N one. The $T_{N\text{-}I}$ values decrease with displaying a typical even-odd alternation on ascending the homologs. The hydrogen derivative of **4** does not exhibit the smectic phase, probably due to the high melting point. The virtual S_A-N transition temperature was estimated by extrapolation of the binary phase diagram of the butoxy and hydrogen homologs, giving ca. 130 °C, which is almost comparable with that for the hydrogen derivative of **1**.

Both alkoxy and alkyl derivatives of **4** exhibit both S_A and S_C phases from the lower homologs. The S_A phase commences from the propoxy homolog, and the $T_{SA\text{-}N}$ values gradually increase with displaying an even-odd alternation on ascending the homologs.

The plot of ΔS vs. R shows fairly different features from those of **1** and **2**, the ΔS values tend to increase on ascending the homologs, where the R values become zero at 0.93 and 0.91 for the propoxy and propyl homologs, respectively, as shown in Fig. 4. The plots of the R values vs. n for alkoxy and alkyl homologs show a similar feature to each other, as shown in Fig. 3b.

These results indicate that both alkoxy and alkyl groups at the R_2 position play some important role for maintaining the smectic layer.

The S_C phase for the alkoxy homologs commences from the butoxy homolog, and the $T_{SC\text{-}SA}$ increases along the S_A-N ones, resulting in a narrow S_A range. The latent heat for the S_C-S_A transition gradually increases as a function of the alkoxy and alkyl chain numbers. A similar trend is observed in the alkyl homologs. These results indicate that the diphenyl terephthalate core essentially favors the layer structure such as S_A and S_C phases.

The diphenyl terephthalate core is the most rigid of all due to the rotational barrier of 8.9 kJ/mol around the phenyl-COO bond, and the rotational barrier should be enough to keep the planarity of the terephthalate moiety. In addition, the linearity of the entire molecular shape should be kept, since the bent nature of the ester groups would be cancelled by the antiparallel orientation of two ester groups. These factors are assumed to be of primary importance for the high smectic properties of **4**.

Conclusion

The effect of molecular structure on the thermal properties of four isomeric ester compounds was examined. The smectic properties are strongly dependent on both relative orientation of two ester groups and chain length of the terminals. In the 4-R_2-phenyl 4-(4-R_1-benzoyloxy)benzoate system the long alkoxy group at the R_1 position is of primary importance for the formation of the S_A phase, and the long alkyl and alkoxyl group at the R_2 position is secondary. The 1,4-dibenzoyloxybenzene core is intrinsically unfavorable for the formation of the smectic layer, probably due to flexibility of the core. The diphenyl terephthalate core intrinsically favors the layer structure, due to its rigid and flat core structure. A subtle change in the structural factors is of primary importance for the mesomorphic diversity of the ester compounds.

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