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THE MESOMORPHIC PROPERTIES OF 1,2,4-TRISUBSTITUTED BENZENES

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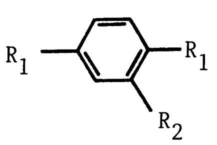
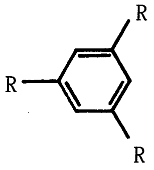
The mesomorphic properties for two series, 1,2,4-tri(4-alkoxyphenoxycarbonyl)benzenes and 1,2,4-tri(4-alkoxybenzoyloxy)benzenes have been examined. For the former series, the nematic and smectic A phases commence from the heptyloxy and nonyloxy homologs, respectively, and the latter series is non-mesogenic.

It is well known that a rod- or a lath-shape of molecule is one of the important factors in displaying mesomorphic properties of molecule. However, recent works have shown that some molecules having large molecular breadth frequently display liquid crystalline properties.[1-4] Their typical molecular structures may be expressed as follows.



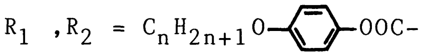
[A]



[B]

When R_2 = H in structure [A], the molecules hold a linearity, displaying stable liquid crystalline phases. Recent works have shown that some molecules having a bulky substituent, i.e., R_2 = phenyl or long alkyl chain in structure [A], also display nematic properties.[1,2] On the other hand, some symmetrically trisubstituted benzenes, i.e., structure [B] with R = 4-alkoxyphenoxycarbonyl group[5] also display liquid crystalline properties, where the mesophases have discotic nature. The structural modification is quite interesting in connection with a boundary between the rod-like and discotic natures.

In this work, we describe the mesomorphic properties of two types of 1,2,4-trisubstituted benzenes, 1 and 2.

1:


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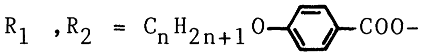

The ester compounds were prepared by the reactions of the corresponding alkoxy phenols and 1,2,4-trichlorocarbonylbenzene or the corresponding 4-alkoxybenzoic acid chlorides and 1,2,4-trihydroxybenzene in dry pyridine. The transition temperatures and the latent heats are summarized in Table 1.

The nematic and smectic phases show schlieren and fan textures which are frequently observed in those of rod-shape liquid crystals. The nematic phase commences from the heptyloxy homolog, and the nematic-isotropic transition

Table 1. Transition temperautres and latent heats for series 1 and 2

Compound	n	C	S_A	N	I	ΔH_{S_A-N}	ΔH_{N-I}
1	1	. 112.8	-	-	.		
	4	. 83.1	-	-	.		
	6	. 54.7	-	-	.		
	7	. 44.7	-	(. 18.4)	.		0.46
	8	. 56.5	-	(. 30.2)	.		0.60
	9	. 53.3	(. 25.5	. 33.6)	.	0.12	1.0
	10	. 58.2	(. 36.5	. 41.0)	.	0.23	1.2
2	8	. 50.9	-	-	.		
	9	. 47.4	-	-	.		
	10	. 49.1	-	-	.		

Transition temperatures and latent heats are given by °C and kJ/mol, respectively. C, S_A , N, and I represent crystal, smectic A, nematic, and isotropic phases, respectively. Parentheses indicate monotropic transitions.

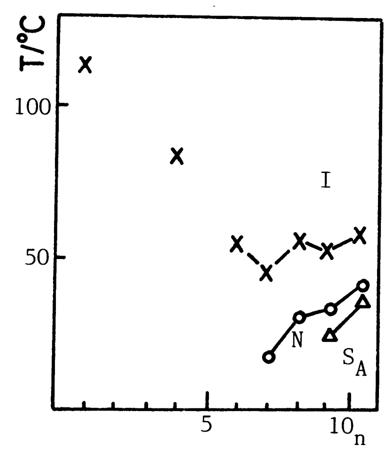

Fig. 1. Transition temperatures against n. X; solid-isotropic, o; nematic-isotropic, Δ; smectic A-nematic.

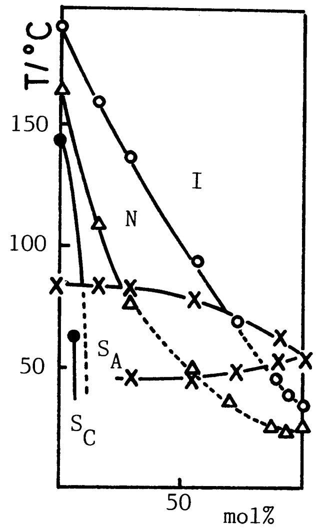

Fig. 2. Phase diagram of 4-octyloxyphenyl 4-(4-octyloxybenzoyloxy)benzoate(on left) and the nonyloxy homolog of **1**(on right).

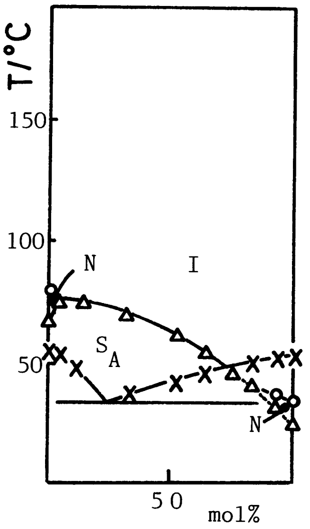

Fig. 3. Phase diagram of 4-cyano-4'-octyloxybiphenyl (on left) and the nonyloxy homolog of **1**(on right).

temperatures increase with increasing carbon number, as shown in Fig. 1. The low members having n = 1 to 6 do not show any mesophase. For example, the fluid obtained by melting the methoxy homolog gave only a highly viscous oil on cooling below room temperature. The smectic phase commences from the nonyloxy homolog, and the smectic-nematic transition temperatures also increase with increasing n. The latent heats for the smectic-nematic and nematic-isotropic transitions are less than 0.2% and 2% of the total transition enthalpies, respectively. The latent heats of the nematic-isotropic and smectic-nematic transitions are quite small compared with those of discotic-isotropic transitions for 1,3,5-trisubstituted benzenes.5)

It would be reasonable to assume that the smectic A phases of 4-octyloxyphenyl 4-(4-octyloxybenzoyloxy)benzoate and N-(4-cyanobenzylidene)-4-octyloxyaniline have monolayer and bilayer arrangements of the molecules, respectively. In Fig. 2, the nematic phase of the nonyloxy homolog is miscible with that of the reference compound, where the nematic-isotropic transition temperatures show weak downward concavity. The smectic phase of the nonyloxy homolog is also miscible with the smectic A phase of the reference compound, while the smectic A-nematic transition temperatures show remarkable deviation from additivity. In the figure, the solid phases are remarkably heterogeneous, perhaps due to large difference in their molecular structures. In Fig. 3, the smectic A-nematic(isotropic) transition temperatures show an upward convexity which is frequently observed in binary mixtures consisting of polar and non-polar liquid crystals.$^{6)}$ These results indicate that the liquid crystalline phases for the series 1 essentially have rod-like nature, while the molecules have very large molecular breadths. The smectic A phase has a monolayer type's arrangement of the molecules, and displays a remarkable enhancement of the thermal stability in polar-non-polar mixture(Fig. 3). On the other hand, the series 2 does not show any mesophase, while these compounds have very similar structures to those of the series 1. Demus et al. reported that some compounds having a long alkyl group at the 2 position in structure [A] exhibited only a nematic phase.$^{2)}$ Similarly, the ester compounds having a phenyl group at the 2 position exhibit a nematic phase.$^{1)}$ However, the nonyloxy and decyloxy homologs of the series 1 exhibit a smectic A phase with monolayer type's arrangement of the molecules. Present results indicate that a packing of the molecules is very important in displaying mesomorphic properties. The X-ray studies are now in progress.

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