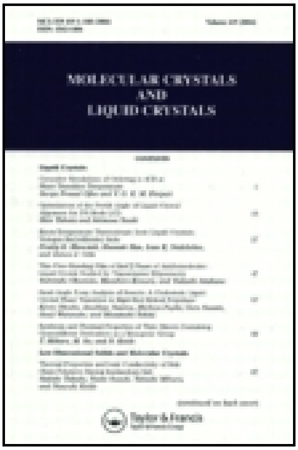


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Structure and Liquid Crystalline Properties: The Effect of Lateral Long Alkoxy Chain on the Thermal Properties of Nematic and Smectic Phases

Shunsuke Takenaka [a] & Hiroshi Yamasu [a]

[a] Department of Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi, 755, Japans

Version of record first published: 04 Oct 2006.

To cite this article: Shunsuke Takenaka & Hiroshi Yamasu (1994): Molecular Structure and Liquid Crystalline Properties: The Effect of Lateral Long Alkoxy Chain on the Thermal Properties of Nematic and Smectic Phases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 238:1, 157-165

To link to this article: http://dx.doi.org/10.1080/10587259408046924

Mol. Cryst. Liq. Cryst., 1994, Vol. 238, pp. 157–165
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Molecular Structure and Liquid Crystalline Properties: The Effect of Lateral Long Alkoxy Chain on the Thermal Properties of Nematic and Smectic Phases

SHUNSUKE TAKENAKA AND HIROSHI YAMASU

Department of Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755, Japan

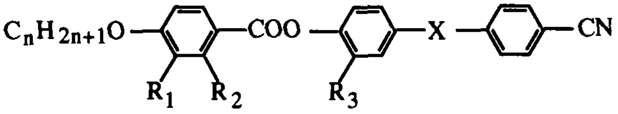
(Received January 11, 1993; in final form April 9, 1993)

Homologous series of 4-cyanophenyl 4-(3-alkoxybenzoyloxy)benzoates, 4-(4-cyanobenzoyloxy)phenyl 3-alkoxybenzoates, and 4-(4-nitrobenzoyloxy)phenyl 3-alkoxybenzoates have been prepared. The nematic-isotropic transition temperature decreases on ascending the series. However, the smectic *A* phase is formed even in the higher members, while the alkoxy group at 3 position would increase the bend of the molecular structure. On the other hand, the related compounds having a long alkoxy group instead of the cyano or the nitro group are non-mesogenic. The formation of the liquid crystalline phases for the polar compounds is discussed in terms of the formation of the antiparallel dimers.

Keywords: syntheses, thermal properties, lateral long alkoxy chain, polar liquid crystals, molecular structure

INTRODUCTION

Generally, rod-like liquid crystals have long alkyl group(s) along the long molecular axis of the core, and the terminal alkyl group(s) plays important roles for displaying liquid crystalline properties. On the other hand, recent works have shown that some compounds having long alkyl group(s) at the lateral position frequently display nematic and/or smectic phases. For example, the ester compounds shown below[1–4] and the related compounds[5–10] display liquid crystalline properties, while these compounds have a long alkoxy group at the lateral position.



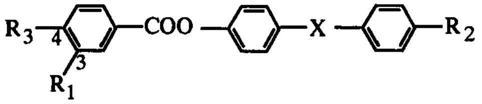
$R_1 = C_nH_{2n+1}O$, $R_2 = R_3 = H$, X = COO , OOC

$R_1 = R_3 = H$, $R_2 = C_nH_{2n+1}O$, X = COO , OOC

$R_1 = R_2 = H$, $R_3 = C_nH_{2n+1}O$  COO, X = COO

For these compounds the lateral alkoxy groups play very interesting roles for mesomorphism, that is, the alkoxy group at 3 position (R_1) enhances the smectic properties, while that at 2 position (R_2) enhances the nematic properties.[1] These facts suggest that the role of the alkoxy group is different from position to position.

In order to clarify the role of the lateral alkoxy group at 3 position, we examined the thermal properties of the following compounds and the related ones.



Compound	R_1	R_2	R_3	X
1	H	NO_2	$C_nH_{2n+1}O$	OOC
2	$C_nH_{2n+1}O$	CN	H	COO
3	$C_nH_{2n+1}O$	CN	H	OOC
4	$C_nH_{2n+1}O$	NO_2	H	OOC
5	$C_nH_{2n+1}O$	CN	$C_nH_{2n+1}O$	COO
6	$C_nH_{2n+1}O$	CN	$C_nH_{2n+1}O$	OOC

This paper describes thermal properties of compounds **1**–**6** and some related ones, and the results will be discussed in terms of the molecular structure.

EXPERIMENTAL

The esterification was carried out according to the method described in a previous paper,[11] and the purity was checked by HPLC (Shimadzu LC-10S) where the ODS column was used, and elemental analysis. Transition temperature was determined by using a Nikon POH polarizing microscope fitted with a Mettler FP-52 heating stage.

RESULTS

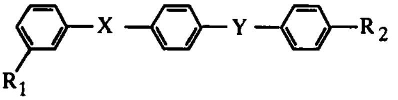
Transition temperatures for compounds **2**–**4** are summarized in Table I.

The compounds have high melting points so that the formation of liquid crystalline phases is monotropic. The nematic and smectic phases have a schlieren texture with a complex birefringence and a fan one, respectively. The smectic phase was identified by examination of the binary phase diagrams for the mixture of 4-(4-nitrobenzoyloxy)phenyl 4-alkoxybenzoates, as shown in Figure 1.

4-(4-Nitrobenzoyloxy)phenyl 4-hexyloxy- and 4-nonyloxybenzoates are known to show a smectic *A* phase having a partially bilayer arrangement.[11] In Figure 1[1] the nematic-isotropic (*N*-*I*) transition shows a linear correlation with the molar composition, and the extrapolation of the *N*-*I* transition gives 100°C as the *N*-*I* transition temperature for the hexyloxy homolog of **4**. This fact indicates that the hexyloxy homolog of **4** is intrinsically mesogenic, though observation of mesophases is not easy because of the high melting point.

TABLE I

Transition temperatures of compounds **2**–**4** (*T*/°C)



Compound	R_1	X	Y	R_2	C		S_A		N		I
2	CH_3O	—COO—	—COO—	CN	·	165	–		(·	138)	·
	C_2H_5O				·	154	–		(·	116)	·
	$C_8H_{17}O$				·	129	(·	106)	–		·
	$C_9H_{19}O$				·	132	(·	109)	–		·
	$C_{10}H_{21}O$				·	127	(·	104)	–		·
3	C_3H_7O	—COO—	—OOC—	CN	·	150	–		(·	110)	·
	C_4H_9O				·	158	–		(·	102)	·
	$C_5H_{11}O$				·	146	·		(·	96)	·
	$C_6H_{13}O$				·	135	·		(·	93)	·
	$C_7H_{15}O$				·	131	·		(·	94)	·
	$C_8H_{17}O$				·	133	·		(·	94)	·
	$C_9H_{19}O$				·	128	(·	99)	·		·
	$C_{10}H_{21}O$				·	131	(·	101)	·		·
4	CH_3O	—COO—	—OOC—	NO_2	·	199	–		–		·
	C_2H_5O				·	195	–		–		·
	C_3H_7O				·	164	–		–		·
	C_4H_9O				·	162	–		–		·
	$C_5H_{11}O$				·	138	–		–		·
	$C_6H_{13}O$				·	142	–		[·	100]	·*1
	$C_7H_{15}O$				·	132	–		–		·
	$C_8H_{17}O$				·	127	(·	97)	–		·
	$C_9H_{19}O$				·	124	(·	109)	–		·
	$C_{10}H_{21}O$				·	132	(·	110)	–		·

Parentheses indicate a monotropic transition. *C*, S_A, *N*, and *I* indicate crystal, smectic *A*, nematic, and isotropic solution, respectively. *1 = An extrapolated transition temperature (see Figure 1[1]).

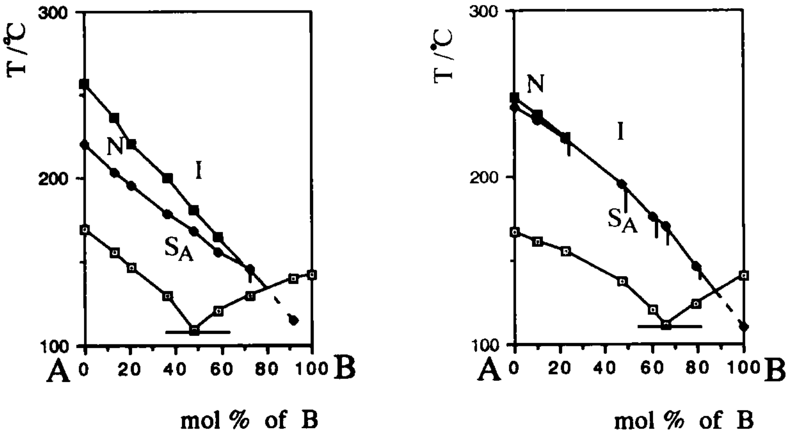
In Figure 1[2], the smectic *A*—isotropic transition (S_A-*I*) shows a linear correlation with the molar composition, and both S_A phases are miscible, though the S_A-*I* transition shows a wide two-phase region. Therefore, we can conclude that the smectic phase for the present compounds is an S_A one having a partially bilayer arrangement, though the thermal properties of both S_A phases may be slightly different.

The transition temperatures are plotted against the carbon number of the alkoxy chain in Figure 2.

DISCUSSION

Generally, liquid crystals are considered to be a rod- or a lath-shape molecule maintaining linearity and rigidity. Strictly speaking, however, most liquid crystals are not linear due to a difference in the bond angles of atoms.

As shown in Figure 3, for example, 4-alkoxybiphenyl and 4-alkylbiphenyl are bent molecules because of the bent angles of the C—O—C (aromatic carbon) bond (120°) and C—C—C (aromatic) one (113°), and the effect of the bend would become remarkable on ascending the series. The difference in the molecular structures must



[1] [2]

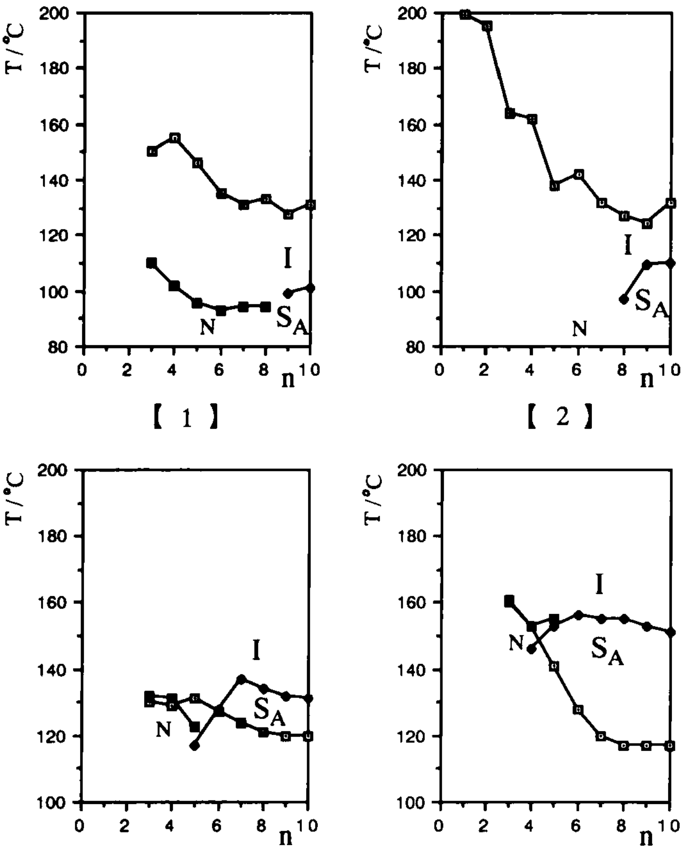
FIGURE 1 Binary phase diagrams for the mixtures of [1] 4-(4-nitrobenzoyloxy)phenyl 4-hexyloxybenzoate (A) and the hexyloxy homolog of 4(B); [2] 4-(4-nitrobenzoyloxy)phenyl 4-nonyloxybenzoate (A) and the nonyloxy homolog of 4(B). Dashed lines indicate a monotropic transition. Vertical lines in the figures indicate a two-phase region of the smectic A phase and the isotropic solution.

be reflected in the liquid crystalline properties. Similarly, a phenyl benzoate core is less linear than a benzylideneaniline core due to the narrow angle of the C (aromatic)—CO—O bond (110°). The effect of the bent structure would become remarkable when the alkoxy groups at 4 and 4′ positions are long.[12]

The present compounds have an alkoxy group at 3 position with respect to the ester linkage, and the molecular structure may be different from usual liquid crystalline molecules. As shown in Figure 4, the methylene groups of the alkoxy group would have a zig-zag conformation so as to minimize the steric repulsion between adjacent methylene groups, maintaining linearity on average.

In 4-substituted compounds two conformers represented by [A] and [B] should be equivalent from an energy point of view. In addition, both conformers are symmetric with respect to the long axis of the core (dashed line in the figure) so that these must be present not only in the isotropic solution but also in liquid crystalline phases. In the 3-substituted compounds two conformers should be also equivalent from an energy point of view. However, the rotational angle (the dashed line) has an angle of 60° to that of the core. Therefore, conformer [B] has a remarkable bent structure and is unfavorable for liquid crystalline properties. There is no doubt that both conformers are present in the isotropic solution, and one of both is present preferentially in the crystalline phase. Our interest is how the equilibrium changes in the liquid crystalline phases. For comparative consideration, the transition temperatures for some related compounds are shown in Table II.

Compound **1** has an alkoxy group at 4 position. As shown in Figure 4, the alkoxy group at 4 position extends along the long axis of the core, and the chain elongation would increase the anisotropy of the molecular structure. As a result, the homologs have high clearing points, and the S_A phase having a partially bilayer arrangement commences from the butoxy homolog.



[1] [2] [3] [4]

FIGURE 2 Plots of transition temperatures against the carbon number: [1] compound **3**, [2] **4**, [3] **5**, and [4] **6**.

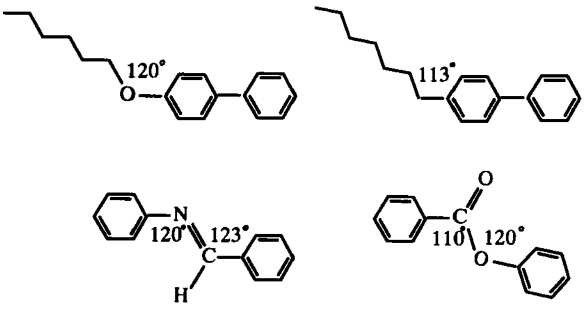


FIGURE 3 Geometries of liquid crystal cores.

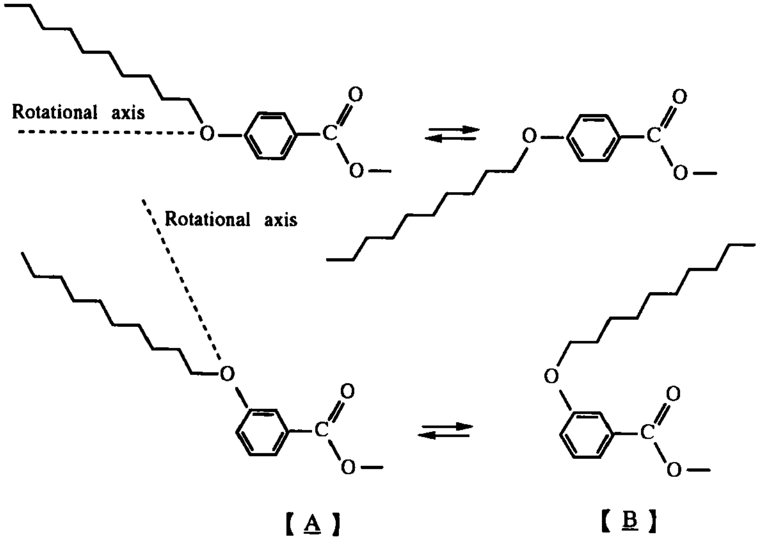
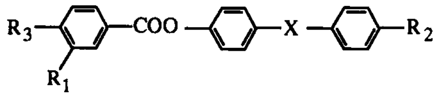


FIGURE 4 Conformations of alkoxy groups at 3 and 4 positions.

TABLE II

Transition temperatures of compounds **1**, **5**, and **6** (T/°C)



Compound	R_1	R_3	X	R_2	C		S_C		S_A		N		I
1[*1]	H	C_3H_7O	—COO—	NO_2	·	201	-		-		·	283	·
		C_4H_9O			·	189	-		(·	172)	·	274	·
		$C_8H_{17}O$			·	165	-		·	239	·	246	·
		$C_9H_{19}O$			·	165	-		·	242	·	243	·
5[*2]	C_4H_9O	C_4H_9O	—COO—	CN	·	129	-		-		·	131	·
	$C_5H_{11}O$	$C_5H_{11}O$			·	131	-		(·	117	·	123)	·
	$C_7H_{15}O$	$C_7H_{15}O$			·	124	-		·	137	-		·
	$C_8H_{17}O$	$C_8H_{17}O$			·	121	-		·	134	-		·
6[*2]	C_3H_7O	C_3H_7O	—COO—	CN	·	160	-		-		·	161	·
	C_4H_9O	C_4H_9O			·	153	-		·	146	·	153	·
	$C_7H_{15}O$	$C_7H_{15}O$			·	120	-		·	155	-		·
	$C_8H_{17}O$	$C_8H_{17}O$			·	117	(·	111)	·	155	-		·

Parentheses indicate a monotropic transition. C, S_C, S_A, N,and I indicate crystal, smectic C, smectic A, nematic phases, and isotropic solution, respectively. *1 Reference 11. *2 Reference 1.

When another alkoxy group is introduced at 3 position (compounds **5** and **6**), the clearing point decreases ca. 100°C. However, the ratio of the S_A-N transition temperature to N-I one[13] rather increases, indicating that the alkoxy group at 3 position increases the smectic properties of the compounds.

When the alkoxy group at 4 position is replaced by hydrogen (compounds **2**–**4**), the clearing point decreases more than 50°C, and the S_A phase having the partially biayer arrangement commences from the octyloxy or the nonyloxy homolog. These facts indicate that the alkoxy group at 3 position does not always prevent the formation of mesophases.

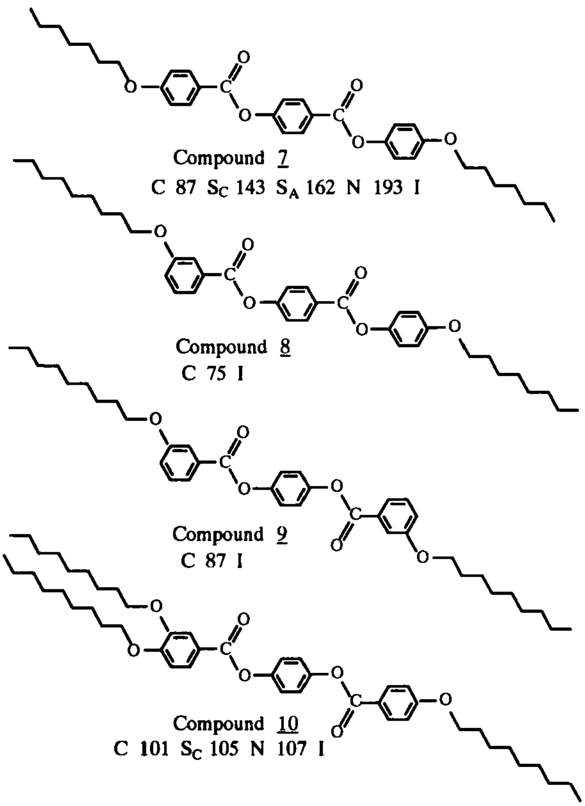
In Table III, the mesomorphic properties of some related compounds having alkoxy groups at both terminal positions are shown.

Compound **7** has alkoxy groups at both 4 and 4′ positions, and the structure of the entire molecule keeps linearity, displaying stable nematic and smectic phases. Compound **8** having alkoxy groups at both 3 and 4′ positions, on the other hand, is non-mesogenic even in the monotropic process (the isotropic solution recrystallized ca. 20°C). As we can see from the table, the molecule is also expected to have linearity as well as **7**, if conformer [A] in Figure 4 is preferentially formed. Similarly, compound **9** having two alkoxy groups at both 3 and 3′ positions is also non-mesogenic. On the other hand, compound **10** having two alkoxy groups at 4 and 4′ positions as well as the alkoxy group at 3 position shows *N* and S_C phases. These facts indicate that in the "non-polar" compounds both alkoxy groups at 4 and 4′ positions are indispensable for displaying the liquid crystalline properties.

An interesting fact is why compounds **8** and **9** are non-mesogenic and **2–4** display *N* and S_A phases. As we can see from Tables II and III, the clearing point of

TABLE III

Transition temperatures for some related compounds (T/°C)



Compound 7
C 87 S_C 143 S_A 162 N 193 I

Compound 8
C 75 I

Compound 9
C 87 I

Compound 10
C 101 S_C 105 N 107 I

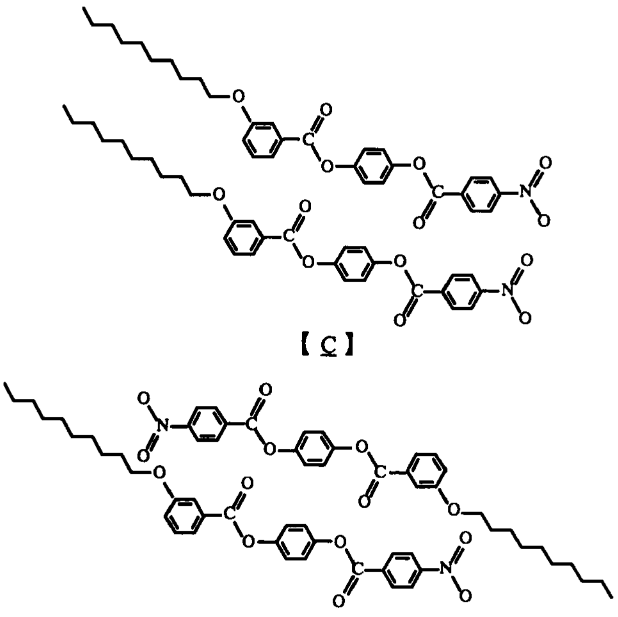


FIGURE 5 Possible models for the molecular arrangement.

compound **10** is lower by 30–40°C than those of **5** and **6** having the cyano group. These facts indicate that the terminal polar group plays a very important role in displaying the mesomorphic properties for the compounds having the alkoxy group at 3 position. Considering the fact that the present compounds tend to display an S_A phase having a partially bilayer arrangement of molecules, it would be reasonable to assume that these molecules form antiparallel dimers such as [C] and/or [D] in Figure 5.

In model [C] the polar groups arrange parallel so tht the electrostatic interaction between them would destabilize the molecular arrangement. In model [D], on the other hand, such disadvantageous interactions are absent. When the antiparallel dimers are suitably stable, the steric hindrance may exclude the unfavorable conformer, [B], to a certain extent, and the formation of the dimers is one of the origins for displaying the liquid crystalline properties. In compounds **7** and **8** such strong interactions would be absent so that the disadvantageous conformers reduce the liquid crystalline properties.

CONCLUSION

Phenyl 4-benzoyloxybenzoates and 4-benzoyloxyphenyl benzoates incorporating an alkoxy group at 3 position instead of 4 position with respect to the linkages display liquid crystalline properties when the cores have a polar group such as a cyano or a nitro group at the other terminal position. The associated dimer may be concerned with the formation of the liquid crystalline phases.

References

1. S. Takenaka, H. Morita, M. Iwano, Y. Sakurai, T. Ikemoto and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **182B**, 325 (1990).
2. S. Takenaka, H. Morita, M. Iwano, S. Kusabayashi, T. Ikemoto, Y. Sakurai and H. Miyake, *Mol. Cryst. Liq. Cryst.*, **166**, 325 (1989).
3. S. Takenaka, Y. Masuda, M. Iwano, H. Morita, S. Kusabayashi, H. Sugiura and T. Ikemoto, *Mol. Cryst. Liq. Cryst.*, **168**, 111 (1989).
4. H. Takeda, S. Takenaka, H. Miyake and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **202**, 111 (1991).
5. V. Gallado and H. J. Muller, *Mol. Cryst. Liq. Cryst.*, **102**, 13 (1984).
6. Nguyen Huu Tinh, J. Malthete and C. Destrade, *Mol. Cryst. Liq. Cryst. Lett.*, **2**, 133 (1985).
7. W. Weissflog and D. Demus, *Mol. Cryst. Liq. Cryst.*, **129**, 235 (1985).
8. W. Weissflog, S. Diele and D. Demus, *Mater. Chem. Phys.*, **15**, 475 (1986).
9. W. Weissflog and D. Demus, *Liq. Cryst.*, **3**, 275 (1988).
10. 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.
11. Y. Sakurai, S. Takenaka, H. Sugiura and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **201**, 95 (1991).
12. Y. Sakurai, S. Takenaka, H. Miyake, H. Morita and T. Ikemoto, *J. Chem. Soc. Perkin Trans. II*, 1199 (1989).
13. W. L. McMillan, *Phys. Rev. A*, **8**, 1921 (1973).