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Liquid crystalline properties of dissymmetric molecules
IX. The effect of a terminal nitro group on the thermal properties of the smectic A phase in 4-nitrophenyl 4-(4-alkoxybenzoyloxyphenyl)benzoates†

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This paper describes the effect of alkoxy chain length on the physico-chemical properties of 4-nitrophenyl 4-(4-alkoxybenzoyloxyphenyl)benzoates. The homologous series shows a smectic A (SmA) phase commencing from the hexyloxy homologue. While the pentyloxy homologue shows only a nematic (N) phase under microscopic observation, X-ray diffraction shows that the N phase has a cybotactic domain with a layer structure of the SmA phase, where the layer spacings are longer than the calculated molecular lengths by *c.* 2 Å. The layer spacings for the heptyloxy–nonyloxy homologues are longer than the calculated molecular lengths by 2.2–4.8 Å and are almost independent of temperature. The layer spacings are correlated with the calculated molecular lengths, and based on these results, a new molecular arrangement model for the SmA phase is proposed.

1. Introduction

A clarification of the molecular arrangement or the layer structure in smectic A (SmA) and smectic C (SmC) phases is a current interest in the liquid crystal field in connection with the ferroelectric properties of liquid crystal (LC) materials. The SmA and SmC phases have been divided into several kinds according to the characteristics of their molecular arrangements, for example, $\mathrm{SmA_1}$, $\mathrm{SmA_d}$, $\mathrm{SmA_2}$, etc, together with the corresponding SmC phases [1–3].

In most LC materials having hydrocarbon chains at both terminal positions of the LC core, the molecular arrangement in the SmA phase has been considered to have a monolayer arrangement of molecules, where the layer spacing almost agrees with the fully extended molecular length; this phase is defined as the $\mathrm{SmA_1}$ phase. On the other hand, so-called polar LC materials, having polar terminal substituents such as a nitro or a cyano group, have been known to form antiparallel dimers due to strong polar interaction and show complicating polymesomorphisms involving SmA and nematic (N) phases. The SmA phase having a layer spacing of 1.0–1.4 times the fully extended molecular length is classified as the $\mathrm{SmA_d}$ modification. Polar LC materials having a layer spacing of twice the fully extended molecular length also form the $\mathrm{SmA_2}$ phase. Strictly speaking, however, the layer spacing is usually less than twice the fully extended molecular length.

In the aromatic ring systems 4-cyano-4′-octyloxybiphenyl (8OCB) and 4-cyanobenzylidene-4-octyloxyaniline (CBOOA), the molecules have been supposed to form antiparallel dimers due to a strong dipole–dipole interaction at the terminal position of the LC core, and the dimers facilitate the appearance of the $\mathrm{SmA_d}$ phase. In these cases, the layer spacings of the $\mathrm{SmA_d}$ phase are close to 1.4 times the molecular length. From these results, the molecular arrangement model shown in figure 1 has been postulated. In the smectic layer most of the aromatic moieties involving the cyano group are considered to be arranged side by side [4].

As mentioned in our earlier paper [5], many LC materials consisting of three aromatic rings with dissymmetrically substituted terminal groups such as halogens, trifluoromethyl, trifluoromethoxy, thiocyanato, etc. tend

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†For part VIII see Wu, J., Okamoto, H., Morita, Y., and Takenaka, S., Liquid Crystalline Properties of Dissymmetric Molecules Part 8: The Effect of Conformation on the Mesomorphic Properties for Liquid Crystal Compounds Having a Lateral Long Alkoxyl Group, *Bull. Chem. Soc. Jpn*, 2001, **74** (12), 2437–2443.

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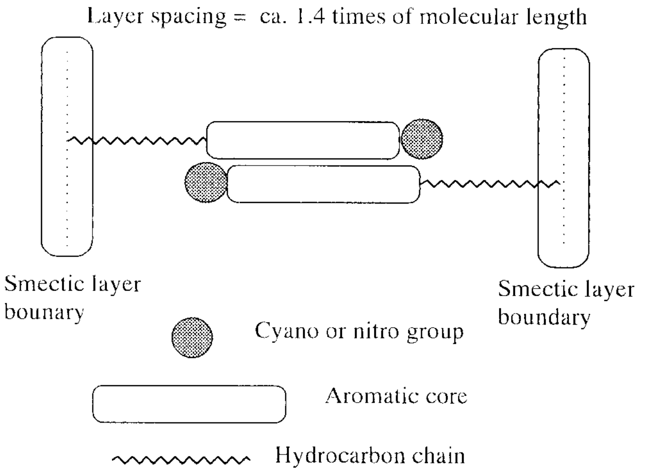


Figure 1. Molecular arrangement model for the SmA$_d$ phase of 4-cyanobiphenyl and 4-cyanobenzylideneaniline compounds [4].

to exhibit preferentially the SmA phase, where the layer spacings are a little greater than the calculated molecular lengths. The SmA phase layer spacings are 2–3 Å longer than the fully extended molecular lengths of these compounds, so the SmA phase may be classified as SmA$_d$. In that paper we supposed that the phase separation or the coherence of the terminal substituents around the boundary of the smectic layer is important for the appearance and stabilization of the SmA$_d$ phase, and we postulated a new molecular arrangement model shown in figure 2.

We consider that the coherence of the substituents is an intrinsic property of dissymmetrically substituted compounds, and that the layer structure is intrinsic in dissymmetric LC materials, so that a similar layer structure should be present in polar LC materials having a terminal nitro or a cyano group. In order to confirm this model, we have examined the smectic properties of the homologous members of the 4-nitrophenyl 4-(4-alkoxybenzoyloxy) benzoate series (**1**). In this paper, we describe the thermal properties and layer structures of the SmA phase of the homologous members of series **1**, and our smectic model is extended to the layer structure of polar LC materials. Some related compounds having a terminal nitro group have already been prepared, and their smectic properties examined [6–23].

2. Experimental

2.1. *Materials*

The materials were obtained by esterification of 4-(4-nitrophenoxycarbonyl)phenol with the required 4-alkoxybenzoic acids according to the conventional method [24]. The purity of the materials was checked by elemental analysis, HPLC with ODS column, and ^{1}H NMR spectroscopy.

2.2. *Characterization*

The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC, with indium (99.9%) as calibration standard (m.p. = 156.6°C, 28.4 J g^{-1}). The DSC thermogram was operated at a heating or a cooling rate of 5°C min^{-1}. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900), with temperatures calibrated with benzoic acid (m.p. = 122.4°C).

X-ray diffraction (XRD) experiments for the smectic phases were performed using a Rigaku denki RINT 2200 diffractometer, with CuK$_\alpha$ ($\lambda = 1.541$ Å) as the X-ray

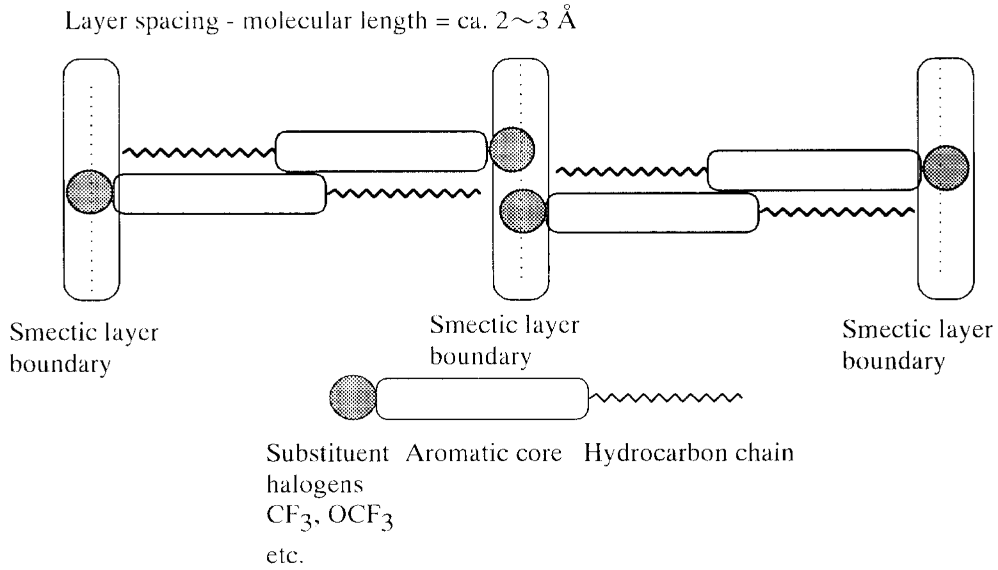
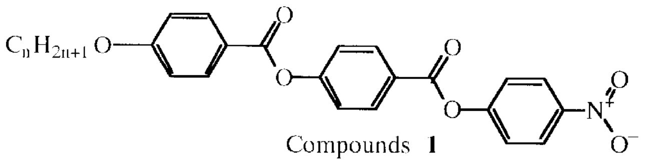


Figure 2. Molecular arrangement model for the SmA phase of dissymmetrically substituted three-aromatic-ring systems [5].



Compounds **1**

Figure 3. Chemical structure of compounds **1**.

source. The reflection angle was calibrated by a comparison of both right and left angles. The temperature was controlled using a Rigaku PTC-20A thermo-controller. The samples filled in the quartz capillaries ($\phi = 1.5$ mm) were oriented by a constant magnetic field (480 G). The samples were placed along the goniometric axis so that the counter movement in the recording plane allowed us to scan the nematic and smectic reciprocal lattice mode along q ($q = 2p/d$ is the reciprocal space vector), i.e. in the direction parallel to the director **n**. The samples were heated to the isotropic temperature, and rapidly cooled below 190°C, since the sample sometimes decomposed, resulting in the appearance of plural reflection peaks in the profile. X-ray profiles were taken during cooling.

The molecular orbital parameters referenced in this paper were obtained by a semiempirical molecular orbital calculation (CS Chem 3D Pro Version 4.0), where minimization of the total energy was achieved by an AM1 method.

3. Results and discussion

3.1. *Thermal properties*

The phase transition behaviour for the homologues is summarized in the table, and the transition temperatures are plotted against the number of alkoxy chain carbon atoms in figure 4. The N phase is formed by the earlier homologues and the N–I (isotropic) transition temperature gradually reduces on ascending the series. Occurrence of the SmA phase commences from the hexyloxy homologues, and the SmA–N or I transition temperature steeply increases on ascending the series. The SmA phase shows a focal-conic fan and isotropic textures under homogeneous and homeotropic alignments, respectively. Under microscopic and thermal examination, the homologues show no LC phase other than N and SmA. For the pentyloxy homologue, the SmA phase was not observed even with rapid cooling of the N phase. The smectic properties of the pentyloxy homologue were further examined with binary phase diagrams; the results are shown in figure 5.

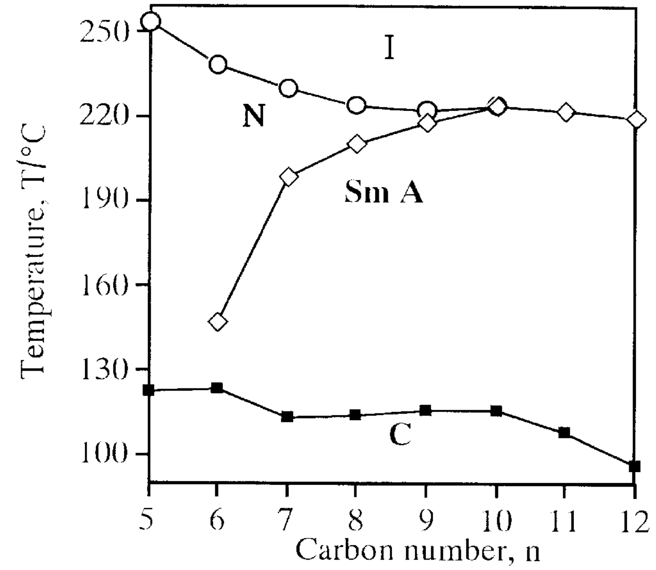


Figure 4. Plots of transition temperature against carbon number, n, for compounds **1**.

For the mixture of the pentyloxy homologue of **1** and 4-(4-butoxyphenoxycarbonyl)phenyl 4-octyloxybenzoate (**2**) [25] in figure 5(*a*), the SmA–N transition temperature shows an upward convexity around the centre of the diagram and steeply decreases on approaching the

Table. Physicochemical properties for compounds **1**. Cr, SmA, N, and I indicate crystal, smectic A, nematic, and isotropic phases, respectively.

	Transition temperatures/°C								Layer spacing (d)[a] and molecular length (l)[b]/Å		
n	Cr		SmA		N		I		*d*	*l*	*d-l*
5	•	123	—		•	254	•		28.0	25.8	2.2
6	•	124	•	147	•	238	•		29.5	27.0	2.5
7	•	113	•	198	•	230	•		31.4	28.2	3.2
8	•	114	•	210	•	224	•		33.2	29.5	3.7
9	•	116	•	218	•	222	•		34.9	30.8	4.1
10	•	116	•	224	•	224	•		36.6	32.0	4.6
11	•	108	•	222	—		•		38.0	33.2	4.8
12	•	96	•	220	—		•		39.1	34.4	4.7

[a] The values were taken at low temperature region.
[b] The longitudinal length for the most linear and stable conformation calculated by MOPAC97.

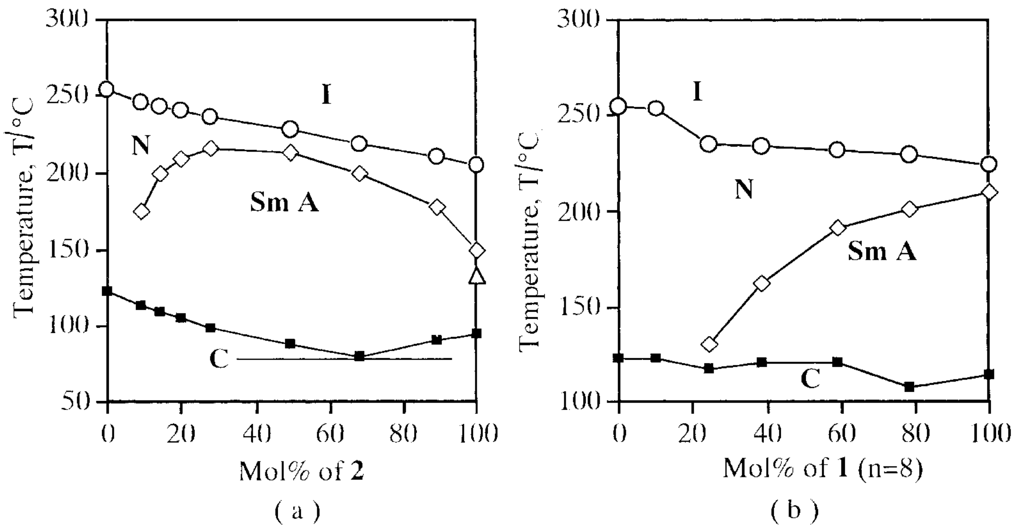


Figure 5. Phase diagrams for the mixtures of: (*a*) 4-(4-butoxyphenoxycarbonyl)phenyl 4-octyloxybenzoate (**2**) (on right) and the pentyloxy homologue of **1** (on left); (*b*) octyloxy homologue (on right) and pentyloxy homologues (on left) of **1**.

pentyloxy homologues. It is known that many binary LC mixtures consisting of so-called 'non-polar' and 'polar' LCs show a notable enhancement of SmA thermal stability or an induction of the SmA phase. In figure 5 (*a*), the components correspond to a polar and non-polar LC pair. In these phenomena, dipole–dipole and electron donor–accepter interactions are considered to play important roles [26–31]. The characteristic feature of figure 5 (*a*) may be influenced by these specific interactions between the two components.

Figure 5 (*b*) shows the phase diagram for a mixture of the pentyloxy and octyloxy homologues of **1**, where the SmA–N transition temperature decreases with increasing the concentration of the pentyloxy homologue, and disappears around the centre of the diagram. These results suggest that the pentyloxy homologue does not readily form an SmA type layer structure, while chain elongation causes a rapid increase in SmA thermal stability. Therefore, the difference in the chain length between pentyloxy and octyloxy homologues strongly affects the layer formation.

3.2. *X-ray diffraction*

The mesophases were further characterized by XRD. Although the pentyloxy homologue shows only an N phase, the X-ray profile shows a broad reflection around

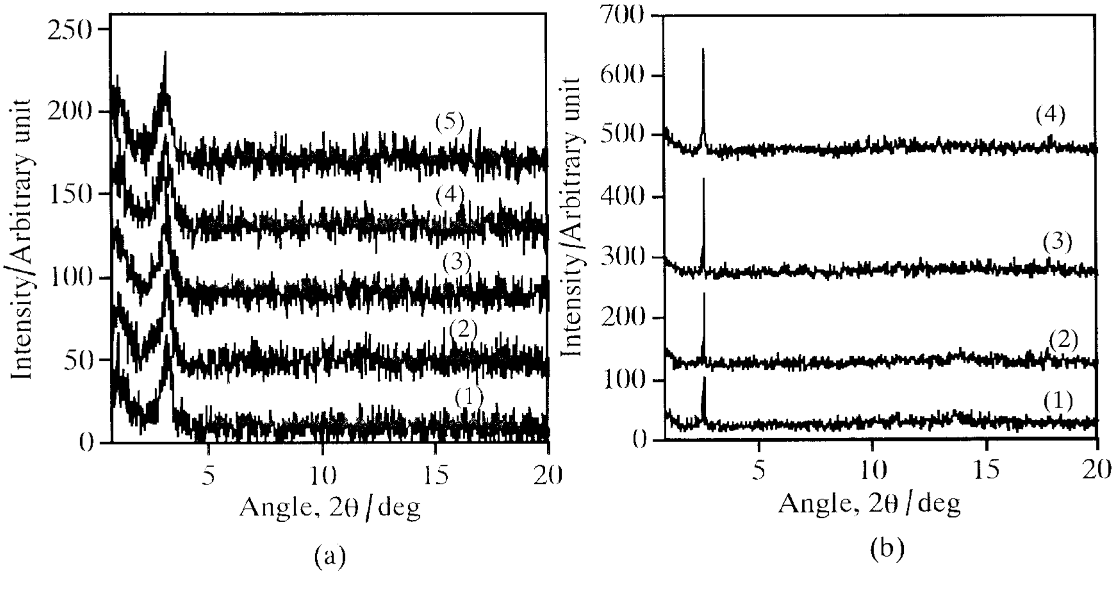


Figure 6. X-ray profiles for: (*a*) the pentyloxy homologue of **1** at: (1) 148, (2) 138, (3) 135, (4) 130, and (5) 125°C; (*b*) the nonyloxy homologue of **1** at: (1) 182, (2) 162, (3) 142, and (4) 122°C.

$2\theta = 2^\circ$–3° arising from the d_{001} direction, as well as a broad one around $2\theta = 20^\circ$, as shown in figure 6 (*a*). In figure 6 (*a*) the reflection peak arising from the d_{001} direction is observed over the whole range of the N phase, and the maximal position and the intensity are almost independent of temperature. The reflection maximum was calculated to be 28.0 Å at 90°C and 28.1 Å at 140°C. This suggest that the N phase consists of a layer structure similar to the SmA phase.

For the profile for the nonyloxy homologue in figure 6 (*b*), on the other hand, the reflection peak arising from the d_{001} direction is intense and sharp. The temperature dependency of the reflection peak for the nonyloxy homologue is again negligible. The layer spacings calculated from the d_{001} peak are 34.9, 35.2, 35.7, and 35.7 Å at 122, 142, 162, and 182°C, respectively.

The temperature dependences of the layer spacings for compounds **1** are shown in figure 7. The plots appear to be continuous in the whole range. Although the layer spacings for the homologues tend to increase with rising temperature, the change is small. Ratna *et al.* reported that the layer spacing for the SmA phase of the hexyloxy homologue shows the same variation as in figure 7; the SmA phase was therefore assigned the SmA$_d$ modification [17].

Minimum layer spacings for compounds **1** are plotted against carbon number in figure 8, in comparison with reference compounds **2**–**5**, whose structures are shown in figure 9. In figure 8 the molecular lengths for the most stable conformation were calculated by an AM1 method (MOPAC); results are summarized in the table. For the comparative consideration, the layer spacings for the homologous members of compounds **2** and **3**, and cyanobiphenyl compounds **4** and **5**, are plotted in figures 8 (*b*) and 8 (*c*), respectively [32].

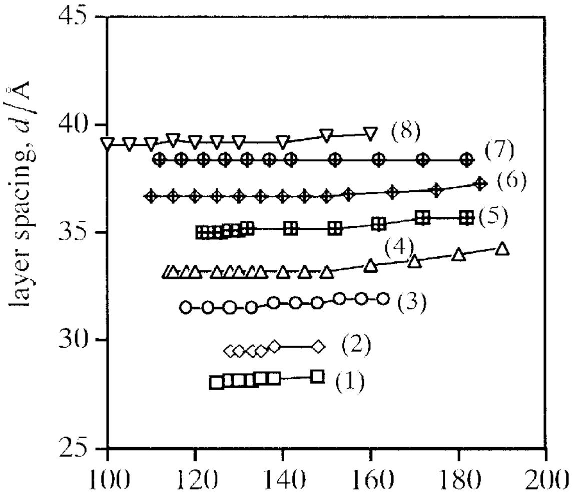


Figure 7. Plots of layer spacings (d) vs. temperature for (1) pentyloxy, (2) hexyloxy, (3) heptyloxy, (4) octyloxy, (5) nonyloxy, (6) decyloxy, (7) undecyloxy, and (8) dodecyloxy homologues of **1**.

Compounds **2** and **3** show the SmA phase from the ethoxy and pentyloxy homologues, respectively; the SmA–N(I) transition temperatures are high and almost independent of the carbon chain length [31]. The observed layer spacings for compounds **2** and **3** are linear against the carbon number, and almost parallel to the calculated molecular lengths. If the average hydrocarbon chain axis is orthogonal to the smectic layer, the layer spacing is expected to increase by 1.24 Å per methylene unit (1.51 sin(111.5°/2), where 1.51 Å and 111.5° are the C–C bond length and C–C–C bond angle of the hydrocarbon chain, respectively). Moreover, in such a condition, the plot of layer spacing vs. carbon number is not expected to show the so-called 'even–odd alternation.' The slope for the observed layer spacing for **2** is 1.20 Å per methylene unit and the plot does not show the even–odd alternation. The good agreement of the value with the calculated one suggests that the terminal hydrocarbon chain arranges almost orthogonal to the SmA layer. On the other hand, the slope of 1.10 Å per methylene unit for **3** is a little smaller, and the plot shows a weak even–odd alternation in the higher homologues. Therefore, it would be reasonable to deduce that the average axis of the terminal hydrocarbon chain tilts a little with respect to the smectic layer. For compounds **2** and **3**, the average differences between the observed layer spacings and calculated molecular lengths are calculated to be 2.31 and 2.25 Å, respectively. The excess layer lengths are close to the longitudinal length of the trifluoromethyl group (2.44 Å). These results indicate that the terminal trifluoromethyl groups cohere around the smectic layer boundary, and the molecules form the SmA$_d$ structure, as shown in figure 2.

In figure 8 (*c*) the layer spacings of the SmA$_d$ phase are plotted for the 4-alkoxy-4′-cyanobiphenyls and the alkyl derivatives reported by Leadbetter *et al.*, together with the molecular lengths calculated in this work [33]. Of course, the slopes for the calculated molecular lengths are 1.24 Å per methylene unit. Interestingly, the slopes for the alkoxy and alkyl compounds, **4** and **5**, are 2.40 and 2.00 Å per methylene unit, and the difference between the layer spacings and calculated molecular lengths are 8.6, 9.7, and 13.4 Å for the octyloxy, decyloxy, and dodecyloxy homologues, respectively. In compounds **4** and **5** the core length between the ether oxygen and nitrogen atom of the cyano group is 11.0 Å in our calculation. Based on these results, the molecular arrangement in figure 1 has been postulated. In this connection, some cyanobiphenyl compounds have been known to show a notable change in crystal structure due to a subtle change in the alkoxy and alkyl chain lengths [34]; STM

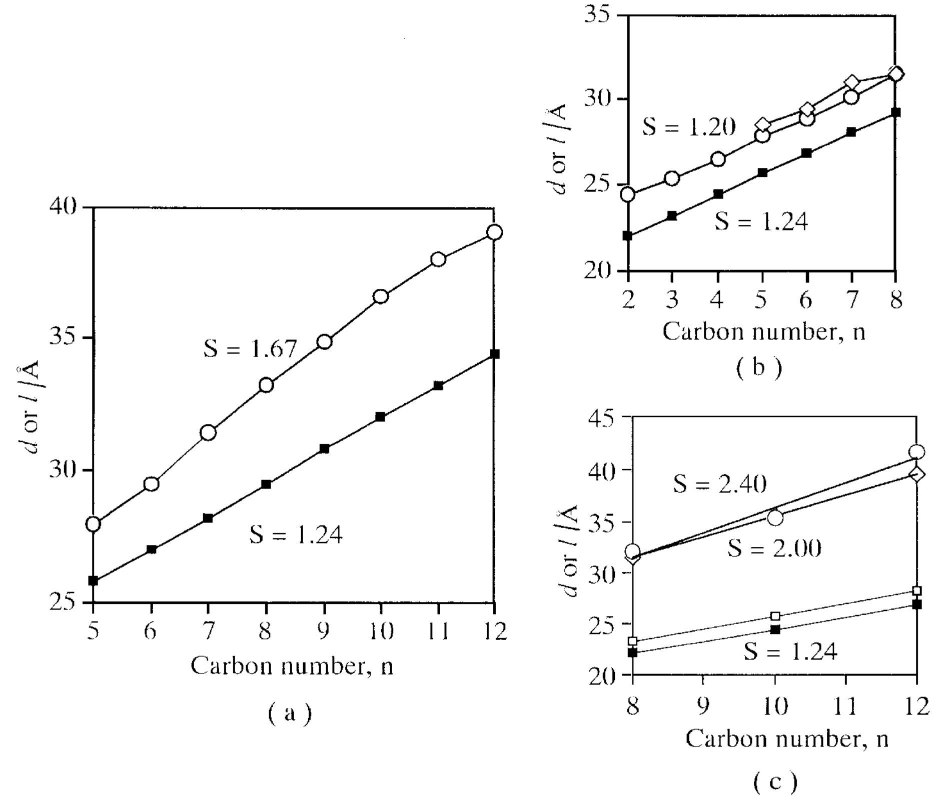


Figure 8. Plots of layer spacings (○ or ◇) and molecular lengths (■ or □) vs. the carbon number, *n*, for (*a*) **1**, (*b*) **2**(○) and **3**(◇), and (*c*) **4**(○) and **5**(◇).

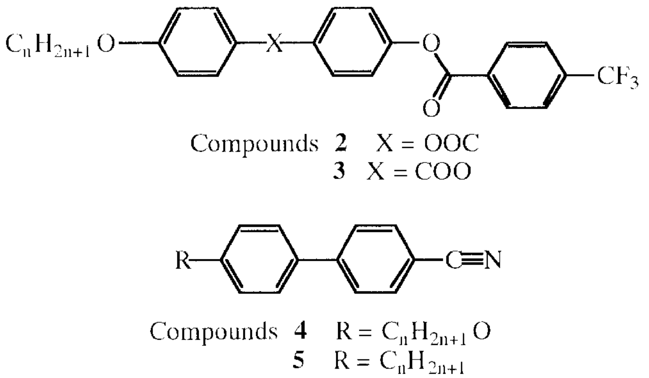


Figure 9. Molecular structures of compounds **2**–**5**.

measurement showed a similar change in molecular arrangement on a MoS surface [35] and graphite surface [36].

On the other hand, as shown in figure 8(*a*), the plot for compounds **1** shows a different tendency from those for **2** and **3**, and **4** and **5**. The difference between the layer spacings and the calculated molecular lengths are 2.2–3.7 Å for the pentyloxy–octyloxy homologues. The values are close to the longitudinal length of the nitro moiety (*c*. 2.5 Å in our calculation). These tendencies are quite similar to those for **2** and **3**. However, the plot for the layer spacings appears to curve subtly, and the slope (1.67 Å per methylene unit) is different from those for **2**–**5**.

As mentioned above, the N phase of the pentyloxy homologue has a layer structure like the SmA phase, so that the correlation length ζ, defined by:

$$\zeta = \lambda/\theta \fallingdotseq \lambda/\sin\theta$$

(where λ and θ are the wavelength of the X-ray and the half width of the reflection peak, respectively), was calculated; the temperature dependency for the pentyloxy and hexyloxy homologues is shown in figure 10.

Although the pentyloxy homologue has a cybotactic domain with the layer structure similar to the SmA phase, the correlation length is quite short compared with that for the nonyloxy compound. For the plot of the hexyloxy homologue, the correlation length becomes longer with decreasing temperature. These results indicate that the layer structure of the SmA-like phase in the N phase of the pentyloxy homologue is very short range compared with those for the other homologues.

3.3. *Layer structure of the SmA phase*

In our earlier paper [5], we reported that the layer spacing of the SmA phase for **3** and **4** is *c*. 2 Å longer than the calculated molecular length, see figure 8(*b*); a

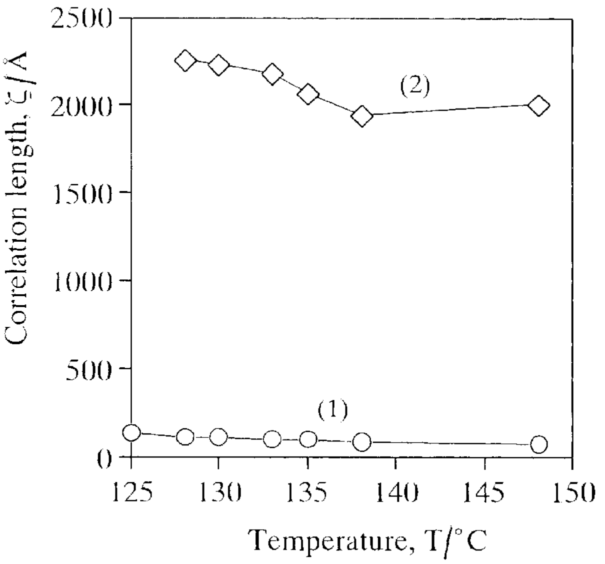


Figure 10. Temperature dependency of correlation length ζ for: (1) pentyloxy and (2) hexyloxy homologues of **1**.

new model for the molecular arrangement in the SmA phase was proposed, as shown in figure 2. In the model, a fluorophilic or polar interaction around the boundary of the smectic layer was considered to be important for the formation of the stable layer structure. As we can see from the comparison of figures 8 (*a*) and 8 (*b*), the slopes of the plots for **1** and **2**/**3**, and the difference between the layer spacings and calculated molecular lengths, are similar to each other, indicating that the layer structures of the SmA phase for **1** and **2**/**3** are similar. Based on the model structure in figure 2, the extended model for compounds **1** is shown in figure 11.

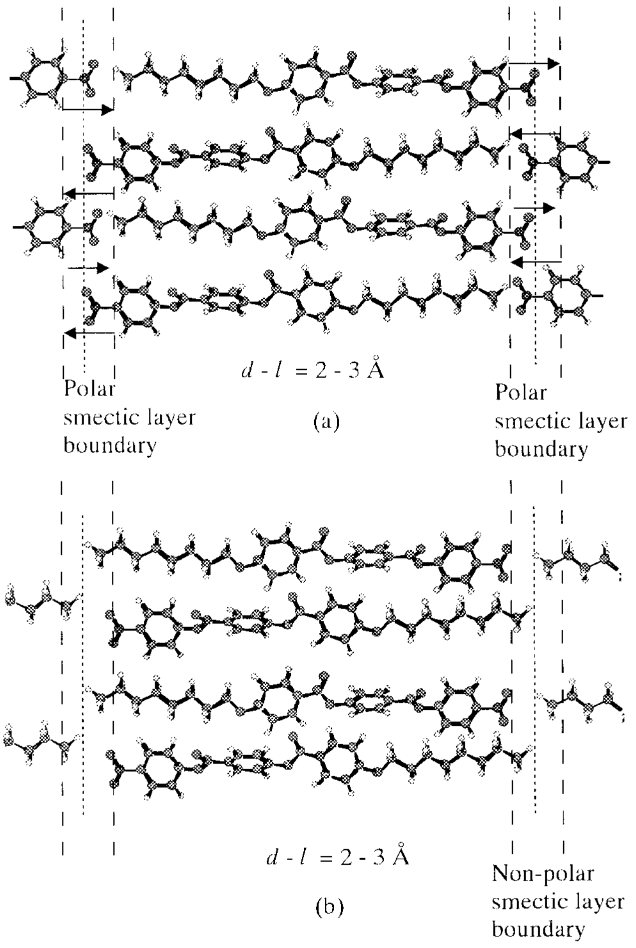


Figure 11. Molecular arrangement models for the SmA phase of **1**.

For LC materials having a polar substituent such as a cyano or nitro group, antiparallel dimers are considered to form in LC phases, where the polar interaction involving the dipoles plays a significant role [1–3]. In our earlier paper, we showed that 4-(2-perfluoroalkylethoxy)-nitrobenzenes exhibit SmA and SmB phases, where the layer spacings are 2–5 Å longer than the calculated molecular length, and are sometimes *c*. twice as long [37]. In the molecular arrangement models, we supposed that the nitro or the nitrobenzene groups cohere and overlap side by side around the layer boundary, and the strong dipole–dipole interaction at a close range is connected with the formation of dimers. The molecular arrangement models shown in figures 11 (*a*) and 11 (*b*) are modified from the arrangement model for 4-(2-perfluoroalkylethoxy)nitrobenzenes. The model in figure 11 (*a*) is similar to that for **2**, where the nitro groups cohere and overlap side by side around the smectic layer boundary. Probably, the difference between the layer spacing and the calculated molecular length 2.6 Å on average, corresponds to the longitudinal length of the nitro group (2.3 Å). In such conditions, the interlayer dipole–dipole interaction may facilitate dimer formation and stabilize the layer structure. In the model, the distance between nitro groups may be determined by the balance between attractive dipole–dipole interaction and charge repulsion on the nitro group. A similar dimer model has been postulated for some LC materials having a terminal cyano group [38, 39].

In the other model shown in figure 11 (*b*), the terminals of the hydrocarbon chains cohere around the layer boundary and cover it, so that the layer boundary is a hydrophobic sphere, and nitrobenzene moieties are covered with the hydrocarbon chains. Under such conditions stabilization of the layer structure by polar interaction around the nitro groups or dimer formation may not be expected. Therefore, the model in figure 11 (*a*) is more suitable for dimers in the SmA and N phases and probably in the isotropic liquid. The dimer structure is probably present in the N and I phases of the lower homologues, where the dimers do not readily form a layer structure. For the SmA phase of the higher homologues, the layer spacings are 3.7 Å longer than the calculated molecular lengths. Therefore, we assume that in the SmA phase not only the nitro group but also a part of the nitrobenzene moiety overlap side by side around the layer boundary, due to strong dipole–dipole interaction around the nitrobenzene moieties.

In compounds **4** and **5**, and CBOOA the model arrangement in figure 1 has been proposed, where the aromatic moieties overlap side by side, and the ratios of the layer spacings to the calculated molecular lengths are *c.* 1.4. However, this model may not be applicable to the present compounds. One reason is that a layer structure having a spacing of 1.4 times the molecular length is hardly formed in the present compounds. The other is that the nitro groups or the nitrobenzene groups in the model are so far apart (*c.* 10 Å) that the dipole–dipole interaction arising from the nitro or nitrobenzene group should be less effective than that in figure 11 (*b*). If the dimers shown in figure 2 are strongly associated by the dipole–dipole interaction we can additionally expect that the layer spacing should increase by 2.4 Å per methylene unit (twice 1.2 Å), as shown in figure 8 (*c*). In practice, the layer spacing increases by 1.7 Å per methylene unit, as shown in figure 8 (*a*). There is no doubt that, however, some LC materials having a terminal nitro or cyano group exhibit the $\mathrm{SmA_d}$ phase with a long layer spacing, 1.4 times the molecular length [13, 40]. This layer structure appears to be more common in two-aromatic-ring systems such as cyanobiphenyl and cyanobenzylideneaniline compounds [7, 41, 42].

4. Conclusion

Compounds **1** exhibit the SmA phase commencing from the hexyloxy homologue, where the layer spacing is *c.* 2.2–4.8 Å longer than the calculated molecular lengths. The pentyloxy homologues has a cybotactic domain of the SmA phase in the N phase. In the SmA phase the interlayer dipole–dipole interaction is considered to play an important role in complex formation. Taking the dipole–dipole interaction around the terminal nitro group into consideration, new models for the SmA phase are proposed. The overlap of the aromatic moieties depends not only on polar interaction around the nitro and ester groups but also on the entire molecular shape.†

References

[1] Levelut, A. M., Tarnto, R. J., Hardouin, F., Achard, M. F., and Sigaud, G., 1981, *Phys. Rev. A*, **24,** 2180.

[2] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals* (Philadelphia: Heyden), p. 134.

[3] Goodby, J. W., 1998, *Handbook of Liquid Crystals*, Vol. 2A, edited by D. Demus (Weinheim: VCH), p. 3.

[4] Cladis, P. E., 1998, *Liq. Cryst.*, **24,** 15 and references cited therein.

[5] Duan, M., Tasaka, T., Okamoto, H., and Takenaka, S., 2000, *Liq. Cryst.*, **27,** 1195.

[6] Galewski, Z., and Sobczyk, L., 1982, *Mol. Cryst. liq. Cryst.*, **88,** 81.

[7] Cladis, P. E., Guillon, D., Daniels, W. B., and Griffin, A. C., 1980, *Mol. Cryst. liq. Cryst. Lett.*, **64,** 93.

[8] Cladis, P. E., Guillon, D., Daniels, W. B., and Griffin, A. C., 1979, *Mol. Cryst. liq. Cryst. Lett.*, **56,** 89.

[9] Dewar, M. J. S., and Goldberg, R. S., 1970, *J. org. Chem.*, **35,** 2711.

[10] Schroeder, D. C., and Schroeder, J. P., 1976, *J. org. Chem.*, **41,** 2566.

[11] Hardouin, F., Sigaud, G., Nguyen, H. T., and Achard, M. F., 1981, *J. Phys.*, **42,** L-63.

[12] Hardouin, F., Nguyen, H. T., Achard, M. F., and Levelut, A. M., 1982, *J. Phys.*, **43,** L-327.

[13] Madhusudana, N. V., Srikanta, B. S., and Subamanya Raj Urs, M., 1982, *Mol. Cryst. liq. Cryst. Lett.*, **82,** 25.

[14] Nguyen, H. T., Hardouin, F., and Destrade, C., 1982, *J. Phys.*, **43,** 1127.

[15] Nguyen, H. T., Gasparoux, H., Malthete, J., and Destrade, C., 1984, *Mol. Cryst. liq. Cryst.*, **114,** 19.

[16] Shashidhar, R., Ratna, B. R., and Krishna Prasad, S., 1984, *Mol. Cryst. liq. Cryst. Lett.*, **102,** 105.

[17] Ratna, B. R., Krishna, S., Shashidhar, P. R., Hepple, G., and Pfeiffer, S., 1985, *Mol. Cryst. liq. Cryst.*, **124,** 21.

[18] Shadhidhar, R., Ratna, B. R., Surendranath, V., Raja, V. N., Krishna Prasad, S., and Nagabhushan, C., 1985, *J. Phys. Lett.*, **46,** L-445.

[19] Nguyen, H. T., Babeau, A., and Destrade, C., 1986, *Mol. Cryst. liq. Cryst. Lett.*, **3,** 69.

[20] Fontes, E., Heiney, P. A., Haseltine, J. L., and Smith, III, A. B., 1986, *J. Phys.*, **47,** 1533.

[21] Takenaka, S., Sakurai, Y., Takeda, H., Ikemoto, T., Miyake, H., Kusabayashi, S., and Takagi, T., 1990, *Mol. Cryst. liq. Cryst.*, **178,** 103.

[22] Sakurai, Y., Takenaka, S., Sugiura, H., and Kusabayashi, S., 1991, *Mol. Cryst. liq. Cryst.*, **201,** 95.

[23] Nounesis, G., Blum, K. I., Young, M. J., Garland, C. W., and Birgeneau, R. J., 1993, *Phys. Rev. E*, **47,** 1910.

[24] Okamoto, H., Umeda, A., and Takenaka, S., 1998, *Mol. Cryst. liq. Cryst.*, **317,** 111.

[25] Tasaka, T., Okamoto, H., and Takenaka, S., *Liq. Cryst.* (in the press).

[26] Schoeder, J. P., and Schroder, D. C., 1968, *J. org. Chem.*, **33,** 591.

[27] Dave, J. S., Patel, P. R., and Vasanth, K. L., 1969, *Mol. Cryst. liq. Cryst.*, **8,** 93.

[28] Park, J. W., Bak, C. S., and Labes, M. M., 1975, *J. Am. chem. Soc.*, **97,** 4398.

[29] Marcos, M., Melenoez, E., Ros, M. B., and Serrano, J. L., 1989, *Mol. Cryst. liq. Cryst.*, **167,** 239.

[30] Demus, D., Hauser, A., Pelzl, G., Bottger, V., and Schonburg, S., 1985, *Cryst. Res. Technol.*, **20,** 381.

[31] Araya, K., and Matsunaga, Y., 1981, *Mol. Cryst. liq. Cryst.*, **67,** 153.

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† The effect of ester groups on layer structure will be the subject of a future publication.

[32] DUAN, M., OKAMOTO, H., PETROV, V. F., and TAKENAKA, S., 1999, *Liq. Cryst.*, **26,** 737.

[33] LEADBETTER, A. J., FROST, J. C., GAUGHAN, J. P., GRAY, G. W., and MOSLEY, A., 1979, *J. Phys.*, **40,** 375.

[34] KURIBAYSHI, M., and HORI, K., 1999, *Liq. Cryst.*, **26,** 809.

[35] HARA, M., IWAKABE, Y., TOCHIGI, K., HASEBE, H., GARITO, A. F., and YAMADA, A., 1990, *Nature*, **344,** 228.

[36] SMITH, D. P. E., HORBER, J. K. H., BINNIG, G., and NEJOH, H., 1990, *Nature*, **344,** 641.

[37] DUAN, M., OKAMOTO, H., PETROV, V. F., and TAKENAKA, S., 1999, *Bull. chem. Soc. Jpn.*, **72,** 1637.

[38] CHIN, E., and GOODBY, J. W., 1986, *Mol. Cryst. liq. Cryst.*, **141,** 311.

[39] MADHUSUDANA, N. V., RAGHUNATHAN, V. A., and SUBRAMANYA RAJ URS, M., 1984, *Mol. Cryst. liq. Cryst.*, **106,** 161.

[40] PETROV, V. F., TASAKA, T., OKAMOTO, H., and TAKENAKA, S., 2000, *Mol. Cryst. liq. Cryst.*, **338,** 11.

[41] ENGELEN, B., HEPPKE, G., HOPP, R., and SCHENEIDER, F., 1979, *Mol. Cryst. liq. Cryst. Lett.*, **49,** 193.

[42] LEADBETTER, A. J., FROST, J. C., GAUGHAN, J. P., GRAY, G. W., and MOSLEY, A., 1979, *J. Phys.*, **40,** 375.