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Shunsuke Takenaka^a, Koichi Nishimura^a & Shigekazu Kusabayashi^a

^a Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita Osaka, 565, Japan

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The Discotic Mesophases of 1,3,5-Trisubstituted Benzenes

SHUNSUKE TAKENAKA, KOICHI NISHIMURA and
SHIGEKAZU KUSABAYASHI

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita
Osaka 565, Japan*

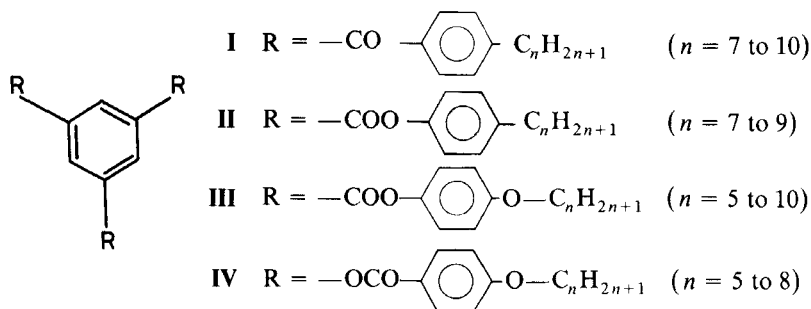
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Some homologous series of 1,3,5-trisubstituted benzenes have been prepared. A homologous series of 1,3,5-tri-(4-alkoxyphenoxy carbonyl)benzenes (the hexyloxy to decyloxy homologs) give rise to discotic mesophases having a nematic-like texture.

INTRODUCTION

It is well known that disc-like molecules having plural alkyl chains of a suitable length frequently give rise to mesomorphic behavior. This mesophase is called a “discotic mesophase” because of the molecular shape.¹ Usually, the discotic mesogens have flat skeletons with highly symmetric axes. For example, benzene hexaalkanoates^{2,3} and hexaalkylphenylbenzenes⁴ have D_6 -symmetric axes. Porphyrine^{5,6} and bipyran^{7,8} compounds have D_4 and D_2 axes, respectively. Furthermore, triphenylene,^{9–11} truxene,^{12–14} anthraquinone,^{15,16} and benzoquinone¹⁷ compounds also give rise to the discotic phases, although they have relatively low symmetric axes. Thus, a skeletal symmetry appears to be very important in determining the mesomorphic behavior of discotic molecules. Moreover, it has been known that an introduction of dissymmetric side chains results in rapid reduction of the mesomorphic stability.¹⁸ From a preparative point of view, 1,3,5-trisubstituted benzenes having C_3 -symmetric axis would be one of the simplest types of discotic molecules. Recently, we reported that some benzene 1,3,5-

triteroid esters gave rise to discotic-like mesophases. However, the liquid state for these compounds is highly viscous so that we could not succeed in reforming of the mesophases on cooling.^{19,20} Therefore, we were interested in the mesomorphic behavior of 1,3,5-trisubstituted benzenes having alkyl or alkoxybenzenes instead of steroid cores. In this paper, we describe the preparation and thermal properties of the following compounds.



The nonyl homolog of **II** has been known to show no mesomorphism.¹

EXPERIMENTALS

Materials

1,3,5-Benzenetricarboxylic acid and phloroglucinol were purchased from Aldrich Chemical, and purified by means of recrystallization from ethanol.

1,3,5-Tri-(4-alkylbenzoyl)benzenes **I** were prepared by a Friedel-Craft reaction of 1,3,5-benzenetricarboxylic acid chloride and alkylbenzenes in nitrobenzene, in which aluminum trichloride was used as a catalyst. The purification was carried out by column chromatography on alumina, in which a solvent mixture of hexane-ether (1:1) was used as the eluent. The recrystallization was carried out from a solvent mixture of ether and ethanol. The esters **II**–**V** were prepared by a condensation of the corresponding phenols and 1,3,5-benzenetricarboxylic acid chloride, or the corresponding acid chlorides and phloroglucinol in a solvent mixture of absolute benzene and pyridine (1:1). The purification was carried out by column chromatography on silica-gel (usually ether:hexane = 2:98), followed by recrystallization from hexane or a solvent mixture of benzene and ethanol. The purity was confirmed by means of elemental analysis. The elemental analysis data are shown in Table I.

TABLE I
Elementary analysis data

Compound	n	Formula	Calcd. (%)		Found (%)	
			C	H	C	H
I	7	C ₄₈ H ₆₀ O ₃	84.16	8.83	84.09	8.91
	8	C ₅₁ H ₆₆ O ₃	84.25	9.15	84.16	9.20
	10	C ₅₇ H ₇₈ O ₃	84.39	9.69	84.31	9.66
II	7	C ₄₈ H ₆₀ O ₆	78.65	8.25	78.63	8.28
	8	C ₅₁ H ₆₆ O ₆	79.03	8.58	78.89	8.59
	9	C ₅₄ H ₇₂ O ₆	79.37	8.88	79.05	8.95
III	5	C ₄₂ H ₄₈ O ₉	72.39	6.94	72.21	6.92
	6	C ₄₅ H ₅₄ O ₉	73.14	7.37	73.07	7.41
	7	C ₄₈ H ₆₀ O ₉	73.82	7.74	73.63	7.89
	8	C ₅₁ H ₆₆ O ₉	74.42	8.08	74.34	8.11
	9	C ₅₄ H ₇₂ O ₉	74.97	8.39	74.78	8.41
IV	10	C ₅₇ H ₇₈ O ₉	75.46	8.67	75.25	8.72
	5	C ₄₂ H ₄₈ O ₉	72.39	6.94	72.21	7.02
	6	C ₄₅ H ₅₄ O ₉	73.14	7.37	73.17	7.29
	7	C ₄₈ H ₆₀ O ₉	73.82	7.74	73.75	7.80
	8	C ₅₁ H ₆₆ O ₉	74.42	8.08	74.32	8.14

Methods

The phase transitions were examined using a Nikon POH polarizing microscope fitted with a Mettler FP 52 heating stage and control unit. The transition enthalpies were measured using a Daini-Seikosha SSC-560 differential scanning calorimeter (DSC). Indium (99.9%) was used as a calibration standard at a heating rate of 5 °C/min. The transition entropies were calculated using the equation: $\Delta S = \Delta H/T$. The DSC measurements were carried out at heating and cooling rates of 5 °C/min at atmospheric pressure, with a sample size of about 5 mg. The transition temperatures in Table II are the onset temperatures of the DSC peaks during heating.

RESULTS AND DISCUSSION

As part of the study, two additional compounds: 1,3,5-trioctyloxybenzene (m.p. 2.5 °C) and benzene 1,3,5-triheptanoate (m.p. 4.5 °C), were prepared but neither was mesomorphic.

The transition temperatures, latent heats, and entropies for the present series are summarized in Table II.

The homologous series of **I** has melting points in the range between 59 and 73 °C. The heptyl and octyl homologs do not give rise to any

TABLE II

Transition Temperatures, enthalpies, and entropies

Compound	<i>n</i>	C · I (<i>T</i> /°C)	Δ <i>H</i> (kJ/mol)	M · I (<i>T</i> /°C)	Δ <i>H</i> (kJ/mol)	Δ <i>S</i> (K/J · mol)
I	7	58.7	61.5			
	8	66.8	30.5			
	10	73.3	41.9	(−22.5)	4.44	17.7
II	7	80.7	37.1			
	8	78.6	44.1			
	9	65.9	39.5	[−15]		
III	5	65.8	40.6			
	6	69.3	34.6	(−12.0)	6.98	26.7
	7	56.2	38.4	(12.5)	9.90	34.7
	8	72.2	54.0	(23.5)	8.63	29.1
	9	78.3	69.7	(22.5)	5.18	17.5
	10	57.5	51.9	(25.5)	8.46	28.3
IV	6	69.8	53.2			
	7	61.3	45.8			
	8	54.6	48.4	[−30]		

The values in the parentheses and brackets indicate the monotropic and virtual transition temperatures, respectively. C · I and M · I indicate the crystal to isotropic, and the mesophase to isotropic transitions, respectively.

mesophase. The DSC thermogram for the decyl homolog showed an exotherm at about -30°C during cooling and an endotherm at -22.5°C on second heating. Although we could not succeed in characterizing of the monotropic transition, the monotropic phase appears to be isomorphous with the mesophase of series **III**, as shown in Figure 4b. In the figure, the mesophase–isotropic transition temperatures show an almost linear correlation with composition from 0–60 mol% of the decyl homolog, and nonlinear behavior thereafter. The DSC thermograms for the octyloxy homolog of **III** are shown in Figure 1. The trace of the first heating shows an endotherm at 72.2°C corresponding to the melting point (run 1). The molten octyloxy homolog of **III** shows an exotherm at about 18°C on the cooling at a cooling rate of $5^{\circ}\text{C}/\text{min}$ (run 2), and an endotherm at 23.5°C , a broad exotherm at about 60°C , and an endotherm at 72.2°C on the second heating stage (run 3). The latter two peaks on the second heating correspond to the recrystallization and melting points, respectively. The molten octyloxy homolog reveals a weak birefringence below 23.5°C , indicating that the endotherm at 23.5°C corresponds to the mesophase–isotropic transition. A similar trend was observed in the hexyloxy, heptyloxy, nonyloxy, and decyloxy homologs. Two noteworthy facts for series **III** are that the entropies for the meso-

phase–isotropic transition account for 10–30% of the total transition entropies, and the texture of their mesophases is very similar to the schlieren texture observed for typical rod-like nematic phase, as well as for discotic nematic phase.^{10,21,22} The polarized light photo micrograph for the mesophase of the nonyloxy homolog is shown in Figure 2. These results suggest that these mesophases are discotic and have a nematic behavior. To further characterize these mesophases, we examined miscibility in some binary phase diagrams. The discotic nematic phases of both octyloxy and nonyloxy homologs of **III** in Figure 3a are apparently isomorphous, since the mesophase–isotropic transition temperatures show an ideal mixture behavior. However, the mesophase of the octyloxy homolog is not isomorphous with the nematic phase of a known rod-like molecule²³ (Figure 3b), indicating the discotic behavior of the mesophase for the octyloxy homolog of **III**. A noteworthy fact in the diagram is that the mixture shows complete phase separation in the solid state. A similar phase separation was observed in a mixture of the octyloxy homolog of **III** and benzene hexahexanoate,¹ in which both discotic phases were not isomorphous.

Sadashiva *et al.* reported that the nonyl homolog of **II** did not give rise to any mesophase,¹ even though series **II** have very similar structures to series **III**. For a comparative study, we examined the phase diagram for a mixture of the octyloxy homolog of **III** and the nonyl homolog of **II**. The results are shown in Figure 4a. The virtual mesophase–isotropic transition temperature for the nonyl homolog of

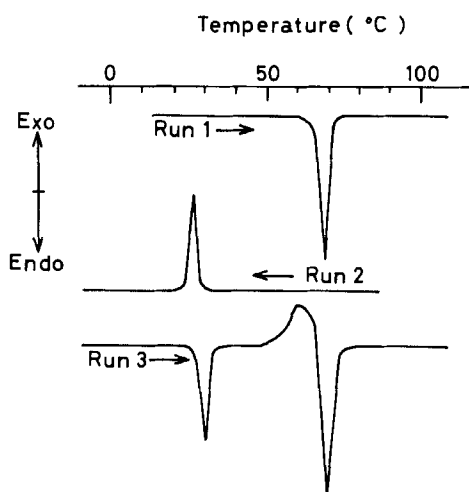


FIGURE 1 The DSC thermogram for the octyloxy homolog of **III**.

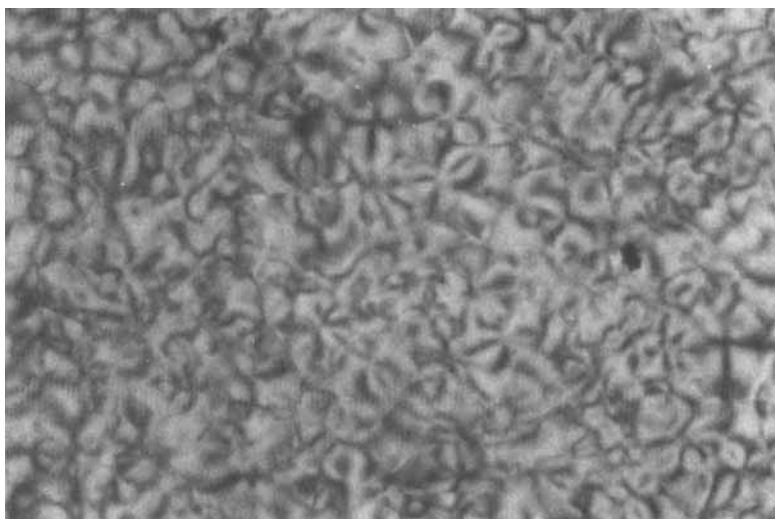


FIGURE 2 A photo micrograph of the mesophase for the octyloxy homolog of **III** at 15 °C(100X).

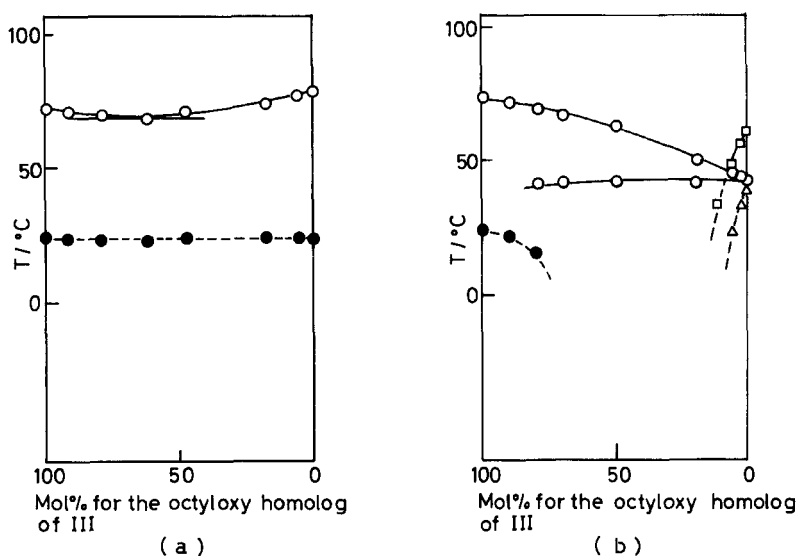


FIGURE 3 Binary phase diagrams. (a) Phase diagram for a mixture of the octyloxy and nonyloxy homologs of **III**. (b) Phase diagram for a mixture of the octyloxy homolog of **III** and 4-pentylphenyl 4'-heptyloxybenzoate. ○; crystal—*isotropic*. ●; mesophase—*isotropic*. □; nematic—*isotropic*, and Δ; smectic A—nematic transitions.

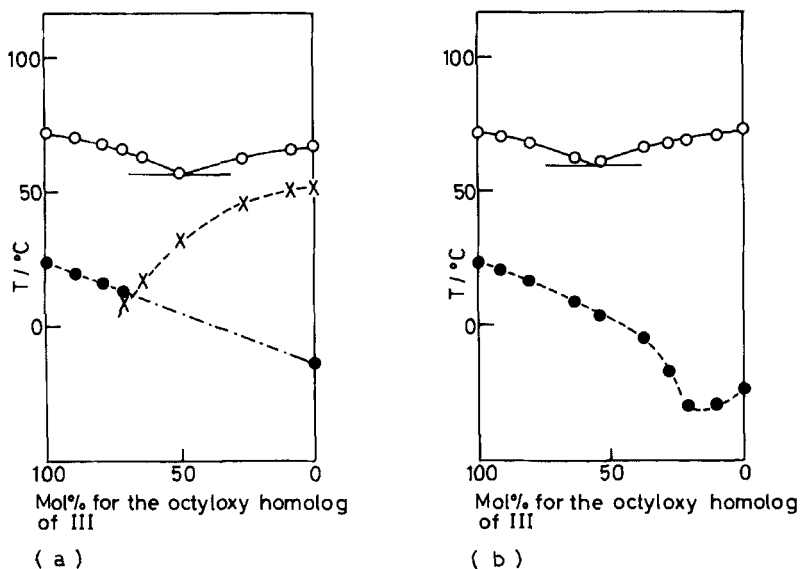


FIGURE 4 Binary phase diagrams. (a) Phase diagram for a mixture of the octyloxy homolog of **III** and the nonyl homolog of **II**. (b) Phase diagram for a mixture of the octyloxy homolog of **III** and the decyl homolog of **I**. \circ ; crystal—*isotropic* and \bullet ; mesophase—*isotropic* transitions. Dashed line indicates the recrystallization point during cooling at a cooling rate of $5^{\circ}\text{C}/\text{min}$.

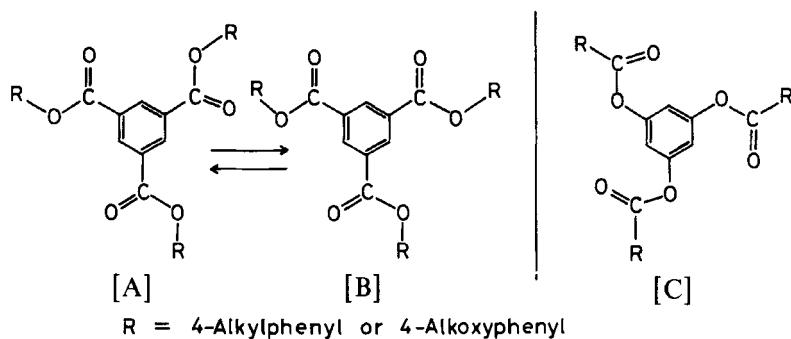
II was determined to be -15°C by extrapolating the mesophase—*isotropic* transition temperatures in the phase diagram, assuming that the mesophase—*isotropic* transition for the components showed an ideal solution behavior because of their structural similarities. This value is about 40°C lower than those of series **III**. Furthermore, the molten nonyl homolog of **II** easily recrystallizes during the cooling (Figure 4a) so that it is not possible to observe the mesophase under usual conditions. A homologous series of **IV** show no mesophase, whereas these are structurally similar to those of series **III**. In order to obtain the virtual mesophase—*isotropic* transition temperature, we examined the phase diagram for a mixture of the octyloxy homologs of **III** and **IV**. In the diagram, the mesophase—*isotropic* transition temperatures rapidly decreased with increasing concentration of the octyloxy homolog of **IV**. Furthermore, the endotherms arising from the mesophase—*isotropic* transitions became broad and weak with increasing concentration of the octyloxy homolog of **IV**, and the endotherm disappears at concentrations of about 30 mol% or higher of the octyloxy homolog of **IV**. From these results, we assume that the

mesophase–isotropic transition temperatures for series **IV** are far lower than those of series **III**.

The effective order for the thermal stability of the discotic phase is:



As mentioned above, molecular symmetry is assumed to be very important in determining the thermal stability of the discotic mesophase. In the present series, a conformational isomerization around the ester groups determines the symmetry of the molecules.



Neglecting the conformation of the aromatic rings at the side chains, conformer [A] has a C_3 axis, while [B] has no symmetric axis. Therefore, it would be reasonable to assume that conformer [A] would result in higher stability for a discotic mesophase than conformer [B]. Usually, the energy difference between both conformers is quite small so that the equilibrium constant is close to unity. For series **II** and **III** the carbonyl groups at the side chains lie on the plane which is occupied by the core benzene ring, and are close to each other. Therefore, the dipole-dipole interaction arising from the carbonyl groups might increase the population of conformer [A]. Such dipole-dipole interaction should be greater in series **III** than in series **II**, since a single bond character of the carbonyl groups is greater in series **III** ($\nu_{\text{COO}} = 1747 \text{ cm}^{-1}$) than in series **II** (1751 cm^{-1}) because of an excellent electron-donating ability of the alkoxy groups in series **III**. This would result in greater stability of the discotic phase for series **III** than for series **II**.

On the other hand, the aryl groups at the side chains in model [C] for series **IV** must be more flexible than those of series **II** and **III**, because a rotation around the phenyl–O bonds in structure [C] is easier than that around the phenyl–CO bonds in conformers [A] and [B]. In addition, the distance between the carbonyl groups in series **IV**

is larger than those in series **II** and **III**. Therefore, the dipole-dipole interactions between the carbonyl groups in series **IV** would be weaker than that in series **II** and **III**. Thus, an increased population of the dissymmetric conformer is proposed to account for the low mesophase stability for series **IV**.

For series **I** three aromatic rings in the side chains will lie out of the plane which is occupied by the core benzene ring due to strong repulsive interaction between ortho hydrogens, while the dipole correlation of the carbonyl groups is similar to that for series **II** and **III**. This results in an increase in the molecular breadth. For series **I** the axial separation of the molecules is proposed to account for the low stability of the mesophase. Thus, we strongly assume that the symmetry of the molecules in the present series is very important in determining the thermal stability of the discotic mesophase.

It is reasonable to assume that molecular polarity and polarisability are also very important in determining the thermal stability of the discotic mesophase, as well as usual rod-like mesophase. For series **III** an increased polarisability due to the alkoxy groups is also responsible for formation of the relatively stable mesophase.

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