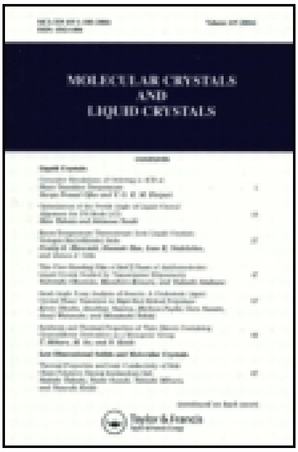

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Mesomorphic Behavior of Compounds Incorporating One-Unit Linking Groups

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Mesomorphic Behavior of Compounds Incorporating One-Unit Linking Groups

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4,4'-Bis[4-(4-alkoxybenzoyloxy)benzylideneamino]diphenyl ether, its 3,4'-analogue, and 1,4-bis[4-[4-(4-alkoxybenzoyloxy)benzylideneamino]phenoxy]benzene have been found to exhibit mostly an enantiotropic nematic phase. The clearing points of these three homologous series are rather close to each other; for example, the methoxy members give 340, 325, and 333°C respectively and the decyloxy members 222, 213, and 231°C, suggesting no substantial difference in the molecular shape though the molecules are not quite linear. On the other hand, the mesophase appearing in 4,4'-bis[4-(4-alkoxybenzoyloxy)benzylideneamino] diphenylmethanes is of the smectic C type. Thus, the importance of the nature of one-unit linking groups as a factor determining the type of mesophase was demonstrated.

Keywords: Nematic, smectic, ether linkage, methylene linkage, non-linear configuration

INTRODUCTION

Mesogens generally consist of two or more aromatic and/or aliphatic rings bearing two terminal substituents and linked together directly or by a linking group in a more-or-less linear, lath-like structure. One-unit linking groups such as —O—, —S—, and —NH— were considered by Vorländer to be unsuitable for liquid crystals due to the resulting nonlinear configurations of the structures.[1] This view is in conformity with the angular correlation parameters of related molecular cores determined by means of depolarized Rayleigh scattering. According to the works reported by Destrade *et al.*[2,3] diphenyl ether molecules tend to be organized with the molecular axes of higher symmetry parallel to each other, but the tendency is much less than those exhibited by typical molecular cores such as biphenyl, N-benzylideneaniline, and stilbene, whereas diphenylmethane does not show such a tendency at all. Nevertheless, Vorländer succeeded in demonstrating that a number of compounds such as 1,2-phenylene bis-[4-(4-ethoxyphenylazoxy) benzoate] and bis [4-(4-methoxyphenylazo) phenyl] isophthalate, for which he supposed acute- and obtuse-angled configurations respectively, are mesogenic.[4,5] Recently, we studied the thermal behavior of 1,2- and 1,3-phenylene bis [4-(4-alkoxyphenyliminomethyl) benzoates] and found that the former compounds

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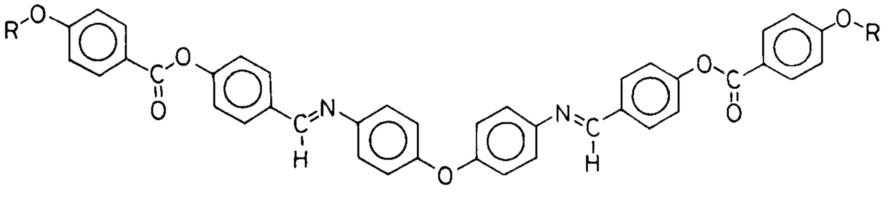
are nematogenic and the latter smectogenic.[6-8] Our work on mesogenic compounds possibly with obtuse-angled configurations has now been extended to three series of compounds incorporating one or two ether linkages (compounds 1 to 3) and a series of compounds incorporating one methylene linkage (compound 4).



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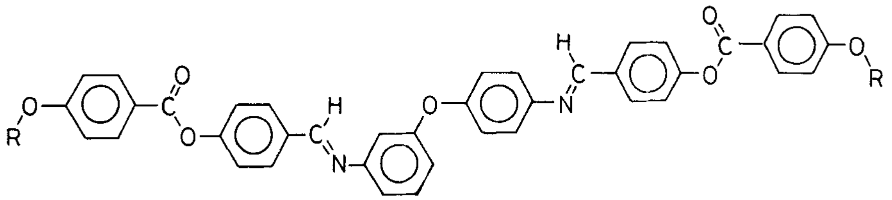

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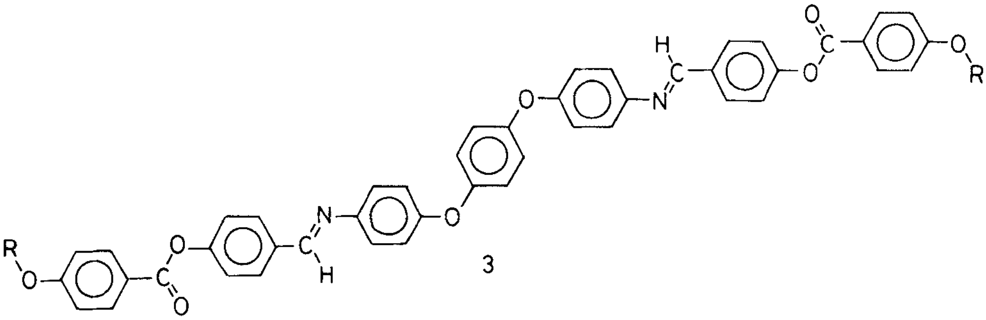

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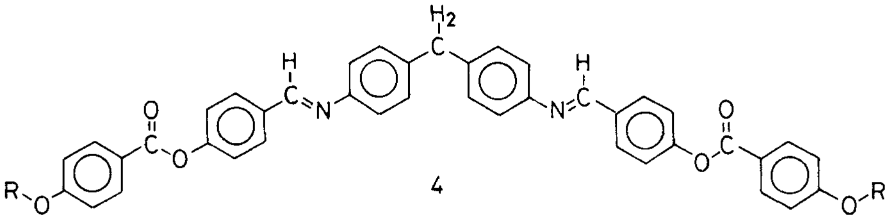

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EXPERIMENTAL

4,4′-Diaminodiphenyl ether, 3,4′-diaminodiphenyl ether, 1,4-bis(4-aminophenoxy)-benzene, and 4,4′-diaminodiphenylmethane are commercially available. The higher homologous members of 4-alkoxybenzaldehyde were prepared by the method proposed in our earlier paper.[9] 4-(Alkoxybenzoyloxy)benzaldehydes were obtained by the reaction between 4-alkoxybenzoic acids and 4-hydroxybenzaldehyde following the procedure of Hassner and Alexanian[10] and then purified by recrystallization from methanol. The aldehyde was condensed with the diamine in a boiling benzene solution by adding a catalytic amount of glacial acetic acid. The crude product was repeatedly recrystallized from benzene, toluene or benzene-ethanol mixtures. For example, Found: C, 78.74; H, 7.21; N, 3.34%. Calcd for $(C_8H_{17}OC_6H_4CO_2C_6H_4CHNC_6H_4)_2CH_2$: C, 78.59; H, 7.17; N, 3.22%. The calorimetric and X-ray diffraction measurements were carried out as described in a previous paper.[7]

RESULTS AND DISCUSSION

The transition temperatures and associated enthalpies of compounds 1 are recorded in Table I. Here, K, S_C, S_A, N, and I denote the crystalline, smectic C and A, nematic, and isotropic liquid phases, respectively. The clearing points for the four lower homologous members are not because of the onset of a superposed exothermal decomposition. Therefore, no reliable enthalpy values could be obtained for these members. All the present compounds possess an enantiotropic N-I transition. The assignment of the nematic phase was made on the basis of a schlieren texture and supplemented by miscibility studies involving the octyloxy homologue and 4-(4-nitrobenzylideneamino)-azobenzene which melts into a nematic phase at 181°C and clears at 228°C. The small enthalpy changes at the clearing point are in conformity with this assignment. The smectic phase appearing in the lower homologous members is characterized to be of the A type because of the achievement of its homeotropic alignment and that appearing in the highest member is of the C type because of its schlieren texture.

TABLE I

Transition temperatures (t/°C) and associated enthalpies (ΔH/kJ mol^{-1})[a] of compounds 1

n[b]	K	S_C	S_A	N	I
1	·230(57)		·270(– – –)	·340(1.3)[c]	·
2	·222(52)		·274(– – –)	·333(1.6)[c]	·
3	·217(54)		·235(– – –)	·299(0.6)[c]	·
4	·235(39)		[·234(– – –)][d]	·291(0.9)[c]	·
5	·234(45)			·276(1.0)	·
6	·228(45)			·261(0.8)	·
7	·225(49)			·248(0.7)	·
8	·223(54)			·240(0.7)	·
9	·220(55)			·229(0.6)	·
10	·215(57)			·222(0.5)	·
12	·202(58)			·208(0.4)	·
14	·194(53)			·201(0.4)	·
16	·190(36)	·196(7.4)		·197(–––)	·

[a] Values in parentheses.

[b] The number of carbon atoms in the alkyl group.

[c] Superposition with an exothermal decomposition

[d] Monotropic transition.

The thermodynamic data for compounds 2 are summarized in Table II. In contrast to the proposition made by Destrade *et al.* that the molecular linearity may be improved by placing two mesogenic branches at the 3- and 4′-positions respectively and that the resulting compounds are more suitable for the formation of the mesophase than 4,4′-disubstituted compounds,[3] the enantiotropic *N*-*I* transition in the present series occurs at a temperature lower by 3 to 29°C, 12°C on average, than that of the corresponding member in the previous one. The melting point is more significantly depressed by this structural change, 47°C on average, and the temperature range of the mesophase is much broadened compared to that of compound 1. It must be emphasized that the enthalpy change by clearing is larger by a factor of almost ten than that of series 1 but still fits in the range complied by Demus *et al.* for *N*-*I* transition (0.84 to 9.63 kJ mol^{-1}).[11] This observation may imply an extensive short-range smectic order within the nematic phase up to the clearing point. The mesophase given by the octyloxy homologue is miscible with the classical nematic phase of 4-(4-nitrobenzylideneamino)-azobenzene as shown in the diagram of the binary system (see Figure 1). The induction of a smectic phase is noted in the composition range from 14 to 72 mol% of the reference mesogen. While no smectic A phase appears in the lower members of this series, a smectic C phase is observed for the dodecyloxy to hexadecyloxy homologues. This phase assignment was made on the basis of a schlieren texture and also by the X-ray diffraction pattern indicative of the absence of in-plane-order. Moreover, the following layer spacings are in support of this assignment: 4.03 nm for the dodecyloxy homologue, 4.23 nm for the tetradecyloxy one, and 4.48 nm for the hexadecyloxy one. The relation between the spacing (d/nm) and the number of carbon atoms in the alkyl group (n) may be approximated by $d = 0.113n + 2.67$. The observed increment per two methylene groups is about one half compared to the value expected when the alkyl chains are perpendicular to the smectic layer. The spacing extrapolated to $n = 0$ is significantly shorter than the estimated distance between the end oxygen atoms, 3.5 nm.

TABLE II

Transition temperatures (t/°C) and associated enthalpies (ΔH/kJ mol^{-1})[a] of compounds 2

n[b]	K	S_C	N	I
1	·222(46)		·325(– – –)[c]	·
2	·238(69)		·304(8.7)	·
3	·167(51)		·286(8.3)	·
4	·192(62)		·274(7.8)	·
5	·155(54)		·258(7.6)	·
6	·168(62)		·247(8.1)	·
7	·160(49)		·236(6.7)	·
8	·165(53)		·228(7.7)	·
9	·158(56)		·219(6.5)	·
10	·154(66)		·213(6.5)	·
12	·151(1.8)	·171(1.8)	·203(6.3)	·
14	·148(69)	·191(5.6)	·198(6.9)	·
16	·145(72)	·194(1.9)		·

[a] Values in parentheses.

[b] The number of carbon atoms in the alkyl group.

[c] Superposition with an exothermal decomposition.

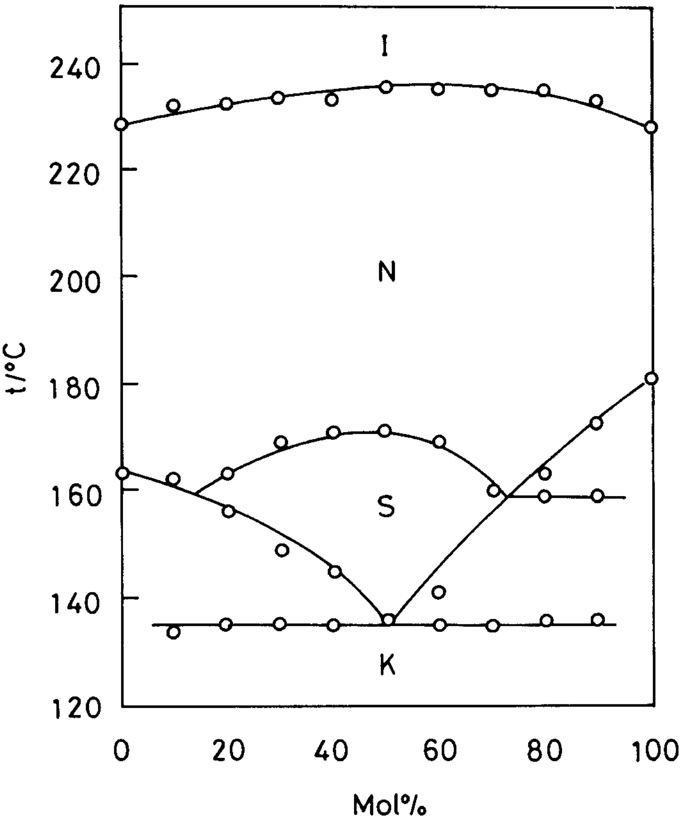

FIGURE 1 Phase diagram of the binary system consisting of the octyloxy homologue of series 2 and 4-(4-nitrobenzylideneamino) azobenzene. The latter compounds is located on the right-hand side.

Thus, the core certainly makes a tilt angle as large as 40° with the layer normal. Moreover, the chains may be extensively interdigitated.

The transition temperature and enthalpy changes of compounds 3 incorporating the two one-unit linking groups are listed in Table III. All the members are purely nematogenic. Miscibility studies between the octyloxy homologue and the above-mentioned reference nematogen firmly established that this mesophase is also a classical nematic one. Both the melting and clearing points in most of the members are promoted relative to those of series 1, 16 and 12°C on average, respectively. The consequence of these trends is a metastable mesophase for the last three homologous members. The enthalpy changes at the clearing point are as large as those in series 2. The high orientational order in the nematic phase may account for the difficulty in supercooling this mesophase even though the *N-I* transition is located only a few degrees below the melting point. For this reason, no reproducible enthalpy change at the *I-N* transition could be recorded for these members. Therefore, the value given in the table is the largest one recorded for each homologue.

The striking feature of the thermal data in Tables I to III is the close similarity in the trends of the *N-I* transition temperature (see Figure 2). As the molecules contain six or

TABLE III

Transition temperatures ($t/^{\circ}C$) and associated enthalpies (ΔH/kJ mol^{-1})[a] of compounds 3

n[b]	*K*	*N*	*I*
1	·257(54)	·333(---)[c]	·
2	·257(66)	·332(---)[c]	·
3	·251(66)	·319(---)[c]	·
4	·243(70)	·302(7.4)[c]	·
5	·231(69)	·282(1.4)[c]	·
6	·230(70)	·275(6.4)	·
7	·231(75)	·261(6.0)	·
8	·233(69)	·256(5.7)	·
9	·231(72)	·247(5.8)	·
10	·225(79)	·231(5.4)	·
12	·223(78)	[·221(4.7)][d]	·
14	·216(81)	[·214(5.4)][d]	·
16	·211(66)	[·209(9.3)][d]	·

[a] Values in parentheses.
[b] The number of carbon atoms in the alkyl group.
[c] Superposition with an exothermal decomposition.
[d] Monotropic transitions.

seven benzene rings and are markedly elongated, tha actual molecular shape in the nematic phase may not be very different from each other. The observed *N*-*I* transition temperatures are considerably higher than those for the formerly-studied bent or kinked molecules; that is, 229°C given by 4,5-dichloro-1, 3-phenylene bis[4-(4-ethoxybenzylideneamino)benzoate] and 213°C given by *N*,*N*′-bis[4-(4-ethoxybenzoyloxy) benzylidene]-3,3′-diaminodiphenylsulfone.[8,12] The higher transition temperature may mean that the effective molecular shape in these three series is fairly linear though it is not exactly so. Linear ring systems are known to provide a thermally more stable nematic phase even by molecules composed of only five benzene rings. For example, Vorländer reported that bis[4-(4-ethoxyphenylazo)phenyl] terephthalate melts at 240–242°C and decomposes between 340 to 348°C without clearing.[4]

Table IV presents the thermodynamic data of compounds 4 incorporating an alternative one-unit linking group. They yield no nematic phase but one or two smectic phases. The mesophases appearing at higher temperatures are denoted by S_1 and those at lower temperatures by S_2. A broken-fan shaped texture is exhibited by the former phase of the lower homologous members but no well-developed texture could be obtained by the higher members. The following observations suggest strongly that the S_1 phase is of the C type. Firstly, the X-ray diffraction patterns recorded for the S_1 phase of the propoxy to pentyloxy homologues are characteristic of the unstructured smectic phase regardless of a large variation in the S_1-*I* transition enthalpy. Secondly, the layer spacing observed for the propoxy member is as short as 2.01 nm, indicating that the molecular axis cannot be perpendicular to the smectic layer. Finally, the S_1 phase of the tetradecyloxy homologue is continuously miscible with the smectic C phase given by 1,3-phenylene bis[4-(4-tetradecyloxyphenyliminomethyl)benzoate] as is shown in Figure 3. A newly induced smectic phase covering the composition range from 38 to 96 mol% of the 1,3-phenylene compound is denoted by S_3. The broad

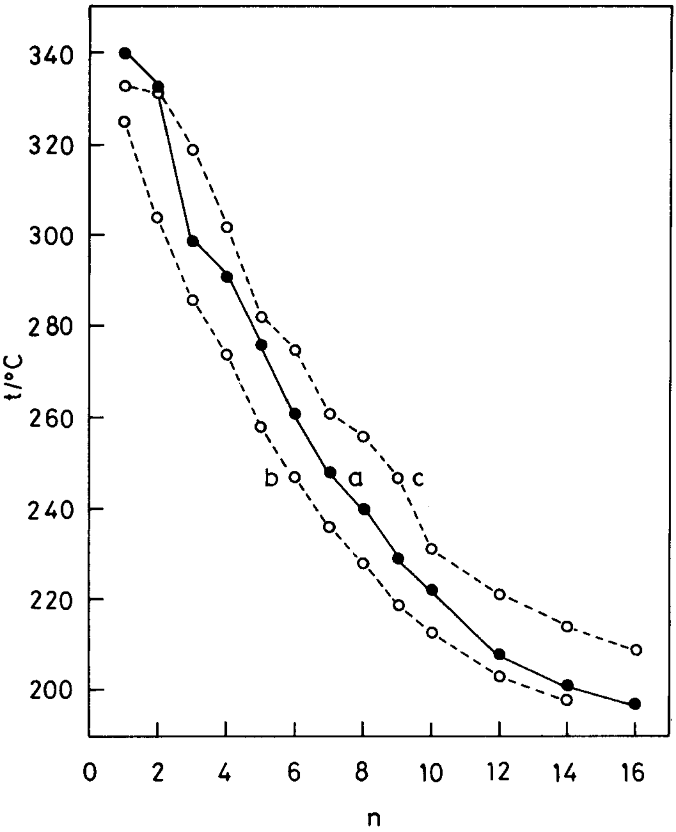

FIGURE 2 Plots of *N-I* transition temperatures against the number of carbon atoms (*n*) in the alkyl group. (a) compound 1, (b) compound 2, and (c) compound 3.

TABLE IV

Transition temperatures (t/°C) and associated enthalpies (ΔH/kJ mol^{-1})[a] of compounds 4

n[b]	K	S_2	S_1	I
1	·223(41)		·235(3.7)	·
2	·188(39)	·190(3.8)	·239(4.3)	·
3	·200(38)	·202(4.2)	·216(5.1)	·
4	·198(29)		·215(13)	·
5	·190(26)		·211(15)	·
6	·180(20)		·210(16)	·
7	·173(20)		·202(21)	·
8	·174(22)		·203(23)	·
9	·174(23)		·198(23)	·
10	·171(25)		·195(23)	·
11	·163(26)		·190(24)	·
12	·157(33)		·186(26)	·
14	·150(44)	·155(10)	·180(24)	·
16	·148(54)	·150(9.1)	·179(25)	·
18	·145(72)		·176(26)	·

[a] Values in parentheses.

[b] The number of carbon atoms in the alkyl group.

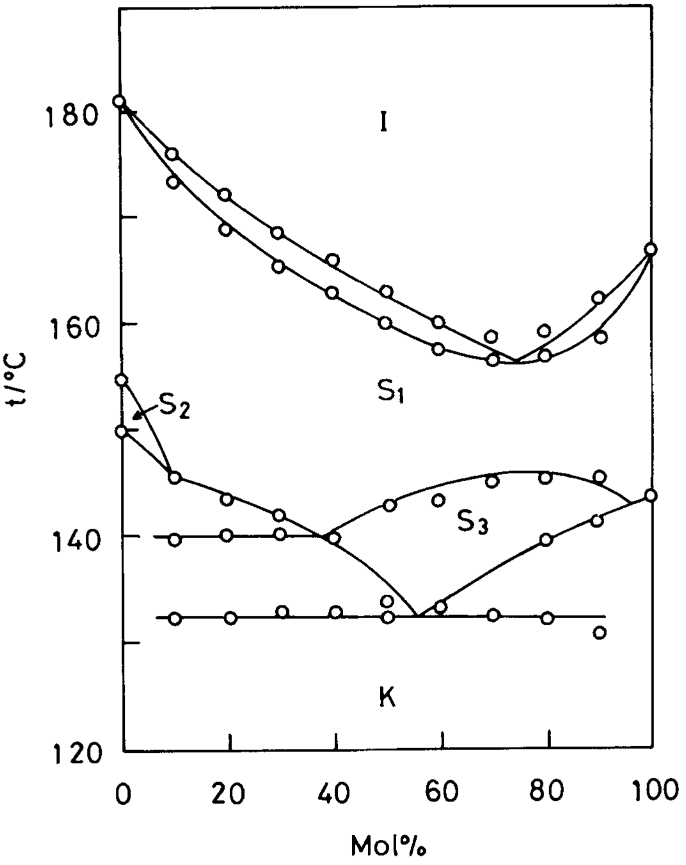

FIGURE 3 Phase diagram of the binary system consisting of the tetradecyloxy homologue of series 4 and 1,3-phenylene bis [4-(4-tetradecyloxyphenyliminomethyl) benzoate]. The latter compound is located on the right-hand side.

maximum is located at 146°C and around 80 mol%. It is noteworthy that the clearing points of these component compounds are not very different from each other, suggesting similarity in molecular configuration. The texture mentioned above is consistent with this assignment.

Comparison between the diphenyl ether and diphenylmethane derivatives reveals that the mesomorphic behavior is highly sensitive to the kind of incorporated one-unit linking group. Two major factors may be conceivable to dominate the way of molecular association. The first is geometrical; namely, bond and torsional angles at the linking group. The bond angle in an ether linkage is less than a tetrahedral one expected for the methylene linkage and so may be less favorable for liquid crystal formation. The energies of torsional motion in diphenyl ether and diphenylmethane molecules were calculated by Kendrick using the ab initio SCF method.[13] The minimum-energy conformation of the diphenyl ether molecule is found at a torsional angle of 77.0° with the barrier heights to a rotation of 31 and 14 kJ mol^{-1} through the planar and book conformations respectively, whereas that of the diphenylmethane molecule is at 115.0°

with 52 and 2 kJ mol^{-1}. Thus, the torsional potential curves suggest that the geometry of the latter molecule is more amenable to a dense molecular packing than the former.

The other major factor is the dipolar interactions between molecular cores. In connection with studies on the thermal properties of phenyl 4-(4-alkoxybenzoyloxy)-benzoates and the three isomeric series, Sakurai *et al.* demonstrated that the longitudinal component of the dipoles in the monomolecular arrangement is always repulsive.[14] Similarly, the repulsive interaction between polar C—O bonds may give rise to a lowering in the positional order. These points may be responsible for the difference in mesomorphic behavior observed for the diphenyl ether and diphenylmethane derivatives.

References

1. D. Vorländer, *Z. Phys. Chem.*, **105**, 211 (1923).
2. C. Destrade, H. Gasparoux and F. Guillon, *Mol. Cryst. Liq. Cryst.*, **40**, 163 (1977).
3. C. Destrade, H. T. Nguyen and H. Gasparoux, *Mol. Cryst. L'iq. Cryst.*, **59**, 273 (1980).
4. D. Vorländer, *Ber.*, **62**, 2831 (1929).
5. D. Vorländer and A. Apel, *Ber.*, **65**, 1101 (1932).
6. M. Kuboshita, Y. Matsunaga and H. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **199**, 319 (1991).
7. H. Matsuzaki and Y. Matsunaga, *Liq. Cryst.*, **14**, 105 (1993).
8. T. Akutagawa, Y. Matsunaga and K. Yasuhara, *Liq. Cryst.*, in press.
9. N. Hoshino, H. Murakami, Y. Matsunaga, T. Inabe and Y. Maruyama, *Inorg. Chem.* **29**, 1177 (1990).
10. A. Hassner and V. Alexanian, *Tetrahedron Lett.*, 4475 (1978).
11. D. Demus, S. Diele, S. Grande and H. Sackmann, "*Advances in Liquid Crystals*," Vol. 6, ed. by G. H. Brown, Academic Press, New York (1983) p. 65.
12. Y. Matsunaga and T. Yuri, *Mol. Cryst. Liq. Cryst.*, **237** 145 (1993).
13. J. Kendrick, *J. Chem. Soc. Faraday Trans.*, **86**, 3995 (1990).
14. Y. Sakurai, S. Takenaka, H. Miyake, H. Morita and T. Ikemoto, *J. Chem. Soc. Perkin Trans.* II, **86**, 3429 (1990).