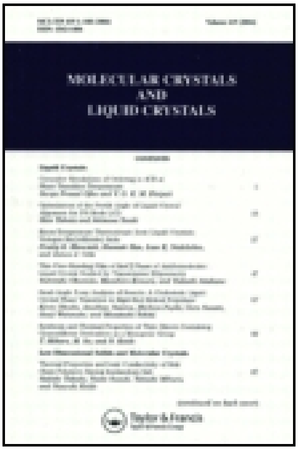

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Mesomorphic Properties of A Homologous Series of 4-Cyanophenyl 3,4- Di(4-alkoxybenzoyloxy) benzoates

S. Takenaka [a] , H. Morita [a] , M. Iwano [a] , S. Kusabayashi [a] , T. Ikemoto [a] , Y. Sakurai [a] & H. Miyake [a]
[a] Department of Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka, 565, Japan

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Mesomorphic Properties of A Homologous Series of 4-Cyanophenyl 3,4- Di(4-alkoxybenzoyloxy)benzoates

S. TAKENAKA, H. MORITA, M. IWANO, S. KUSABAYASHI, T. IKEMOTO, Y. SAKURAI, and H. MIYAKE

Department of Chemical Process Engineering, Faculty of Engineering Osaka University, Suita, Osaka 565, Japan

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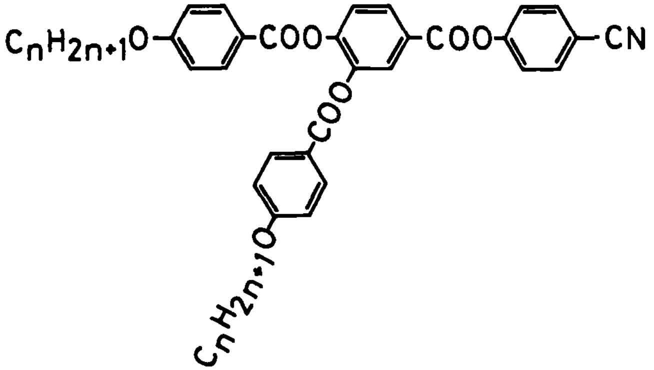
A new homologous series of 4-cyanophenyl 3,4-di(4-alkoxybenzoyloxy)benzoates (from ethoxy to decyloxy homologs) has been prepared. The homologs show both nematic and smectic A phases with fine schlieren and fan textures, respectively, whereas these have extremely large molecular breadth. The series is assumed to form an associated dimer and behave as a partially bilayer type smectic A phase. The dielectric properties have also been examined and the results support the formation of the associated dimer. The results have been discussed in terms of the geometry of the molecules.

Keywords: mesomorphic properties; dielectric properties; polar liquid crystals; associated dimer

It has been known that linearity, rigidity, and polarizability of molecules are indispensable for displaying liquid crystallinity. One of the current interests is study of liquid crystals free from the classical sense. Generally, an increase in molecular breadth has been known to be very unfavorable for liquid crystallinity, because it reduces the anisotropies of both molecular geometry and polarizability. For example, nematic stabilities in some biphenyl systems are inversely proportional to the bulkiness of the lateral substituent attached at the molecule.[1] Recent works, however, have shown that some molecules having extremely large lateral substituents, such as a long alkyl or a phenyl group, display stable mesophases.[2–7] Some twin molecules[8] and bent molecules[9,10] are also examples. Such geometrical variation is one of the current interests in connection with the boundary between the so-called 'rod-like' and 'discotic' liquid crystals. A typical example is that 1,2,4-trisubstituted benzenes which have a rod-like nature,[11] show stable nematic and smectic A phases, while 1,3,5-tri substituted benzenes show a discotic type nematic phase.[12,13] These facts indicate that the geometry of molecules is the most important factor in determining not only mesophase stability but also molecular arrangement in the mesophases. We are especially interested in the liquid crystalline nature of 1,2,4-trisubstituted benzenes, because these have extremely large molecular breadths.

In this paper, we describe the preparation and thermal properties of 4-cyanophenyl 3,4-di(4-alkoxybenzoyloxy)benzoates shown below.



The liquid crystalline properties will be discussed in terms of the molecular geometry.

EXPERIMENTAL

Materials: 3,4-Di(4-alkoxybenzoyloxy)benzoic acids were prepared by esterification of 3,4-dihydroxybenzoic acid with corresponding 4-alkoxybenzoyl chlorides in a solvent mixture of toluene–pyridine (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–pet. ether. The identification of the products was checked by elementary analysis. The transition temperatures of the homologous series are summarized in Table I.

A homologous series of 4-cyanophenyl ester was prepared by condensation of corresponding 3,4-di(4-alkoxybenzoyloxy)benzoic acids with 4-cyanophenol by the DCC method in dried dichloromethane. The products were purified by column chromatography on silica-gel, followed by recrystallization from a solvent mixture

TABLE I

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

Carbon number	*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

of ether–petroleum ether. The identification of the products was carried out by elementary analysis and thin layer chromatography on silica-gel.

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 (48.0°C).

Transition enthalpies were measured with a Daini-Seikosha SSC-560 differential scanning calorimeter, thereby indium (99.9%) was used as a calibration standard with a heating rate of 5°C/min. Dielectric constants were measured by using an Ando-denki TR-10 precision capacitance measurement system. The capacitor cell consisted of two indium-coated glass electrodes separated by a 10 μm spacer. The cell temperature was controlled by means of a brass housing. The applied voltage was 0.4 V. The alignment of the molecules in the cell was achieved by applying ca. 1 *T* magnetic field. The capacitor cell was calibrated by highly purified benzene and acetonitrile. The static dielectric constants were measured in the cooling stage.

RESULTS

The transition temperatures and the latent heats for the homologous series are summarized in Table II.

A nematic phase commences from the butoxy homolog, and the formation is monotropic, except for the hexyloxy homolog. A smectic phase commences from the heptyloxy homolog, and the nonyloxy and decyloxy homologs show only a smectic one. The microscopic textures are shown in Figure 1.

The nematic phase shows a schlieren texture. The nematic phase appears to have high viscosity because the change of the texture in the cooling stage was slightly slow. The smetic phase has a fine fan texture.

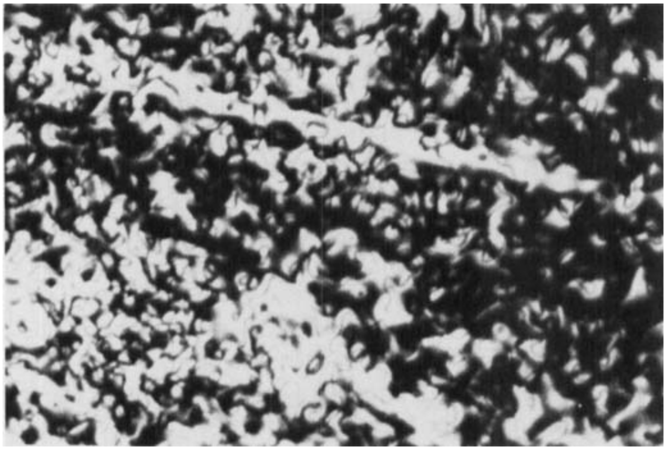
The transition temperatures and latent heats are plotted against the carbon number *n* in Figure 2.

TABLE II

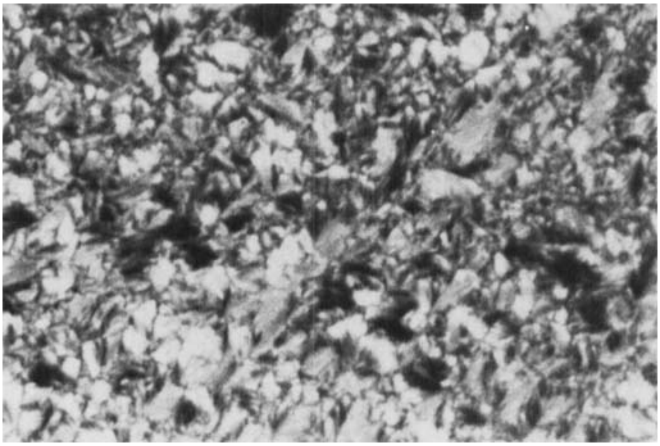
Transition temperatures (T/°C) and the latent heats (kJ/mol)

n	C	S_A	N	I	ΔH_{mp}	ΔH_{SA-N}	ΔH_{N-I}
2	. 145	-	-	.	39		
3	. 145	-	-	.	44		
4	. 124	-	(.	46).	42		*1
5	. 132	-	(.	54).	24		*1
6	. 68	-	.	81 .	80		1.1
7	. 120	(.	73 .	80).	50	*1	*1
8	. 114	(.	87 .	89).	47	1.2	1.0
9	. 109	(.	93)-	.	48	4.1	
10	. 107	(.	101)-	.	47	5.2	

Parentheses indicate monotropic transitions. *1 The latent heats were not evaluated because of simultaneous recrystallization.



(A) See Color Plate V.



(B) See Color Plate VI.

FIGURE 1 Microscopic pictures of the octyloxy homolog: (A) nematic phase at 88°C, and (B) smectic A phase at 80°C. A Konica high sensitive film(ASA 3200) was used.

Both nematic-isotropic and smetic-nematic(isotropic) transition temperatures tend to increase with the increasing carbon number. In the figure, the melting point of the hexyloxy homolog show a remarkable depression. An abnormal behavior is also recognized in the latent heats for the pentyloxy homologs in Figure 2B.

In order to characterize the smectic phase, binary phase diagrams were examined, and the results are shown in Figure 3.

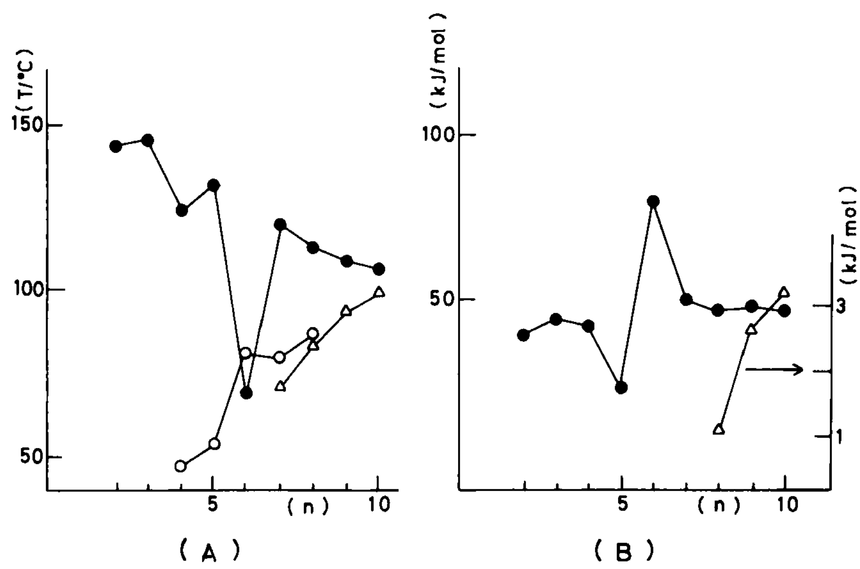


FIGURE 2 Plots of: (A) transition temperatures, and (B) the latent heats against the carbon numbers. ○; nematic-isotropic, △; smectic A-nematic (isotropic), ●; melting point.

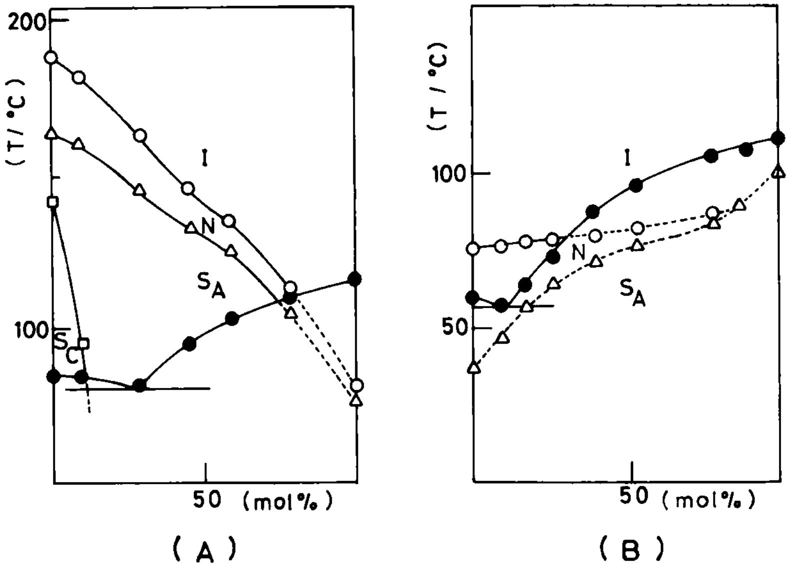


FIGURE 3 Binary phase diagrams of: (A) the octyloxy homolog (on right) and 4-octyloxy phenyl 4-(4-octyloxybenzoyloxy)benzoate (on left). (B) the nonyloxy homolog (on right) and 4-nonyloxyphenyl 3,4-di(4-nonyloxybenzoyloxy)benzoate (on left). Dashed lines indicate monotropic transitions.

In Figure 3A, both the smectic and nematic phases of the octyloxy homolog are miscible with a monolayer type smectic A and nematic ones of 4-octyloxyphenyl 4-(4-octyloxybenzoyloxy)benzoate.[14] In the diagram the nematic-isotropic and smectic A-nematic transitions show a weak non-ideal solution behavior. The smectic A phase of the nonyloxy homolog is also miscible with that of 4-nonyloxyphenyl 3,4-di(4-nonyloxybenzoyloxy)benzoate,[15] as shown in Figure 3B. In the figure the smectic A-nematic (isotropic) transitions show a weak enhancement around the center of the diagram. The smectic A phase also has an affinity with the partially bilayer type smectic A phase of 4-cyanophenyl 4-(4-nonyloxybenzoyloxy)benzoate[16] and 3,4-dioctyloxybenzylidene-*N*′-4′-(4″-cyanobenzoyloxy)aniline.[17] Thereby, the smectic A-nematic (isotropic) transitions show almost linear correlation with additivity. These results suggest that the molecules form the associated dimer, and the smectic A phase behaves as a partially bilayer arrangement (S_{Ad}).

The dielectric constants of the homologs were examined under a magnetic field. The temperature dependency of the hexyloxy homolog is shown in Figure 4.

The dielectric constant in the isotropic medium is ca. 14, and the dielectric anisotropy in the nematic phase ($T_{N-I}-10$) is ca. 12. As is evident from the figure, the mean value ($\bar{\epsilon}$ = 12.7) calculated by ($\epsilon_{\parallel}$ + $2\epsilon_{\perp}$)/3 does not agree with the dielectric constant in the isotropic medium. For the nonyloxy homolog the dielectric constant in the isotropic medium is ca. 12.5.

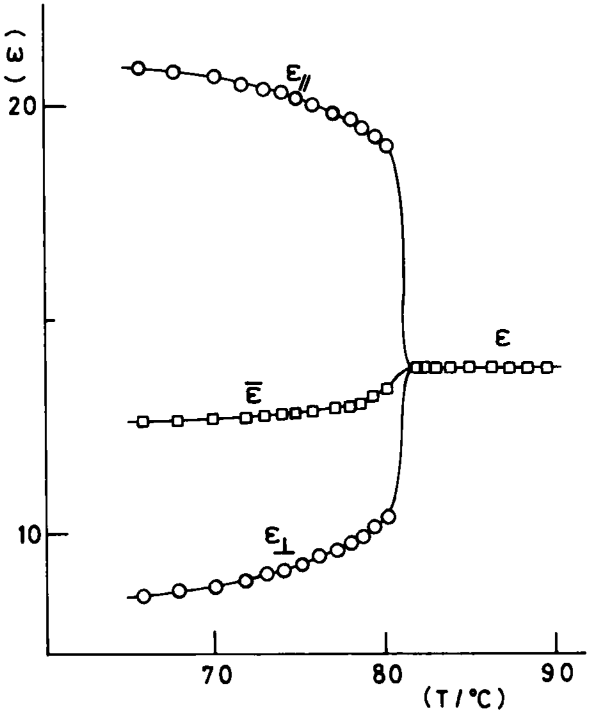
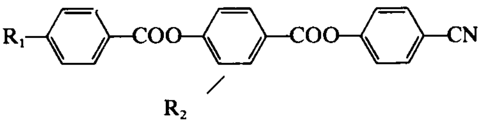
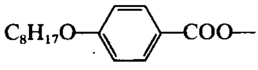


FIGURE 4 Temperature dependence of dielectric constants for the hexyloxy homolog at 1 kHz. Experimental conditions are shown in the experimental section.

TABLE III

The effect of lateral substituent



R_1	R_2	*C*	*N*	S_A	*N*	*I*
$C_8H_{17}O$	H	. 116	–	–	.	229 .[16]
$C_9H_{19}O$	H	. 121	(. 116)	. 198	.	229 .[16]
$C_8H_{17}O$		. 114	–	(. 87	.	89).
$C_9H_{19}O$		. 109	–	(. 93)	–	

DISCUSSION

The homologous series shows the nematic and smectic A phases of general rod-like liquid crystals. The thermal stabilities of both nematic and smectic A phases interestingly increase with the increasing chain length. The latent heats for both transitions are analogous to those of usual rod-like liquid crystals.

The following comparison expresses the mesomorphic characteristics of the present series (Table III).

The lateral substituent apparently decreases the nematic stability, but it enhances the smectic nature relative to the nematic, that is, an increase of the ratio, T_{S_A-N}/T_{N-I}.

In order to understand the mesomorphic properties of the series, we have to know the molecular geometry. It is not easy to realize the correct molecular geometry, because the molecules have three rotatable linkages which determine the gross geometries of the entirety of the molecules. Therefore, we supposed that the ester bonds at positions 3 and 4 orient so as to minimize the sterical repulsion between the ester groups, and the ester bond at the position 1 orients so as to keep the best linearity of the entirety of the molecule and the alkoxy chains are fully extended. The estimated molecular structure of the octyloxy homolog is shown in Figure 5.

The circles in the figure indicate van der Waals radii for respective atoms (H = 1.2, C = 1.5, O = 1.4, and N = 1.5 Å). As is evident from the figure, the geometries of the present series are quite unfavorable for mesomorphic phenomena. The octyloxy homolog is ca. 32 Å long and 20 Å width. Thereby, the ratio of the molecular length to breadth is 1.6 which is too small for usual rod-like liquid crystals, and probably too large for discotic ones. Nevertheless, the homologous series shows not only nematic but also smectic A phases having a rod-like nature. The homologous series of 3,4-di(4-alkoxybenzoyloxy)benzoic acids also shows a more stable nematic phase (see Table I) and the nematic-isotropic transitions show

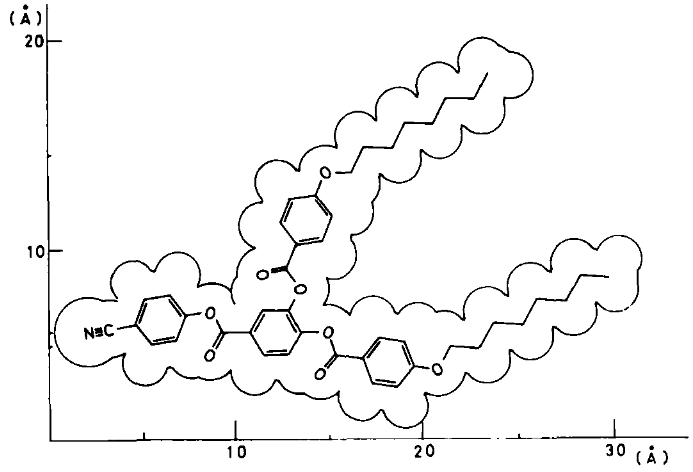


FIGURE 5 The estimated molecular structure of the octyloxy homolog.

a remarkable even-odd effect, while these homologs also have very unfavorable geometries for liquid crystalline properties. It has been known that 4-alkyl and 4-alkoxybenzoic acids show highly stable nematic and smectic *C* phases, while the molecules have only one aromatic ring. The mesomorphic properties have been interpreted by the formation of the hydrogen-bonded dimer.[18] For 3,4-di(4-alkoxybenzoyloxy)benzoic acids the ratio of molecular length to breadth would be improved over 3 by the formation of a similar associated dimer. The value would be large enough to display rod-like liquid crystals.

In very polar liquid crystals such as 4-cyanophenyl or 4-nitrophenyl 4-(4-alkoxybenzoyloxy)benzoates, the molecules have been known to form an antiparallel dimer, enhancing the mesomorphic properties. In these cases dipole-dipole interactions around the core and the polar group are considered to be the origin of the formation of the asociated dimer.[19] Considering these facts, it would be reasonable to assume that the present series also forms a similar associated dimer, and the formation favors reduction of the excluded volume. In fact, the smectic phase of the present series has an affinity with various kinds of smectic A phases having a monolayer and partially bilayer nature, without showing any abnormal behavior in the binary phase diagrams. One interesting fact in the dielectric properties is that the average dielectric constant in the nematic phase is lower (by 1.3) than the value in the isotropic medium. Further studies are underway.

References

1. G. W. Gray and B. M. Worrall, *J. Chem. Soc.*, 1545 (1959).
2. N. H. Tinh, J. Malthete, and C. Destrade, *Mol. Cryst. Liq. Cryst. Lett.*, Vol. **2**, 133 (1985).
3. W. Weissflog and D. Demus, *Mol. Cryst. Liq. Cryst.*, **129**, 235 (1985).
4. V. Gallardo and H. J. Muller, *Mol. Cryst. Liq. Cryst.*, **102**, 13 (1984).
5. R. J. Cox, W. Volksen, and B. L. Dawson, 'Liquid Crystals and Ordered Fluids,' ed. by A. C. Griffin and J. F. Johnson, Plenum Press, New York (1984), Vol. 4, p. 33.

6. S. Diel, W. Weissflog, G. Pelzel, H. Manke, and D. Demus, *Liquid Crystals*, **1**, 101 (1986).
7. W. Weissflog and D. Demus, *Cryst. Res. and Techn.*, **18**, K 21 (1983).
8. A. C. Griffin, S. F. Thames, and M. S. Bonner, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 135 (1977).
9. G. Sigaud, F. Hardouin, and H. Gasparoux, *Mol. Cryst. Liq. Cryst. Lett.*, **92**, 217 (1983).
10. M. Koden, T. Yagyu, S. Takenaka, and S. Kusabayashi, *J. Phys. Chem.*, **87**, 4731 (1983).
11. S. Takenaka, Y. Masuda, and S. Kusabayashi, *Chem. Lett.*, 751, (1986)
12. N. Nishimura, S. Takenaka, and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **104**, 347 (1984).
13. S. Takenaka, K. Nishimura, and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **111**, 227 (1984).
14. J. P. van Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, **22**, 285 (1973).
15. Unpublished results in our laboratory.
16. G. Sigaud, N. H. Tinh, F. Hardouin, and G. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **69**, 81 (1981).
17. N. H. Tinh, J. Malthete, and C. Destrade, *Mol. Cryst. Liq. Cryst. Lett.*, **2**, 133 (1985).
18. G. W. Gray, 'The Molecular Physics of Liquid Crystals' ed. by G. R. Luckhurst and G. W. Gray, Academic Press, New York. (1979), p. 1 References cited therein.
19. G. W. Gray and J. W. Goodby, 'Smetic Liquid Crystals' ed. by G. W. Gray and J. W. Goodby, Heydon & Son Inc., Philadelphia (1984), p. 134.