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Novel Liquid Crystals Having a Large Dielectric Anisotropy

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A homologous series of 4-cyanophenyl 4-(2,4-dialkoxybenzoyloxy)benzoates(from the pentyloxy to decyloxy homologs) shows a monotropic nematic phase, and the lower members show a large positive dielectric anisotropy in the mesophase.

It has been known that geometrical factors such as linearity and rigidity, and polarisability anisotropy of molecule are the most important factors in determining the mesomorphic properties.[1)] However, recent works have shown that some molecules having a large lateral substituent such as a long alkyl[2-5)] or a phenyl group[6)] also have liquid crystalline properties. Such structural modification will give us important information about the liquid crystallinity of molecule. In this work, we describe the thermal and dielectric properties of a homologous series of 4-cyanophenyl 4-(2,4-dialkoxybenzoyloxy)benzoates(1). The homologous series was prepared by two step esterification of 2,4-dialkoxybenzoic acids, as shown below. In the scheme, the first esterification was carried out according to the method of Dubois et al.,[7)] where the carboxy group of

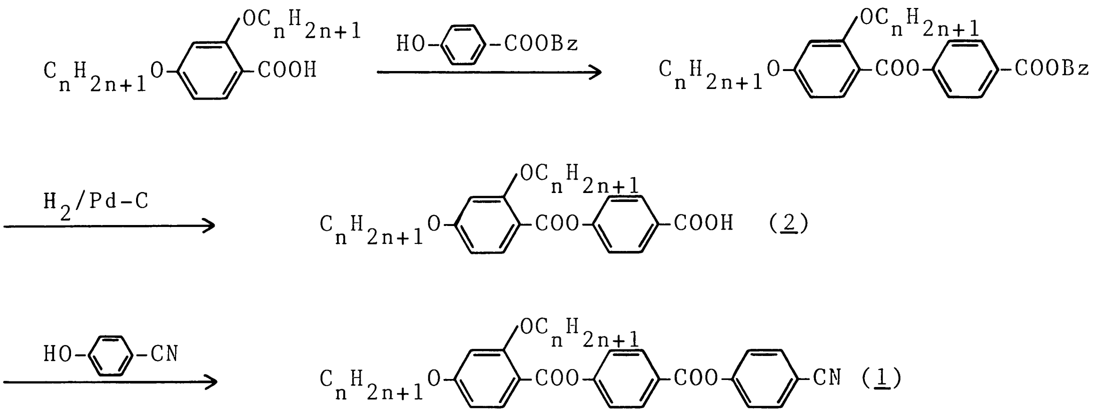

Table 1. Transition temperatures for the homologous series of 1 and 2(T/°C)

Carbon number	Compd 1						Compd 2				
n	C		N		Ia)	ΔH_{N-I}/kJ.mol^{-1} c)	C		N		I
5	.	90	(.	60)	.b)	0.3	.	156	(.	108)	.
6	.	84	(.	59)	.	0.4	.	143	(.	107)	.
7	.	76	(.	57)	.	0.4	.	119	(.	102)	.
8	.	68	(.	60)	.	0.9	.	99	.	100	.
9	.	69	(.	56)	.	0.6	.	96	.	96	.
10	.	72	(.	58)	.	1.2	.	97	(.	95)	.

a) C, N, and I abbreviate crystal, nematic phase, and isotropic solution, respectively. b) Parentheses indicate monotropic transitions. c) ΔH_{N-I} indicates the latent heat for the nematic-isotropic transition.

4-hydroxybenzoic acid was protected with a benzyl group(Bz in the scheme) which was removed by a catalytic hydrogenation with paradium-carbon. The second esterification was accomplished by a DCC method.

The transition temperatures and the latent heats for the homologous series of 1 and 4-(2,4-dialkoxybenzoyloxy)benzoic acids(2) are summarized in Table 1.

Both series show a fairly stable nematic phase having a schlieren texture, in spite of the large molecular breadth. The nematic thermal stabilities for both series are almost independent of the carbon number of the alkoxy chains. The latent heats for the nematic-isotropic transition are an order of 1 kJ/mol, and are comparable with those of the usual rod-like liquid crystals. Throughout the homologs, any smectic phases could not be observed.

The molecular structure of the nonyloxy homolog of series 1 was estimated by calculation, where the geometrical parameters used in the calculation were indicated in a previous paper.4) A possible molecular structure is shown in Fig. 1. As is evident from the figure, the alkoxy group attached at the position 2 extends toward the lateral direction of the molecule, and extremely increases the molecular breadth. In addition, the alkoxy group is located adjacent to the ester linkage so that the steric hindrance between these groups would change the molecular structure. Similar to the case of the homologous series of 1,4-bis[4-alkoxybenzoyloxy]-2-n-alkylbenzenes,3) the alkoxy group at the position 2 may be more or less distorted in order to minimize the molecular breadth, when the alkoxy chain is considerably long. Considering these geometrical disadvantages, series 1 must be unfavorable for the mesomorphic phenomena.

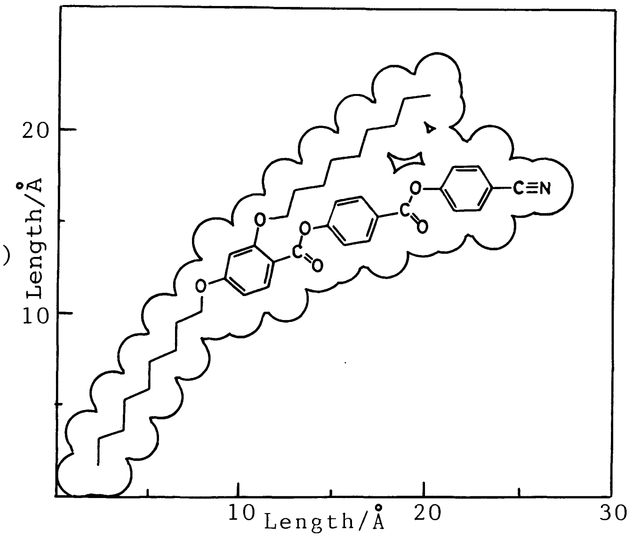

Fig. 1. The calculated molecular structure of the nonyloxy homolog. Circles indicate the van der Waals radii for respective atoms(C=1.5, H=1.2, O=1.4, and N=1.5 Å).

It has been known that liquid crystals having a polar terminal substituent such as a nitro or a cyano group form the associated dimer, and show interesting polymesomorphisms involving a reentrant phenomenon. The present series is also expected to form a similar dimer, though the tighter packing of the dimer in the nematic phase may be difficult because of the large lateral alkoxy group. However, the associated dimer is not essential for the appearance of the mesomorphic properties, since the alkoxy derivatives of series 1 are also mesogenic. For example, 4-nonyloxyphenyl 4-(2,4-dinonyloxybenzoyloxy)-benzoate shows the nematic phase(T_{N-I}=67 °C). Series 2 shows more stable nematic phase than series 1, whilst the molecular structure is apparently less favorable. The mesomorphic properties of the acids must be originated from the hydrogen-bonded dimer, similar to benzoic acid derivatives.1)

We are interested in the dielectric properties of series 1, in connection with the abnormal molecular structure. The dielectric properties were taken under a magnetic field of ca. 10 kG. The results are shown in Fig. 2. The dielectric constants tend to decrease with increasing the carbon number of the alkoxy chains. For the pentyloxy homolog the dielectric constant for the longitudinal direction($\varepsilon_{\parallel}$) steeply increases, and the transverse($\varepsilon_{\perp}$) one decreases with lowering temperature, and the values are 48 and 13 at 50 °C

(T_{N-I}-10 °C), respectively. The dielectric anisotropy($\varepsilon_{\parallel}$ $-\varepsilon_{\perp}$ =35) is one of the largest values hitherto reported. Similarly, the dielectric anisotropy for the nonyloxy homolog is 21 at 46 °C(T_{N-I}-10 °C). The increase in the dielectric anisotropy might be concerned with the monomer-dimer equilibrium of the cyano compounds. A large dielectric anisotropy has been observed in some 4-cyano-3-fluorophenyl ester compounds, and discussed in terms of the monomer-dimer equilibrium.[8)]

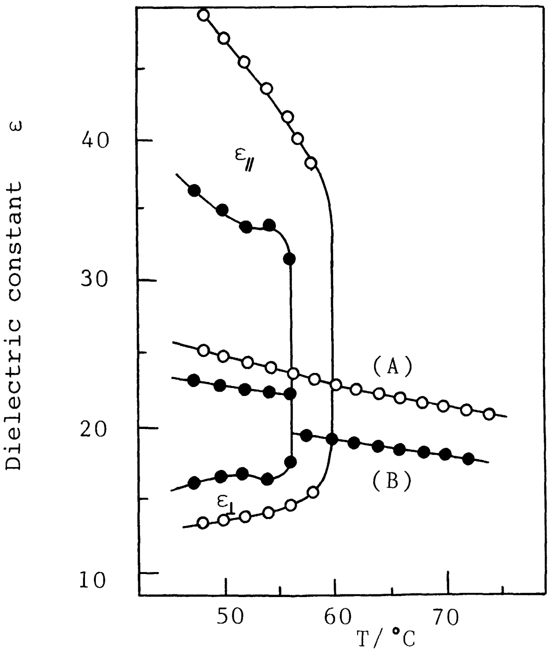

Fig. 2. Temperature dependence of dielectric constants for the pentyloxy(A) and nonyloxy homologs(B).

Conclusively, an introduction of the long alkyl group at the lateral position results in a depression of melting point, and an increase in dielectric anisotropy, while it depresses the mesophase thermal stability. The present results are a useful guide for the molecular design of new liquid crystals.

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