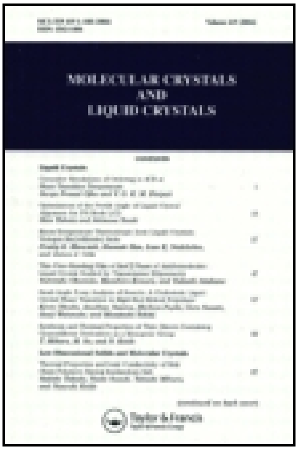

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Thermal Properties of 4-Alkoxyphenyl 3,4-Di(4-alkoxybenzoyloxy)benzoates

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Thermal Properties of 4-Alkoxyphenyl 3,4-Di(4-alkoxybenzoyloxy)benzoates

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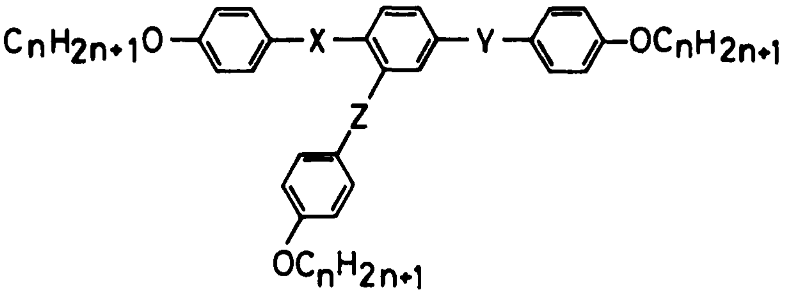
A homologous series of 4-alkoxyphenyl 3,4-di(4-alkoxybenzoyloxy)benzoates has been prepared. All the members (from the ethoxy to nonyloxy homologs) show a nematic phase having a fine schlieren texture, and the nonyloxy homolog also shows a smectic A phase having a fine fan texture. The plot of the nematic–isotropic transition temperatures against the carbon number of the alkoxy chains shows a remarkable even-odd effect. The mesophases have an affinity with the nematic and smectic A phases of the usual rod-like liquid crystals. The nematic phase is highly viscous. The thermal properties are discussed in terms of the molecular structure. A geometrical boundary between rod-like and discotic liquid crystals has been discussed.

Keywords: preparation, lateral substituent, mesomorphic properties, discotic liquid crystals.

It is one of the current interests to clarify a qualitative relation between molecular structure and mesomorphic properties.

A rod- or a lath-shape molecule has been considered to be an indispensable factor in displaying mesomorphic properties in a classical sense.[1] About ten years ago, the classical concept was denied by discovery of the so-called 'discotic' liquid crystals.[2] An important requisite for discotic mesogens is that the molecule possesses a symmetric plane and a relatively large hard core. However, one question for chemists still remains: What is the geometrical boundary between the rod-like and discotic liquid crystals? In order to answer this question, we have opened some studies on mesomorphic properties of poly-substituted benzenes. In an earlier paper, we stated that some 1,3,5-trisubstituted benzenes show the nematic and cholesteric phases having no affinity with those of the rod-like liquid crystals, and are classified as discotic liquid crystals.[3,4] More recently, we also reported that 1,2,4-trisubstituted benzenes show nematic and smectic A phases which are miscible with those of the rod-like liquid crystals.[5] These facts suggest that the geometrical difference between 1,3,5-trisubstituted benzenes and 1,2,4-trisubstituted benzenes is close to the geometrical boundary between the rod-like and discotic liquid crystals. In this meaning, it is very important to clarify the mesomorphic properties of poly-substituted benzenes.

In this paper, we describe preparation and mesomorphic properties of a homologous series of 4-alkoxyphenyl 3,4-di(4-alkoxybenzoyloxy)benzoates.[1]



	X	Y	Z
1	–COO–	–COO–	–COO–
2	–OOC–	–COO–	–OOC–
3	–COO–	–OOC–	–COO–

(n = 2 ~ 9)

The present results have been compared with the thermal properties of the related compounds **2** and **3**, and have been discussed in terms of the molecular structures and the electrostatic properties of the ester linkages. A geometrical boundary between the rod-like and discotic liquid crystals has been also discussed.

EXPERIMENTAL

Materials: 3,4-Di(4-alkoxybenzoyloxy)benzoic acids were prepared by the reaction of benzyl 3,4-dihydroxybenzoate with corresponding 4-alkoxybenzoyl chloride in a solvent mixture of pyridine-toluene (1:1). The products were purified by column chromatography on silica-gel where chloroform was used as an elution solvent, followed by recrystallization from a solvent mixture of ether and petroleum ether. The benzyl group, the protecting group of the carboxy group, was removed by catalytic hydrogenation (Pd–C) in a solvent mixture of toluene–ethanol (1:1). The products were purified by recrystallization from ethanol. A homologous series of 3,4-di(4-alkoxybenzoyloxy)benzoic acids is mesogenic. The transition temperatures are summarized in Table I, and are plotted against the carbon number(n) of the alkoxy chain in Figure 1B.

The homologous series **1** was prepared by the reaction of 3,4-di(4-alkoxybenzoyloxy)benzoic acids with corresponding 4-alkoxyphenols. The materials were

TABLE I

Transition temperatures of 3,4-di(4-alkoxybenzoyloxy) benzoic acids (T/°C)

n	C–I	N–I
2	174	108
3	168	84
4	134	111
5	133	102
6	141	108
7	134	107
8	117	109
9	112	108

purified by column chromatography on silica-gel where chloroform was used as an elution solvent, followed by recrystallization from a solvent mixture of ether-petroleum ether.

Method: Transition temperatures were determined by using a Nikon POH polarizing microscope fitted with a Mettler FP52 heating stage and control unit. Benzophenone was used as a calibration standard with a heating rate of 5°C/min (48°C). Transition enthalpies were measured with a Daini-Seikosha SSC-560 differential scanning calorimeter. Indium (156.6°C) was used as a calibration standard with a heating rate of 5°C/min.

RESULTS

Transition temperatures and latent heats for series **1** are summarized in Table II. For comparative studies the thermal properties for series **2** and **3** are also shown in Table II.

TABLE II

Transition temperatures(T/°C) and latent heats(kJ/mol) for series **1–3**

Compounds	*n*	m.p.	T_{N-I}	ΔH_{N-I}	T_{SA-N}	ΔH_{SA-N}
1	2	129	73	0.45		
	3	106	40	0.47		
	4	98	74	0.48		
	5	77	65	0.50		
	6	68	77	0.64		
	7	57	72	0.83		
	8	70	75	0.82		
	9	60	76	1.25	37	1.27
2	7	45	18	0.46		
	8	57	30	0.60		
	9	53	34	1.0	26	0.12
	10	58	41	1.2	37	0.23
3	8	51				
	9	47				
	10	49				

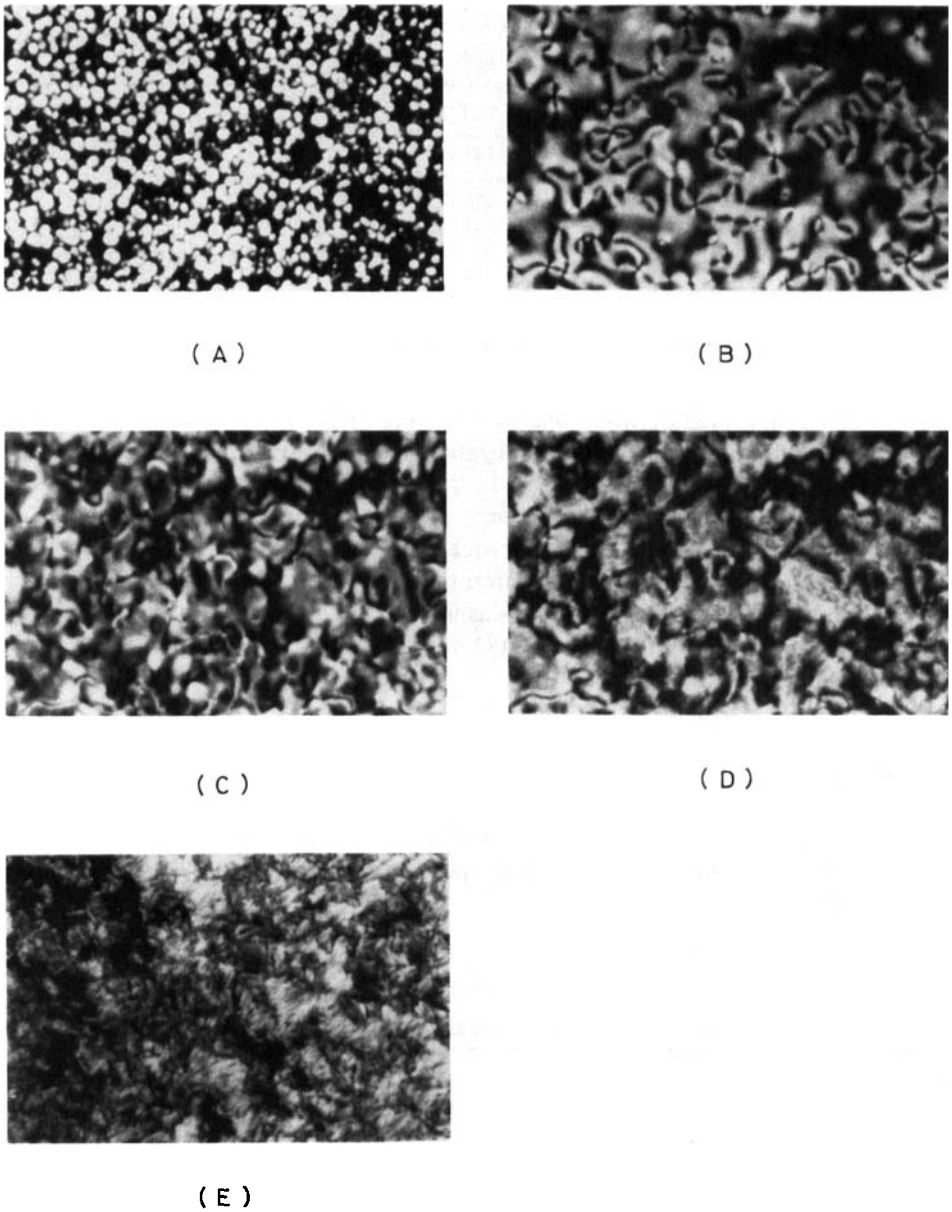


FIGURE 1 Microscopic textures for the nonyloxy homolog of **1**: (A) nematic phase (appearance of domains) at 74°C, (B) after 10 sec. at 74°C, (C) after 30 sec. at 74°C, (D) after 10 min. at 40°C, and (E) smectic A phase at 30°C. These pictures were taken with Konica film (ASA 3200, 100 ×). See Color Plates, 1A, 1B, 1C, 1D, and 1E.

The nematic phase shows a fine schlieren texture which is quite similar to that of series **2**.[5] The smectic A phase shows a fan texture. An interesting fact is that the nematic phase formed by cooling the isotropic solution shows fine particles in the early stage, changes gradually, and gives a steady state with a fine schlieren texture, as shown in Figure 1.

The gradual change continued about 5 min, indicating that the nematic state is fairly viscous.

The transition temperatures are plotted against the carbon number (n) of the alkoxy chains in Figure 2.

In Figure 2A, the plot of the nematic–isotropic transition temperatures against the carbon number of the alkoxy chains for series **1** shows a remarkable even-odd effect, where the nematic-isotropic transition temperatures for the even members are almost independent of the carbon number, while those for the odd members increase with increasing the carbon number. A similar trend is also observed in the nematic–isotropic transition temperatures for 3,4-di(4-alkoxybenzoyloxy)benzoic acids, as shown in Figure 2B. The characterization of the mesophases was carried out by binary phase diagrams, as shown in Figure 3.

In figure 3A, the nematic phase of the present series is miscible with that of a typical rod-like liquid crystal, 4-octyloxyphenyl 4-(4-octyloxybenzoyloxy)benzoate, while the nematic phase has a very wide two-phase region around the center of the diagram. A similar behavior was observed in many binary phase diagrams involving the present series.

The binary phase diagram for a mixture of di(4-octyloxyphenyl) isophthalate and the octyloxy homolog of **1** is shown in Figure 3B. The thermal stability of the nematic phase for the octyloxy homolog of **1** steeply decreases with increasing the concentration of the isophthalate ester, and the nematic phase disappears in the diagram. This fact indicates that the isophthalate ester is intrinsically non-mesogenic, and for series **1** the 4-alkoxybenzoyloxy group at position 4 is indispensable for displaying the liquid crystalline properties.

Figure 3C shows the binary phase diagram for a mixture of two adjacent homologs of series **1**. The nematic phases for two homologs have a good affinity, while two adjacent homologs have fairly different nematic–isotropic transition temperatures. Figure 3D shows the phase diagram for a mixture of 4-cyanophenyl 3,4-di(4-nonyloxybenzoyloxy) benzoates[6] and the nonyloxy homolog of **1**. The mixture corresponds to the so-called 'polar-nonpolar' system, and the smectic A-nematic (isotropic) transition temperature shows a weak upward convexity around the center of the diagram.

DISCUSSION

Most liquid crystals hitherto reported have a rod-like molecular shape, and the others have a discotic one. On the other hand, some molecules having extremely large substituents at the lateral positionl[7–10] and a bent geometry around the center of the molecules[11,12] also show considerably stable mesophases.

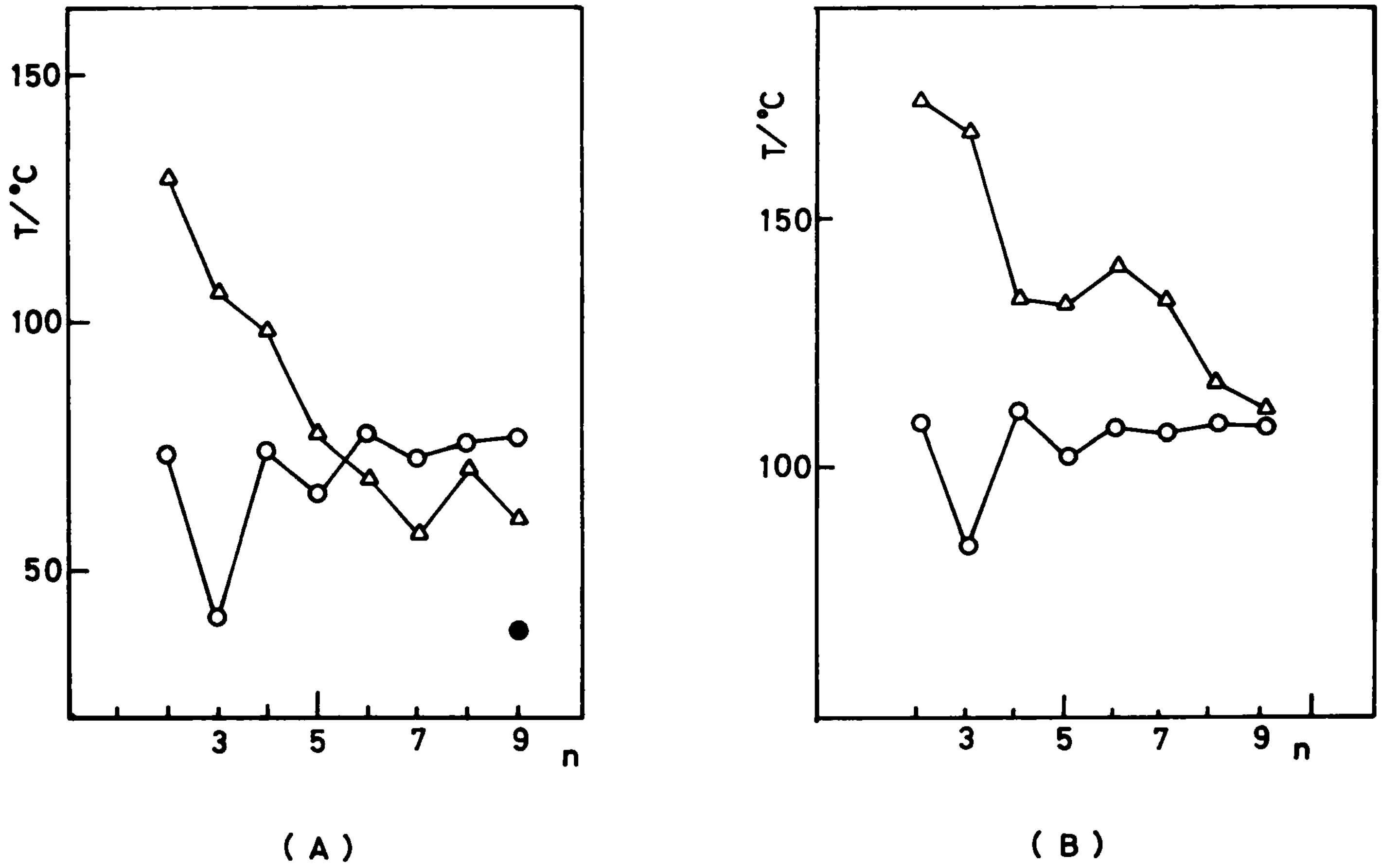


FIGURE 2 Plots of transition temperatures against the carbon numbers: (A) Series **1**, (B) 3,4-di(4-alkoxybenzoyloxy)benzoic acids. ○; nematic-isotropic transition, ●; smectic A–nematic transition, △; melting point.

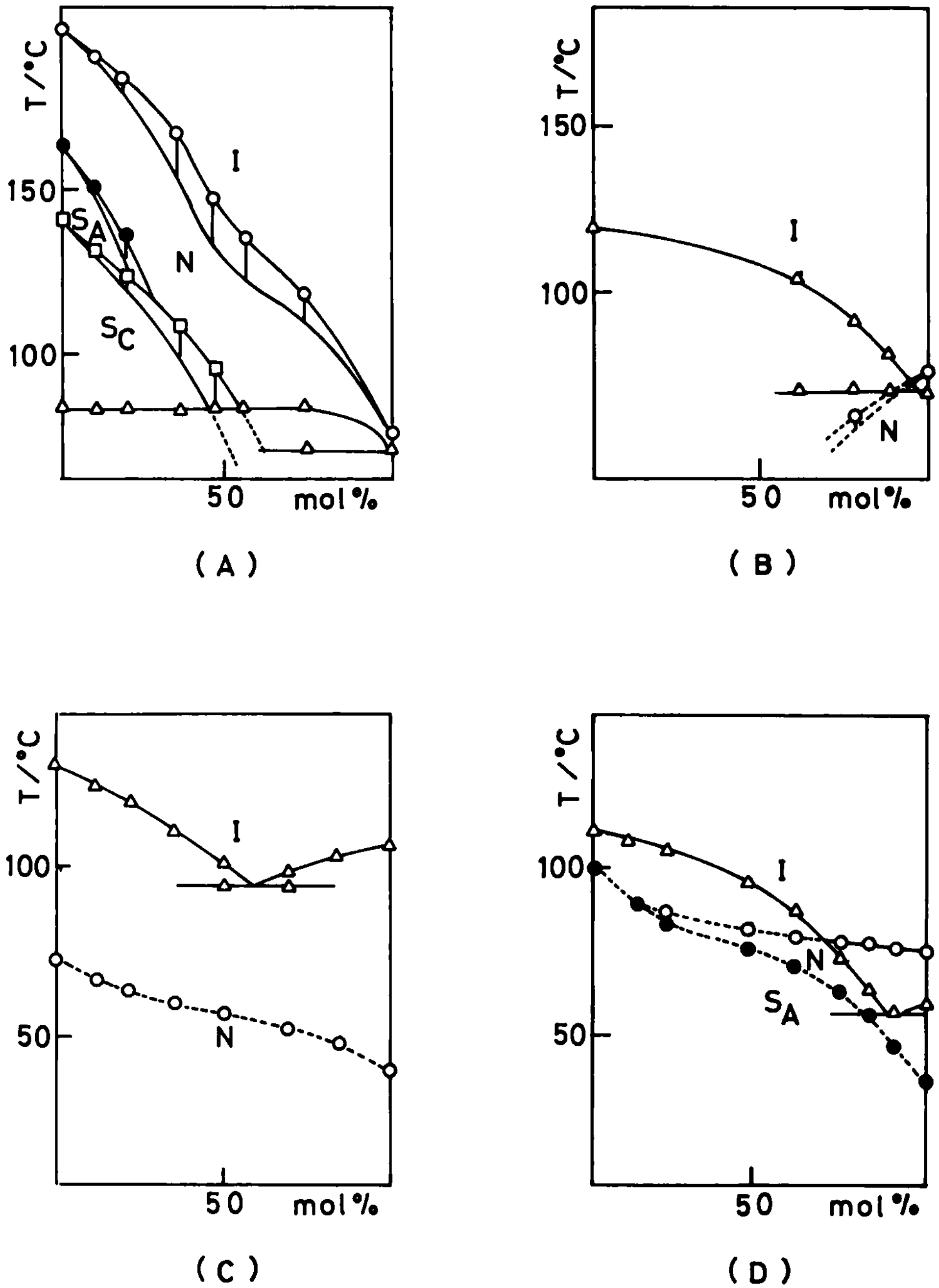


FIGURE 3 Binary phase diagram of: (A) 4-octyloxyphenyl 4-(4-octyloxybenzoyloxy)benzoate (on left) and the octyloxy homolog of series 1 (on right), (B) di(4-octyloxyphenyl) isophthalate (on left) and the octyloxy homolog of series 1 (on right), (C) the ethoxy (on left) and propoxy homologs (on right) of series 1, (D) 4-cyanophenyl 3,4-di(4-octyloxybenzoyloxy)benzoate (on left) and the octyloxy homolog of series 1 (on right). Dashed lines indicate monotropic transitions.

The present series is one of these cases. The thermal characteristics for the 1,2,4-trisubstituted benzenes are summarized as follows:

1. The homologous series shows a nematic phase, and the thermal stability of the nematic phase is strongly dependent on the orientation of the linkages.
2. The plot of the nematic–isotropic transition temperatures against the carbon number of the alkoxy chains for series **1** shows a remarkable even-odd effect.
3. The smectic nature for the series is considerably poor, whereas the smectic A phase commences from the nonyloxy homolog of both series **1** and **2**.
4. The nematic phase for series **1** and **2** has a high viscosity.
5. The transition enthalpies for the nematic-isotropic and smectic A-nematic transitions are almost comparable with those of the usual rod-like liquid crystals.

The molecular structures of the present series are fairly different from the usual rod-like liquid crystals. Therefore, we tried to calculate one of the possible geometries of the present series by using a microcomputer. Figure 4 shows the results where the parameters used in the calculation are also indicated.

The molecule involves many bonds being rotatable and the geometry of the entirety of the molecule is strongly dependent on the conformation of the bonds. In the calculation, therefore, we supposed that the conformation around the ester and ether oxygens is arranged so as to keep the best linearity of the molecule and minimize a steric hindrance between the ester groups at positions 3 and 4. In the model, we supposed that three alkoxy groups are fully extended. The circles indicate the van der Waals radii for respective atoms. In the liquid crystalline states, of course, the molecule must rotate violently and cannot have a fixed conformation.

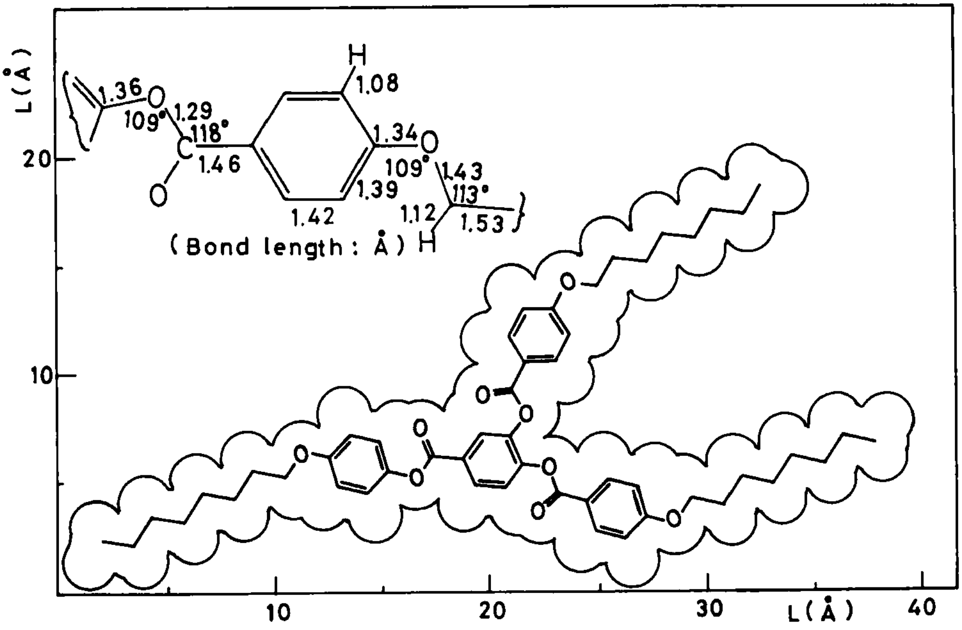


FIGURE 4 The molecular structure of the octyloxy homolog of series **1**.

However, it would be reasonable to assume that the molecule in the mesophases keeps the geometrical characteristics such as the molecular length and breadth and the bulk geometry. Apparently, the 4-alkoxybenzoyloxy group at position 3 results in a marked increase of the molecular breadth; that is, the excluded volume of the molecule. As mentioned in the result section, the nematic phase has a high viscosity. This may be concerned with the extremely large molecular breadth.

When the terminal groups are the octyloxy ones, the calculated molecular geometry is ca. 40 Å length and 20 Å breadth. The ratio of the molecular length to the breadth, ca. 2, may be too small to display liquid crystalline properties. The materials of the present series, 3,4-di(4-alkoxybenzoyloxy)benzoic acids, also show a nematic phase. Thereby, the nematic–isotropic transition temperatures show a quite similar even-odd effect to series **1**. Furthermore, the nematic thermal stability is higher than that of series **1**, while the acids appear to have less favorable geometries for the mesomorphic phenomena. Generally, the mesomorphic properties of 4-alkyl- and 4-alkoxybenzoic acids have been interpreted in terms of the formation of the hydrogen-bonded dimer.[1] For 3,4-di(4-alkoxybenzoyloxy)benzoic acids the formation of a similar hydrogen-bonded dimer is expected and is responsible for the mesomorphic properties.

In an earlier paper, we said that 4-cyanophenyl 3,4-di(4-alkoxybenzoyloxy)benzoates, the related compounds of the present series, show both nematic and smectic A phases.[6] Thereby, we supposed that the molecules form an antiparallel dimer, and form a partially bilayer arrangement in the smectic A phase. For the formation of the dimer, the cyano group at the terminal position is supposed to play some important role. It would be reasonable to assume that the present molecules in the mesophases also form some particular arrangement, probably in order to minimize the molecular volume. For unsymmetric molecule such as the present series, a possible arrangement is an antiparallel one, since such an arrangment would reduce the increased excluded volume.

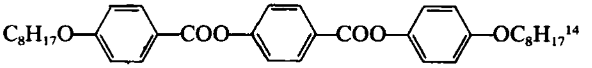
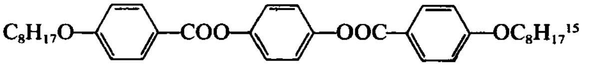
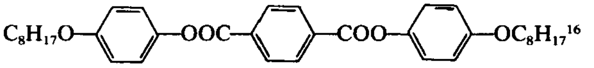
In fact, some non-polar liquid crystals are known to form preferentially an antiparallel arrangement[11,12] or an interdigited one.[13]

In Table III, the thermal properties of the present series are compared with those of related compounds having a rod-like geometry.

In general, in rod-like liquid crystals, a change in the orientation of the ester linkages does not affect the nematic thermal stability so much, since the nematic thermal stability is mainly determined by the geometrical and polarizability anisotropies. On the contrary, the smectic thermal stability is frequently strongly dependent on the orientation of a polar group incorporated in the molecule, since polar local interactions play some important role in determining the thermal stability of the layer arrangement.[17] The related compounds of **7** in Table III are just such cases. The nematic thermal stabilities for series **1**–**3** are fairly different but only in the orientation of the ester linkages. The nematic thermal stabilities decrease by the order of **1** > **2** > **3**. These results indicate that the nematic thermal stabilities of the present series are strongly affected by the molecular geometry. For the octyloxy homolog of series **3**, a replacement of the ester linkage at position 1 by an azomethine linkage remarkably enhances the nematic thermal stability: T_{N-I} = 79°C.[16] This fact indicates that the rigidity of the linkage at position 1 is important

TABLE III

The effect of linkage on mesophase stabilities (T/°C)

Compounds	S_C		S_A		N		I
 [14]	·	141	·	163	·	188	·
 [15]	·	136	–		·	194	·
 [16]	·	180	·	183	·	191	·

	S_A-N	N-I
1	37*1	74*2
2	26*1	30*2
3		< 0*3

*1: the nonyloxy homolog. *2: an average of heptyloxy-nonyloxy homologs. *3: The value was estimated from the binary phase diagram for a mixture of the octyloxy homologs of **2** and **3**.

in enhancing the nematic thermal stability. Although for series **1** and **2** the ester linkages at position 1 have an identical orientation, the nematic thermal stability for series **1** is higher by 44°C than that of series **2**. In this connection, we have to pay attention to the orientation of the ester linkages at positions 3 and 4. For series **2**, two ester linkages at positions 3 and 4 have a large steric hindrance between them so that two ester groups must twist with respect to the plane of the central aromatic ring. The geometrical disadvantage is assumed to be the cause of the low nematic thermal stability for series **2**.

Conclusively, 1,2,4-trisubstituted benzenes intrinsically show liquid crystalline phases having a rod-like nature. The mesophase thermal stabilities are strongly dependent on the molecular geometry—especially in the linearity and rigidity of the straight line passing through positions 1 and 4 of the central aromatic ring. The molecules in the mesophases are assumed to arrange antiparallel in order to avoid the geometrical disadvantage.

The boundary between rod-like and discotic liquid cystals: We have reported that 1,3,5-trisubstituted benzenes show a nematic phase having a discotic nature.[4] In this paper, we also say that 1,2,4-trisubstituted benzenes show a nematic phase having a rod-like nature.[5] In this section, we want to discuss the boundary between the rod-like and discotic liquid crystals in terms of the molecular structure. For this purpose, we also prepared some related compounds shown in Table IV.

The molecular structures of the octyloxy derivatives of **1–9** were estimated by calculation with the parameters shown in Figure 4, and the results are shown in Figure 5.

The perpendicular and horizontal axes are the molecular length and breadth which are defined in the figure, respectively. We can assume that from the geometrical point of view, the discotic properties of molecules increase when both L and D increase simultaneously, along the L/D = 1 line. On the other hand, the

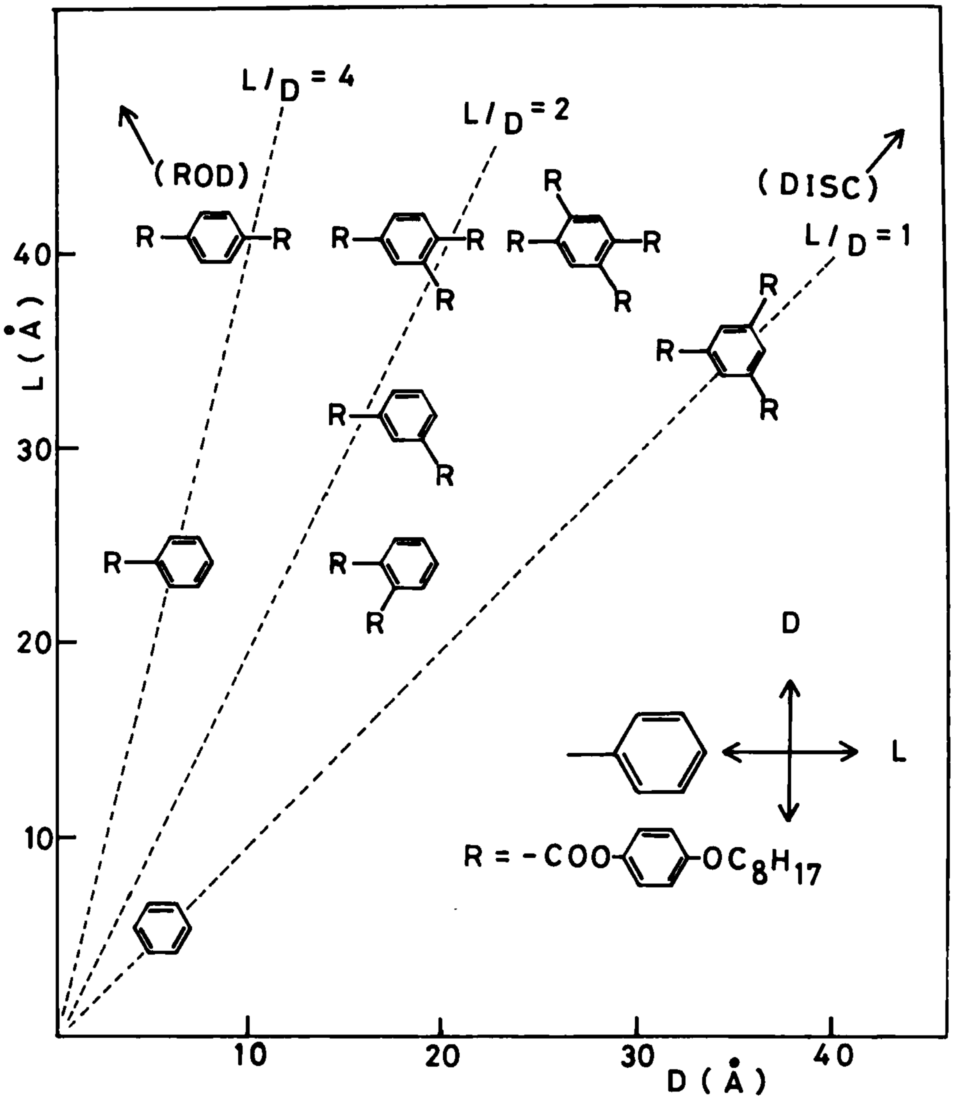
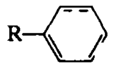
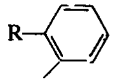
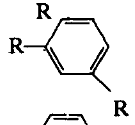
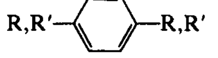
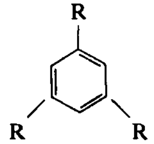
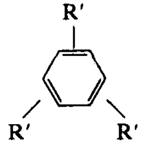
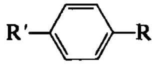
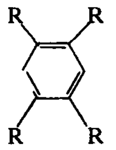


FIGURE 5 Plot of molecular length(L) against the breadth (D).

rod-like properties of molecule increase when the molecular length independently increases, *i.e.*, an increase of the L/D value. As is evident from the figure, benzene has a D_6 symmetry and is expected to have discotic properties. But, the entirety of the molecule is probably too small to show any mesophases. Although compound **4** is classified into rod-like liquid crystals from the geometrical point of view, it is non-mesogenic, probably because of low polarizability anisotropy. Certainly, an introduction of a substitutent, such as alkoxy, halogen,[17] or cyano groups,[18] induces the mesomorphic properties involving the nematic and smectic phases.

TABLE IV

Transition temperatures for related compounds (T/°C)

Compounds	Structures	Transition temperatures	
4		C.58.I (7)	C.59.I (8)
5		C.56.I (7)	C.62.I (8)
6		C.119.I (7)	C.120.I (8)
7		see Table III.	
8		C-72(.D.24).I (8)	C-78(.D.23).I (9)
8′		C.61.I (7)	C.55.I (8)
1		see Table II.	
2		see Table II.	
9		C.89.I (8)	C.89.I (9)

The values in parentheses indicate the carbon number(n) of the alkoxy chains. R and R′ represent the 4-alkoxybenzoyloxy and 4-alkoxyphenoxycarbonyl groups, respectively.

From the geometrical point of view, compounds **5** and **6** are classified neither into rod-like nor discotic liquid crystals. In fact, both compounds are non-mesogenic and have poor mesomorphic properties (refer to Figure 3B).

The para-substituted benzenes **7** have a typical rod-like molecular structure so that the homologs show stable nematic and smectic phases. A notable fact is that the nematic thermal stabilities are almost independent of the orientation of the ester linkage, as shown in Table III.

1,3,5-Trisubstituted benzenes have a geometrical symmetry and the L/D ratios are one so that these are expected to show discotic properties. In practice, however, only compound **8** shows discotic phases, and the related compound **8′** is non-mesogenic, indicating that the thermal stabilities of the discotic phases are strongly dependent on the orientation of the ester linkages. In this connection, we pointed out the importance of the geometrical symmetry of the molecules.[4]

1,2,4-Trisubstituted benzenes, **1** and **2**, have unsymmetrically substituted molecular shapes, and there are more than two L/D ratios. As mentioned above, series **1** shows the most stable nematic and smectic A phase, having an affinity with those of the rod-like liquid crystals, while the mesophases sometimes have a wide two-phase region in the binary phase diagrams (see Figure 3A). As is evident from Table II, the nematic thermal stabilities for series **1**–**3** are strongly dependent on the orientation of the ester linkages. The thermal characteristics resemble those of the discotic liquid crystal **8** rather than those of rod-like liquid crystals **7**. The mesophases of **1** and **8**, of course, have no affinity.

Although 1,2,4,5-tetrasubstituted benzenes **9** have higher symmetric axes, the L/D value is larger than one, but less than two. Therefore, the homologs are non-mesogenic. In addition to the geometrical unsymmetry, the increased molecular thickness due to a repulsive interaction between the ester groups attached at the ortho positions cannot favor the mesomorphic phenomena for the 1,2,4,5-tetrasubstituted compounds. While **9** is non-mesogenic, we are interested in the potential mesomorphic properties.

In order to test the miscibility relation between compounds **8**, **1**, and **9**, some

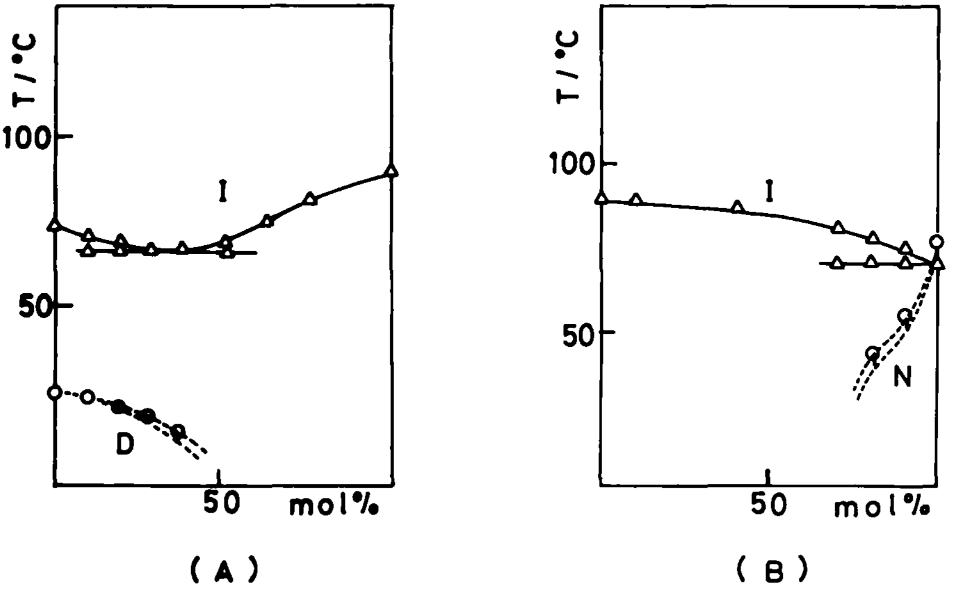


FIGURE 6 The binary phase diagrams for a mixture of: (A) the octyloxy homolog of **8** (on left) and the octyloxy homolog of **9** (on right), (B) the octyloxy homolog of **9** (on left) and the octyloxy homolog of series **1** (on right). ○; mesophase-isotropic transition, △; melting point.

binary phase diagrams involving these compounds were examined, and the results are shown in Figure 6.

In Figure 6A, the discotic-isotropic transition temperature for the octyloxy homolog of compound **8** gradually decreases with increasing the concentration of the octyloxy homolog of **9**. On the other hand, the nematic-isotropic transition temperature for the octyloxy homolog of **1** in Figure 6B steeply decreases with increasing the concentration of the octyloxy homolog of **9**. These facts indicate that from the thermodynamical point of view, compound **9** is rather classified into the discotic liquid crystals, though the homologs are potentially non-mesogenic.

Conclusively, 1,2,4- and 1,3,5-trisubstituted benzenes are classified into the rod-like and discotic liquid crystals, respectively, and 1,2,4,5-tetrasubstituted benzenes are close to the boundary between them. The most important factor distinguishing the two classes is the molecular geometry, that is, the molecules on the L/D = 1 line are most suitable in displaying the discotic properties. Destrade et al. also pointed out the importance of a structural symmetry for displaying the discotic properties.[20]

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