Intermolecular Interactions in Crystal Structures of Isomeric Mesogens with Two Ester Linkages

Kyoko Tamura and Kayako Hori*

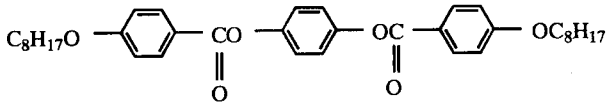
Graduate School of Humanities and Sciences, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112-8610

(Received October 25, 1999)

In order to make clear the influence of more than one polar group on packing modes of molecules and hence on liquid crystalline behavior, crystal structures have been determined for five mesogens with a general formula, $C_nH_{2n+1}O$–C_6H_4–X–C_6H_4–Y–C_6H_4–OC_mH_{2m+1}: **I** (n = m = 8, X = COO, Y = OCO), **II** (n = m = 8, X = OCO, Y = COO), **VI** (n = 8, m = 1, X = COO, Y = OCO), **V** (n = 8, m = 1, X = OCO, Y = COO), and **VI** (n = 8, m = 1, X = OCO, Y = OCO). Two symmetrical molecules **I** and **II**, in which the dipole moments cancel, have quite different crystal packings. Compounds **II** and **V** with the same core (the moiety except for chains) have similar packing modes in spite of different chain lengths. These facts are interpreted in terms of two factors: overlappings of planar moieties in cores, formed by the conjugation of a benzene ring with the attached ester linkage(s), and dipole–dipole interaction of polar groups. The crystal structures are closely related to the liquid crystalline phase sequences: imbricated structures (half-and-half overlapping of molecules) to the nematic character and smectic-like layer structures with the smectic one.

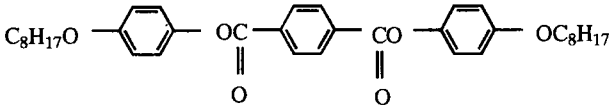
Different arrangements of two or more polar groups in a molecule have a significant influence on liquid crystalline behavior. Thus compounds with different directions of two ester linkages have mesophase sequences as shown:[1]

p-phenylene bis(4-octyloxybenzoate) (**I**)



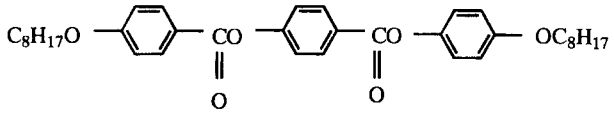
cryst.-122–Sm C–126-nem.–194–iso. (in °C)

bis(4-octyloxyphenyl) terephthalate (**II**)



cryst.-144–Sm C–180–Sm A–183-nem.–194–iso.

4-octyloxyphenyl 4-(4-octyloxybenzoyloxy)benzoate (**III**)

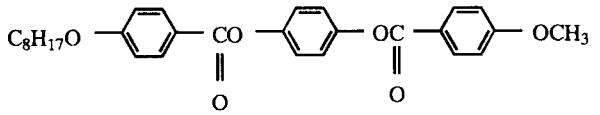


cryst.-84–Sm C–141–Sm A–163-nem.–188–iso.

In compound **I**, the nematic phase is more dominant than the smectics, while compounds **II** and **III** have smectic phases in a wider temperature range than the nematic phase. It is noteworthy that two symmetrical molecules **I** and **II**, in which dipole moments cancel as a whole, form different mesophase seqences, while the non-symmetrical, polar molecule of **III** forms the same mesophases as **II**. In order to investigate the influence of intra- and intermolecular interactions of the two ester linkages on the packing modes of molecules, crystal structure determination has been attempted for the isomers. As was preliminarily reported,[2] quite different crystal packings of **I** and **II** show the significant local interaction of polar groups.

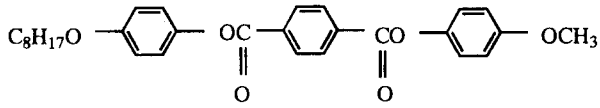
In order to study the local interaction of polar groups on packing modes, crystal structure analysis has been extended to the following related compounds, in which one of the octyloxy groups of the previous series is replaced by a methoxy group:

p-phenylene 4-methoxybenzoate 4-octyloxybenzoate (**IV**)



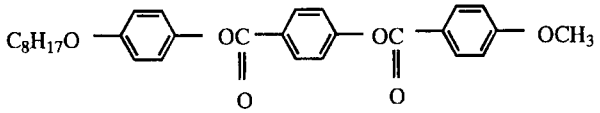
cryst.-124–nem.–224–iso.[3]

4-methoxyphenyl 4-octyloxyphenyl terephthalate (**V**)



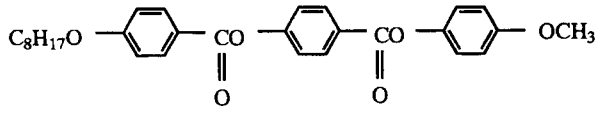
cryst.-167–(Sm A–125-)nem.–224–iso.[3]

4-octyloxyphenyl 4-(4-methoxybenzoyloxy)benzoate (**VI**)



cryst.-101–nem.–214–iso.[3]

4-methoxyphenyl 4-(4-octyloxybenzoyloxy)benzoate (**VII**)



cryst.-107–Sm A–122-nem.–226–iso.[3)]

In these four compounds, the nematic phase is dominant. The smectic A phase is shown only in compound **VII** in a narrow temperature range and in **VI** monotropically.

This paper discusses the influence of the different directions of two ester linkages on molecular packings and liquid crystalline behavior, based on the crystal structures of **I**, **II**, **IV**, **V**, and **VI**. Crystal structures of **III** and **VII** have not been determined, as mentioned in the Experimental section.

Experimental

Compounds. All the compounds except for **V** were synthesized in a conventional way[1,3–5] Compound **V** was obtained by one-step esterification of an equimolar mixture of terephthaloyl chloride with 4-octyloxyphenol and 4-methoxyphenol. The compound was separated from the reaction mixture by column chromatography on silica gel using CH_2Cl_2–hexane (2 : 1) as an eluent (yield, 43.3%) and recrystallized from ethyl acetate. Transition temperatures of all the compounds determined by DSC were consistent with the reported values.[1,3]

Crystal Structure Analysis. Cell parameters and reflection intensities (up to $2\theta = 120°$) were measured on a Rigaku AFC-7R diffractometer with Cu $K\alpha$ radiation (λ = 1.54184 Å). Three standard reflections were measured after every 150 reflections. No significant change was observed. The intensity data were corrected for Lorentz and polarization factors but not for extinction and absorption. Detailed experimental conditions and crystal data are summarized in Table 1.

Structures were solved by using SHELXS86[6] and refined by the full-matrix least-squares method on F^2 by using SHELXL93.[7] Scattering factors were taken from the International Tables for Crystallography.[8] Non-hydrogen atoms except for disordered ones (see below) were refined anisotropically. Benzene rings of **IV**, **V**, and **VI** and the peripheral ring of **I** were constrained to the ideal hexagons. Hydrogen atoms calculated geometrically were included in intensity calculations but not refined. For crystal **IV**, there were three crystallographically independent molecules A, B, and C, which were refined in a three-blocked matrix. Because of the remarkably large displacement parameters, atoms of alkyl chains (C(1A), C(2A), C(1B)–C(7B), and C(1C)–C(5C)) were treated as disordered with fixed occupancies of 0.5. Atoms of the disordered chains were refined with isotropic displacement parameters, many of which still became large and so were fixed to be 0.3. The high R value (12.7%) is considered to be due to this highly disordered structure. The final R value for **V** is also high (11.8%), probably

Table 1. Experimental Details, Crystal Data, and Final Results of Refinements

	I	**II**	**IV**	**V**	**VI**
Formula	$C_{36}H_{46}O_6$	$C_{36}H_{46}O_6$	$C_{29}H_{32}O_6$	$C_{29}H_{32}O_6$	$C_{29}H_{32}O_6$
Formula weight	574.73	574.73	476.55	476.55	476.55
Solvent for crystal growth	Ethyl acetate/ methanol	$CHCl_3$/methanol	$CHCl_3$/ isobutanol	$CHCl_3$/methanol	Ethyl acetate/ isobutanol
Crystal shape	Needle	Plate	Plate	Plate	Needle
Crystal size / mm	0.6×0.05×0.04	0.5×0.4×0.02	0.4×0.2×0.02	0.3×0.3×0.01	0.6×0.1×0.1
l.s. for cell const[a)]	25 (56—57°)	21 (56—57°)	25 (38—45)	18 (46—50)	25 (51—57)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Pn
a/Å	26.788(7)	7.699(3)	11.901(2)	7.833(2)	30.924(5)
b/Å	4.195(11)	38.61(2)	42.088(6)	60.70(2)	15.157(8)
c/Å	14.733(12)	5.544(3)	8.0589(13)	5.503(2)	5.587(4)
α/°	90	91.42(4)	94.187(13)	101.39(2)	90
β/°	99.77(3)	90.66(4)	100.985(13)	90.37(2)	92.66(5)
γ/°	90	93.44(4)	83.240(12)	86.44(2)	90
V/Å^3	1632(5)	1644.5(13)	3929.7(10)	2560.3(11)	2615(2)
Z	2	2	6	4	4
d_X/Mg m^{-3}	1.17	1.16	1.21	1.24	1.21
μ/mm^{-1}	0.624	0.619	0.680	0.696	0.681
Scan mode	2θ–ω	2θ–ω	2θ–ω	ω	2θ–ω
No. of unique refls	2809	4897	11657	7599	4482
No. of refls ($> 2\sigma(I)$)	1548	3740	3210	3563	3321
$(\Delta/\sigma)_{max}$	0.168	0.043	0.424	0.044	0.089
$\Delta\rho$(max)/e Å^{-3}	0.239	0.277	0.428	0.496	0.184
$\Delta\rho$(min)/e Å^{-3}	−0.229	−0.336	−0.445	−0.480	−0.270
R(int)[b)]	0.072	0.030	0.070	0.058	0.068
R_1[c)]	0.0624	0.0779	0.1272	0.1182	0.0611
R_{w2}[d)]	0.1708	0.2799	0.4136	0.3351	0.1891
S	1.100	0.844	1.027	0.946	1.094

a) The number of reflections with the 2θ range in the parenthesis. b) Based on F ($> \sigma(F)$). c) $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$ for observed reflections. d) $R_{w2} = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$ for observed reflections. $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P = (F_o^2+2F_c^2)/3$ with a = 0.1144, b = 0.4324 for **I**, a = 0.2457, b = 1.9685 for **II**, a = 0.3314, b = 0.0 for **IV**, a = 0.3107, b = 7.0316 for **V**, and a = 0.1403, b = 0.6056 for **VI**.

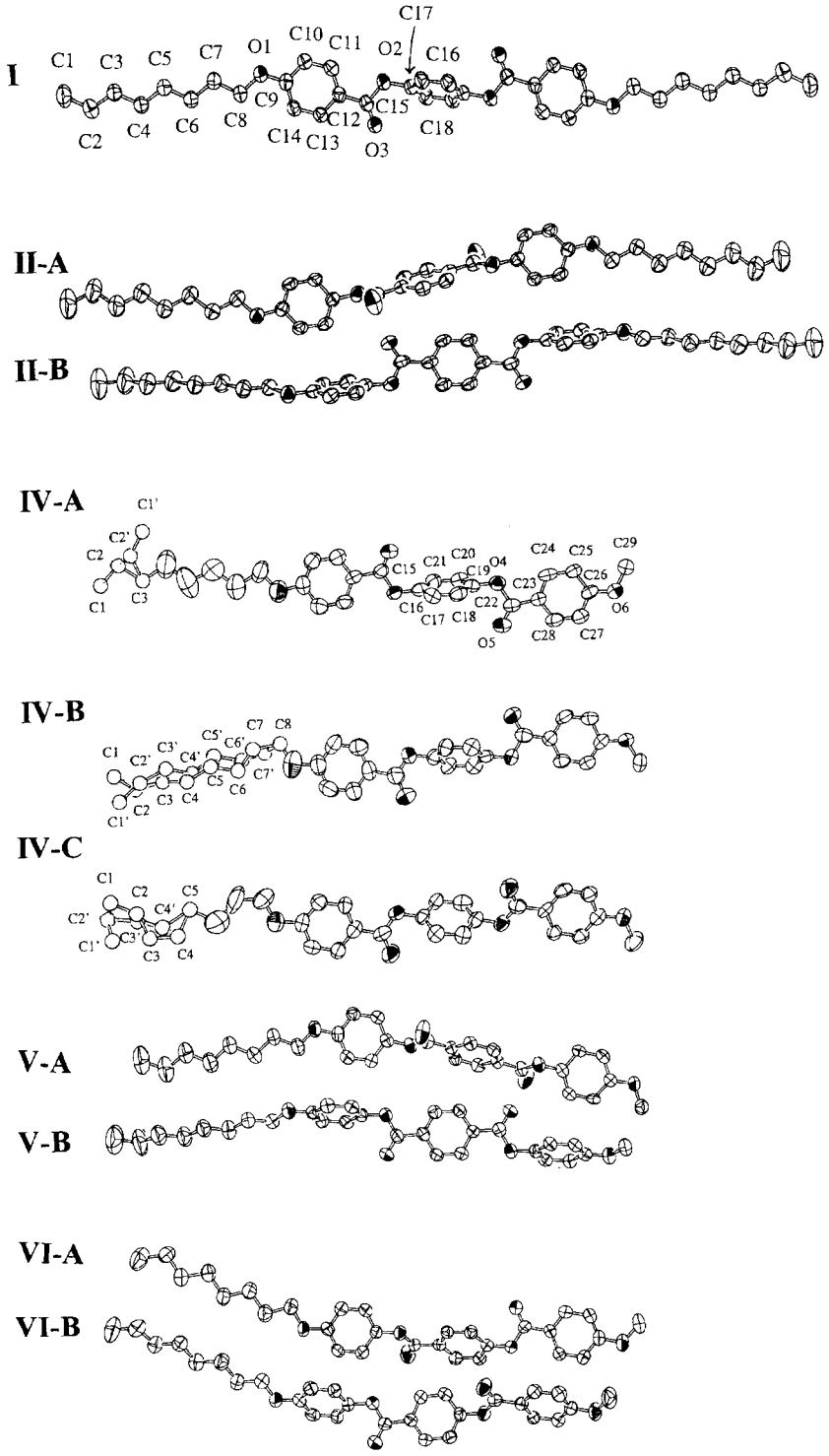


Fig. 1. ORTEP drawings of molecules with the numbering schemes. All the molecules are numbered in a similar way. Thermal ellipsoids are drawn with 50% probabilities. Hydrogen atoms are omitted for simplicity. Atoms refined isotropically are shown by small spheres with arbitrary diameter to show the conformations of disordered chains more clearly.

caused by the weak intensity data. Final results of the refinements are summarized in Table 1. Crystallographic data have been deposited at the CCDC, cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 140467-140471 and also deposited as Document No. 73022 at the Office of the Editor of Bull. Chem. Soc. Jpn.

For crystal **III**, data collected at room temperature (for the crystal data: $P2_1/c$, a = 36.965(6), b = 14.979(2), c = 5.503(8) Å, β = 92.78(6)°) converged to the final R value of 16%. Another data set was obtained at 180 K for the same crystal, because there were no other better crystals. Crystal data were found to be $P2_1/c$,

a = 159.19(2), b = 14.592(18), c = 5.480(15) Å, β = 90.1(2)°, the dimension of the a axis being four times longer than that obtained at room temperature. Following measurement for the same crystal at room temperature showed the four-time periodicity again. Thus, it is considered that this crystal has the long unit-cell, which was not detected in the first run, although the possibility of a phase transition can not be completely neglected. The structure, however, has not been solved, probably because the data were insufficient for four crystallographically independent molecules. Single crystals suitable for data collection have not been obtained for crystal **VII**, either, in spite of the repeated attempts at crystal growth.

Results and Discussion

Molecular Conformations. Figure 1 shows the molecular structures of **I**, **II**, **IV**, **V**, and **VI**. Molecules **I** and **II** have an inversion center on the center of the central benzene ring. A half of the molecule is crystallographically independent in crystal **I**, while there are two crystallographically independent half-molecules A and B in crystal **II**. In crystal **I**, the peripheral ring is coplanar with the attached ester linkage, with the dihedral angle of 4.2(4)°. In crystal **II**, both of the ester linkages are coplanar with the central benzene ring, with the dihedral angles of 3.0(5)° and 1.6(6)° for molecules A and B, respectively.

In crystal **IV**, there are three crystallographically independent molecules: A, B, and C. Dihedral angles of peripheral rings with the attached ester linkages are 2(2)–6(2)° except for the ring of the methoxy side of molecule C, 13(2)°. Each terminal chain is twisted and largely disordered, especially in molecules: B and C. In crystal **V**, there are two crystallographically independent molecules, A and B. Both of the ester linkages are coplanar with the central benzene ring with the dihedral angles of 1.9(9)–4(1). There are two crystallographically independent molecules A and B also in crystal **VI**. Each ester linkage is approximately coplanar with the benzene ring, to which the C atom of the ester linkage is attached, with the dihedral angles of 0.4(4)–5.3(4)°. Consequently, approximately planar moieties are formed by a benzene ring and the attached ester linkage(s), showing the conjugation between them in all the molecules. Terminal chains have all-*trans* conformation in all the crystals except for **IV**.

Crystal Packings. Figure 2 shows the crystal packing of **I** viewed along the b and c axes. Molecules are arranged so that the planar moieties with conjugation from C=O to an alkoxy O atom via a benzene ring (–O–C_6H_4–COO–) come close between adjacent molecules. Here, one of the oppositely directed moieties in a molecule is close to an adjacent molecule, while the other is close to another molecule, resulting in an imbricated structure. Figure 2(b) shows that adjacent molecular long axes are not parallel but slightly tilted (20°) away from each other. The distances between ester linkages are 3.79 Å for O(2)(x, y, z)···C(15)(x, $y-1$, z) and 3.82 Å for O(2)(x, y, z)···O(3)(x, $y-1$, z)).

Figure 3 shows the crystal packing of **II**. The central planar moieties are fully ovelapped, leading to the separate aggregation of core moieties and alkyl chains, a distinct lamellar

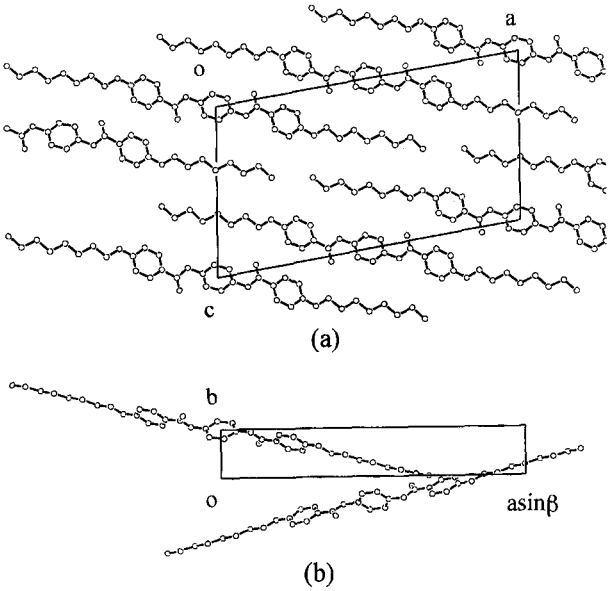


Fig. 2. Crystal structure of **I** viewed along the b (a) and c (b) axes.

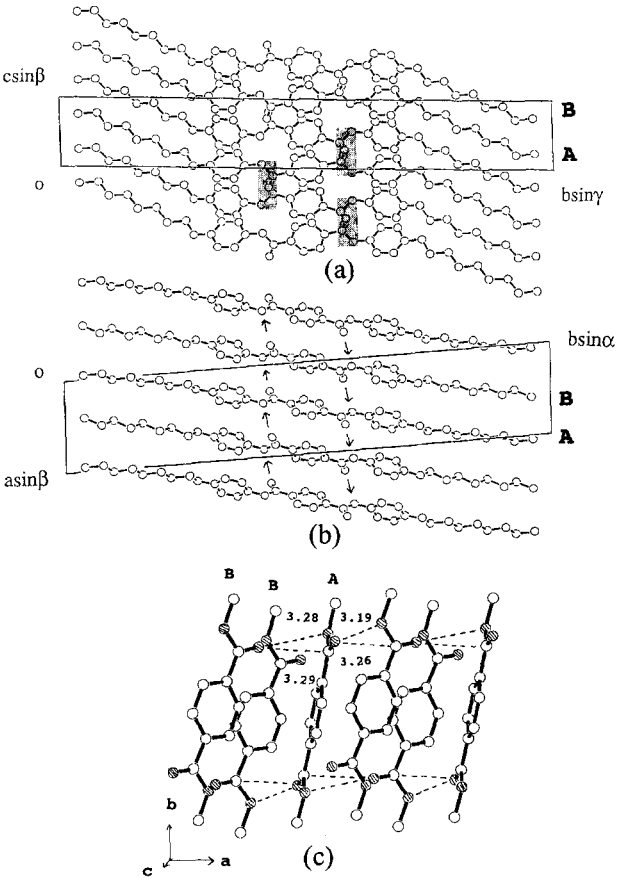


Fig. 3. Crystal structure of **II** viewed along the a (a) and c (b) axes and the arrangement of ester linkages (c). Close arrangements of ester linkages are marked in (a).

structure. Figure 3(a) shows that ester linkages come close to each other between adjacent molecules; one of the ester linkages of a molecule A comes close to that of an adjacent B molecule, while the other comes close to that of another

B molecule and vice versa. In Fig. 3(b), ester linkages are aligned along the a axis in two rows, the directions of which are opposite to each other, as shown by arrows. The distances of ester linkages are shown in Fig. 3(c).

Crystal **IV** has a lamellar structure with the layer plane parallel to the *ac* plane, as shown in Fig. 4. Molecular long axes are largely tilted (ca. 45°) with respect to the layer normal. Crystallographically independent molecules, A, B, and C are arranged in a parallel set of molecules. The three-molecule-sets are stacked in a head-to-head way, i.e. methoxy and octyloxy groups facing methoxy and octyloxy groups, respectively, leading to a bimolecular layer structure. The planar moiety (O–C_6H_4–COO) of a molecule C in the methoxy side has an antiparallel overlapping with the inversion-related C molecule, leading to the shift of three-molecule-sets along the molecular long axes and hence the large tilt in

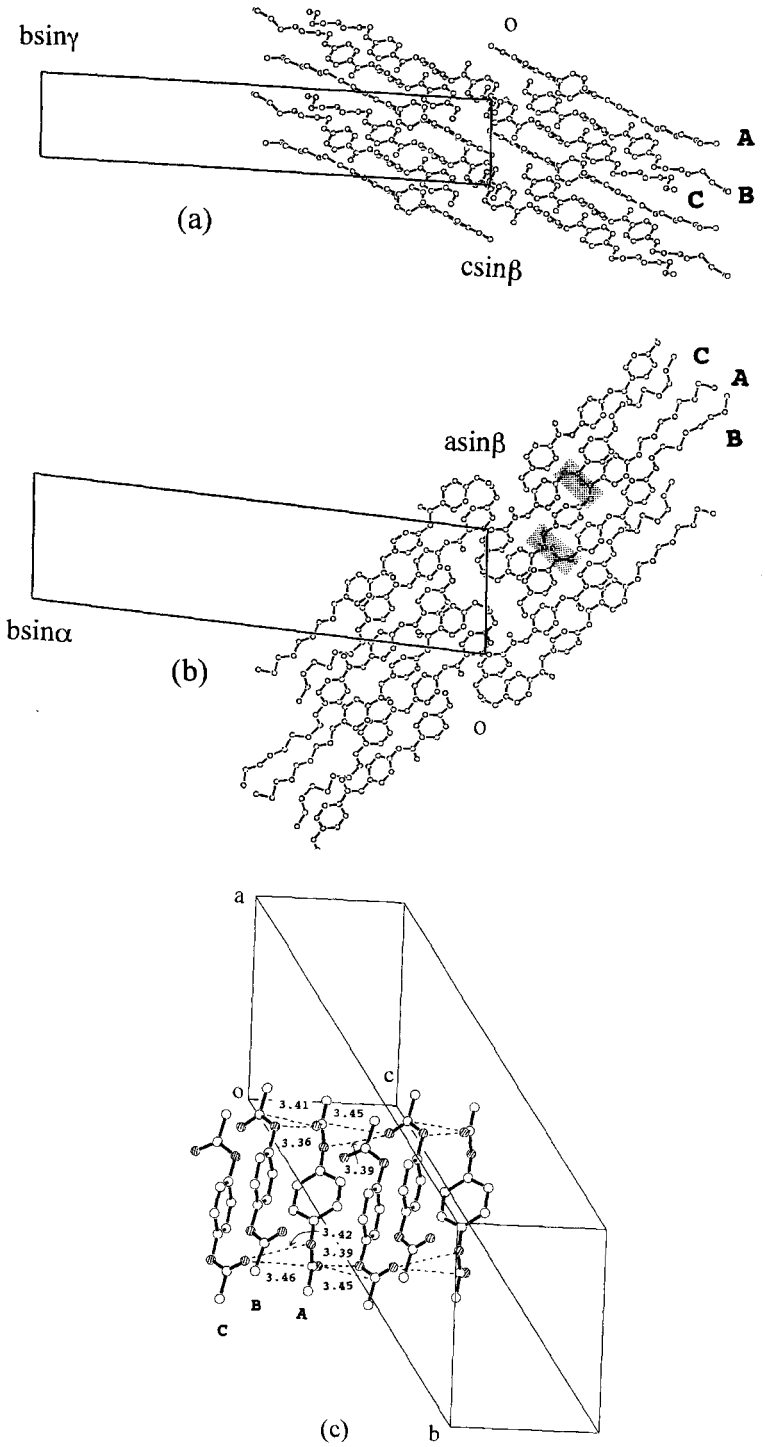


Fig. 4. Crystal structure of **IV** viewed along the *a* (a) and *c* (b) axes and the arrangement of ester linkages (c). Only one of the disordered atoms in chains are shown for simplicity. Close arrangements of ester linkages are marked in (b).

the smectic-like layer structure. Chains of close contacts of ester linkages are formed along the c axis between molecules A and B and between A and C, as shown in Fig. 4(c).

Figure 5 shows the structure of crystal **V**, in which methoxy and octyloxy groups meeting methoxy and octyloxy groups, respectively, forming a bimolecular lamellar structure, as in crystal **IV**. The resultant structure is, however, very similar to that of crystal **II**, with the large overlapping of core moieties and the segregation of cores and chains. Figure 5(c) shows the arrangement of ester linkages in crystal **V**, which is very similar to that in crystal **II**.

Figure 6 shows that molecules A and B form parallel pairs in crystal **VI**. The pairs are arranged in a head-to-tail way (facing of methoxy and octyloxy groups) throughout the crystal, resulting in a polar structure, because two ester linkages are in the same direction in a molecule. The distances between methoxy groups and ester linkages (3.32 and 3.45 Å for (29A)···O(2A) and C(29B)···O(2B), respectively) are close to van der Waals contact (3.22 Å),[9] suggesting a considerable interaction between them. On the other hand, ester linkages are rather far from each other between adjacent molecules: 3.94 Å for O(2A)(x, y, z)···O(3A)(x, y, $z-1$), 3.80 Å for O(4A)(x, y, z)···O(5A)(x, y, $z+1$), 3.87 Å for O(2B)(x, y, z)···O(3B)(x, y, z-1)), and 3.73 Å for O(4B)(x, y, z)···O(5B)-(x, y, $z+1$).

Factors Controlling Crystal Structures. All the molecules have approximately planar moieties formed by the conjugation of a phenyl ring with the attached ester linkage(s). The planar moieties have a tendency of coming close (overlapping) between adjacent molecules. The extent of overlapping determines the type of crystal packings: i.e. imbricated (**I** and **VI**) or smectic-like layer (**II** and **V**) structures. In molecule **I**, the locations of the planes are at both ends of the core, leading to a partially overlapped structure of the core moieties. In molecule **II**, both ester linkages are coplanar with the central benzene ring, leading to largely overlapped structures of the core. Therefore, the quite different crystal packings shown by the two symmetrical molecules,

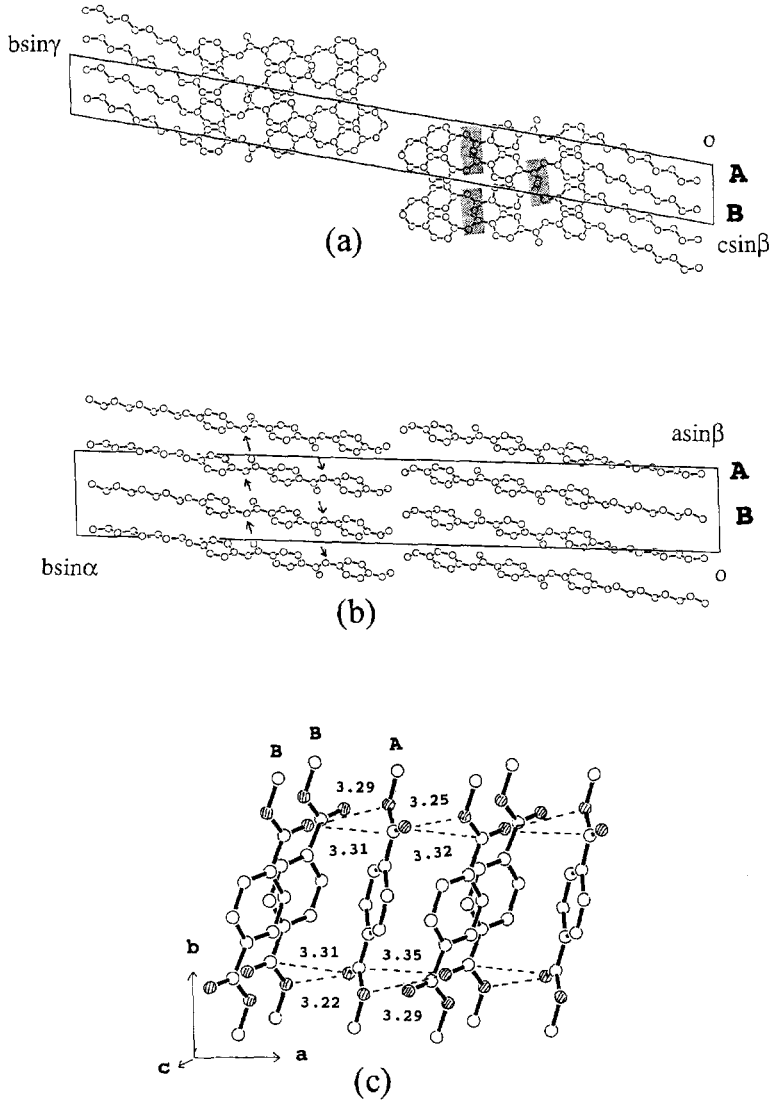


Fig. 5. Crystal structure of **V** viewed along the b (a) and c (b) axes and the arrangement of ester linkages (c). Close arrangements of ester linkages are marked in (a).

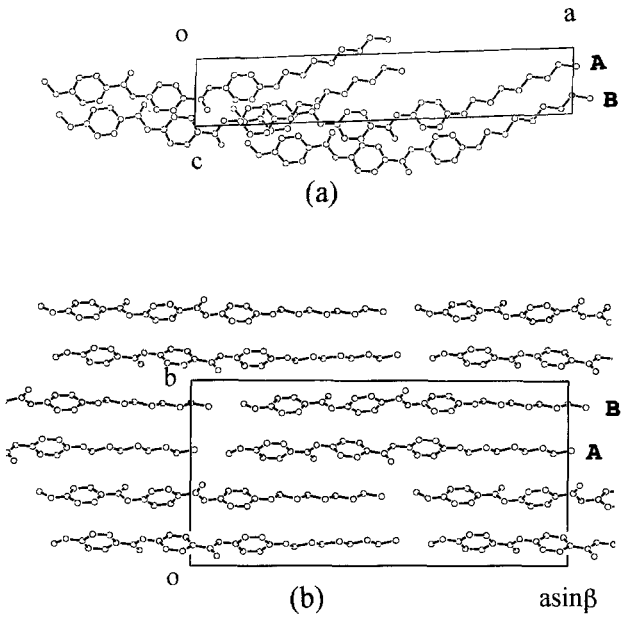


Fig. 6. Crystal structure of **VI** viewed along the *b* (a) and *c* (b) axes.

in which dipole moments cancel as a whole, are derived from the location of the planar moieties in the cores. In crystal **IV**, which has a common core with **I**, an antiparallel arrangement of the planar moieties, O–C_6H_4–COO, as is found in crystal **I**, is partly observed, which leads to a largely tilted layer structure. In crystal **V**, planar central moieties, the same as those in crystal **II**, are fully overlapped, resulting in a distinct lamellar structure similar to that of crystal **II**. It may be pointed out that the planar moiety comprising a benzene ring and two ester linkages in molecules **II** and **V** is larger than that composed of a benzene ring and an ester linkage in molecules **I** and **IV**, so that the former controls the crystal structures more definitely. In crystal **VI**, which is the only example for an unsymmetrical core, molecules form parallel pairs with overlapping of the planar moieties. However, pairs shift along the long axes of molecules, resulting in the imbricated structure. Thus, it is concluded that the arrangements of core moieties are controlled by the location and the size of the conjugated plane in a molecule.

Dipole–dipole interaction of ester linkages is another factor controlling the crystal structures. In crystals **II** and **V**, ester linkages are closely arranged almost in the same way, as shown in Figs. 3(c) and 5(c), leading to almost the same smectic-like layer structures of crystals **II** and **V**, in spite of the difference in chain lengths. In crystal **IV**, close arrangements of ester linkages are found among three parallel molecules. On the other hand, ester linkages are rather far from each other in crystals **I** and **VI**.

Relationships between Crystal Structures and Mesophase Behavior. The characteristics of crystal structures are closely related to the mesophase sequencies. In compound **I** the nematic phase is more dominant than the smectics and compounds **IV** and **VI** have only the nematic. All these compounds have imbricated or largely tilted layer structures in crystalline states. Compound **II** has smectic phases over a wider range than the nematic, in accordance with the layer structure in the crystal. On the other hand, compound **V** has the Sm A phase only monotropically, although the crystal has a distinct layer structure. It is considered that the crystal **V** is so stable that it does not melt until a high temperature is reached (167 °C) and that the high melting point hides the smectic phases. It is also pointed out that crystals **II** and **V** with large overlapping of core moieties and dipole–dipole interaction due to the close arrangements of ester linkages have higher melting points than others, showing the relationship of structures and thermal properties.

Takenaka and his co-workers[10] found that layer spacings in Sm A measured by means of X-ray diffraction are in good agreement with the molecular lengths calculated for lower homologues of compound **II**, while those for higher homologues are significantly shorter (2.1 Å for the octyloxy compound) than the calculated lengths. Based on these data, they proposed a model in which terminal moieties of long chains deviate from the extended conformation. The model is consistent with the strong interactions among cores shown in the crystal structure of **II**.

On the other hand, Hikmet et al. synthesized diacrylates with the same cores as compounds **I**, **II**, and **III**.[11] The compound with the same core as **I** is nematogenic with the monotropic Sm C, while those with the same cores as **II** and **III** have only Sm A. The mesophase character (nematic or smectic) is very similar to that of **I**, **II**, and **III** and was discussed in terms of the flexibility, which corresponds to the planarity in our discussion, of cores as well as intermolecular interaction between dimers. The absence of Sm C in the acryloyloxy compounds in contrast to the octyloxy compounds is, however, considered to be due to the bulky acryloyloxy group in the end position of each chain, which would reduce lateral intermolecular interaction, leading to the more disordered Sm A and to their lower clearing points (140—152 °C).

Conclusions

Crystal structures have been determined for mesogens with two ester linkages, two with the same terminal chains (octyloxy) and three with different ones (octyloxy and methoxy). Comparing the crystal structures and mesophase sequences, we conclude as follows.

1) Two symmetrical molecules, in which dipole moments cancel as a whole, have quite different crystal packings, showing the significance of the local intermolecular interaction: overlapping of planar moieties of cores and dipole–dipole interaction.

2) Compounds with central planar core moieties have similar packing modes in spite of quite different chain lengths, showing the important role of the size and the location of the planar moieties.

3) The resultant crystal structures are closely related to the liquid crystalline phase sequences; imbricated structures to the nematic phase and layer structures with smectic phases.

We are grateful to Ms. Hiroko Uchida for the preliminary

study of crystal **I** and to Professor Shunsuke Takenaka of Yamaguchi University for his useful discussion concerning the layer spacings in Sm A. This work was supported by a Grant-in-Aid for Scientific Research No. 08640638 from the Ministry of Education, Science, Sports and Culture.

References

1 S. Takenaka, Y. Sakurai, H. Takeda, T. Ikemoto, H. Miyake, S. Kusabayashi, and T. Takagi, *Mol. Cryst. Liq. Cryst.*, **178**, 103 (1990).

2 K. Tamura, H. Uchida, and K. Hori, *Mol. Cryst. Liq. Cryst.*, **330**, 201 (1999).

3 Y. Sakurai, S. Takenaka, H. Miyake, H. Morita, and T. Ikemoto, *J. Chem. Soc., Perkin Trans. 2*, **1989**, 1199.

4 W. R. Young, I. Maller, and D. C. Green, *J. Org. Chem.*, **41**, 2566 (1972).

5 J. C. Dubois and A. Beguin, *Mol. Cryst. Liq. Cryst.*, **47**, 193 (1978).

6 G. M. Sheldrick, "SHELXS86. A Program for the Solution of the Crystal Structures," University of Götingen (1986).

7 G. M. Sheldrick, "SHELXL93. Program for the Refinement of the Crystal Structure," University of Götingen (1993).

8 "International Tables for Crystallography," ed by A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht (1992), Vol. C.

9 A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

10 H. Okamoto, T. Tasaka, V. F. Petrov, and S. Takenaka, to be submitted to *Liq. Cryst.*

11 R. A. M. Hikmet, J. Lub, and A. J. W. Tol, *Macromolecules*, **28**, 3313 (1995).