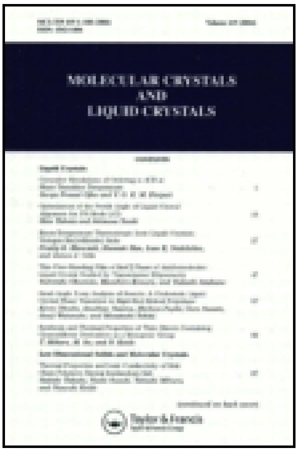

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Intermolecular Interaction Revealed in the Crystal Structures of Chiral Smectogenic Biphenyl Esters

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Intermolecular interactions revealed in the crystal structures are discussed in terms of the lateral overlapping of the core moities and the arrangements of the polar groups for chiral smectogenic biphenyl esters. It is found that the packing modes of the molecules within a layer, which are closely related to the liquid crystal phase sequences, are dependent on the length of the moiety sandwiched by the two polar groups.

Keywords: crystal structure, biphenyl esters, X-ray diffraction, chiral smectogens

INTRODUCTION

Good correlations between liquid crystal behavior and crystal structures have been shown for three series of biphenyl esters having a 2-methylbutyl group with slightly different liquid crystal phases by systematic single crystal X-ray analyses. Details of the crystal structures and the procedures of the structure determination were reported elsewhere.[1–4] Here, we discuss the intermolecular interaction revealed in the crystals in terms of the two factors: the lateral overlapping of molecules and the interaction between polar groups. Preliminary results for the biphenyl esters with a 1-methylheptyloxy group are also briefly discussed.

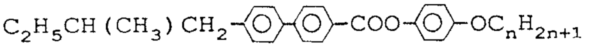
RESULTS AND DISCUSSION

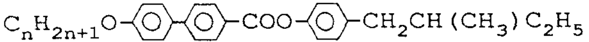
Structural features of the crystals are summarized in Table I. All the crystals have smectic-like layer structures. Figure 1 shows schematic diagrams of the crystal

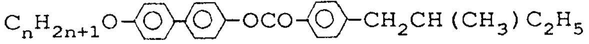
TABLE I

Summary of the crystal structures

	n	paraffin chain	biphenyl link	tilt angle	phase sequence	ref
I	5	all-trans	coplanar	50°	X-(C*)-chol	(1)
	7	extended$^{\#}$	53°	60	X-C*-chol	(1)
II	7	twisted	coplanar	30	X-C*-A-chol	(2)
	8	twisted	coplanar	30	X-C*-A-chol	(2)
III	6M	all-trans	coplanar	60	X-X'-I*-C*-chol	(4)
	6T	twisted	20,40°	45	X-X'-I*-C*-chol	(4)
	7M	twisted extended	coplanar	45	X-I*-C*-chol	(3)
	7T	isomorphous with III-6T			X-J*-I*-C*-chol	(3)

I 

II 

III 

X, X' denote crystals.

with a twisted moiety of O-C-C-C.

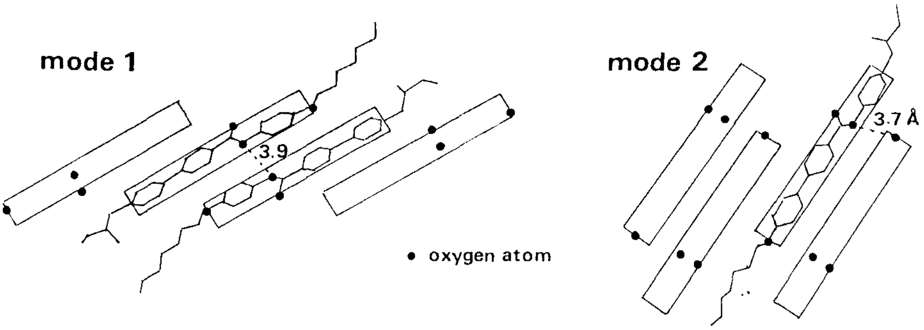


FIGURE 1 Schematic diagrams of the crystal structures of the series I and II.

structures of the series I and II. Intermolecular interactions constructing layer structures are considered to be divided into two factors: overlapping of molecules and the interaction between the polar groups. In the crystals of the series I, only the ester groups are associated with each other with the antiparallel arrangement between the neighboring molecules (mode 1). On the other hand, the ester and ether groups are in proximity at the two positions between the two molecules (mode 2) in the crystals of the series II. Here, whole molecules including paraffin chains participate lateral overlapping of the molecules. The difference is interpreted as follows. A molecule of the series I has a short moiety sandwiched by an ester and an ether group. In this case, the mode 1 is preferred, since the mode 2 diminishes molecular overlapping. For a molecule of the series II, in which a much longer core moiety is sandwiched by the two polar groups, the mode 2 provides large overlapping at the same time. Therefore, overlapping of the core moieties is larger in the crystals of the series II than that in the series I, indicating that the smectic-like layer structure is more stable in the series II, where Sm*C transforms to Sm A, than in the series I, where Sm*C transforms to a cholesteric.

In the third series, the situation is more complicated. For $n = 7$, two crystal forms were found (abbr. III-7M and III-7T). Figure 2 shows a schematic diagram of III-7M. Here, two of the three crystallographically independent molecules have a parallel arrangement, to which the third one is antiparallel. Paraffin chains between the parallel molecules have close contacts with each other. In addition, both modes of arrangement of polar groups are found. The coexistence of the two modes, as well as the close contacts of paraffin chains within a layer, would enhance the lateral interaction, leading to the transition to the more ordered smectic (Sm*I) than Sm*C.

For III-7T, which transforms to Sm*J, sufficient data have not been obtained. Two forms of the single crystals were obtained for $n = 6$ (III-6T and III-6M). Although both crystals transform directly not to a mesophase but to the same high-temperature crystalline phase, III-6T is approximately isomorphous with III-7T. Thus, the structure of III-6T is expected to be related to Sm*J. The structure is quite different from those mentioned above, in which the contact angles of the phenyl rings are about 60°. In contrary, some of the mutual arrangements of phenyl rings of III-6T is nearly parallel (~20°). This structure suggests the difficulty of molecular free rotation, since the hydrogen atoms attached to these phenyl rings are interdigitated, being closely related to the highly ordered structure of Sm*J. In III-6T, ether and ester groups are in relatively short distances, as is shown in Figure 3(a). On the other hand, for III-6M, the mode 1 is dominant, as is shown in Figure 3(b).

The crystal structures of the series III suggest that the two modes of 1 and 2 are competitive in this series. This is interpreted to be due to the fact that the sandwiched moiety in this case is of intermediate size of the series I and II, as shown in Figure 4. The difference of the length between the series II and III is very small. However, the conjugation between the ester group and the biphenyl moiety, which

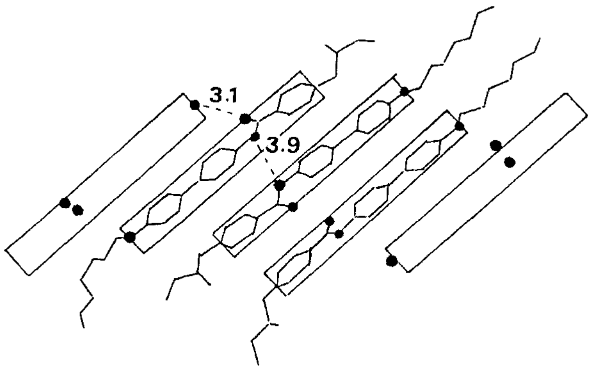


FIGURE 2 Schematic diagram of the crystal structure of III-7M.

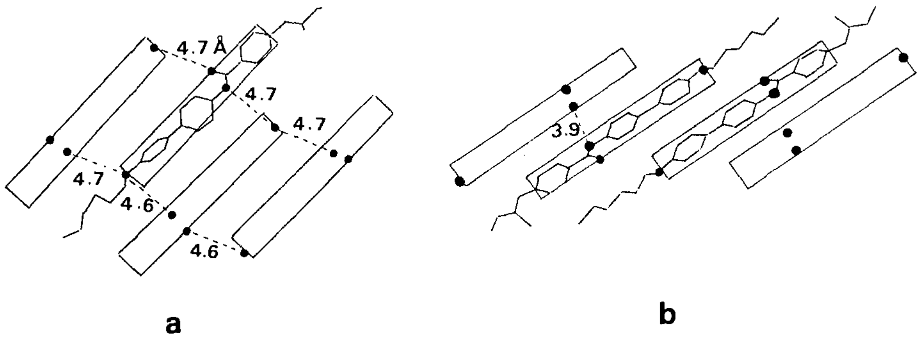


FIGURE 3 Schematic diagrams of the crystal structures of III-6T (a) and III-6M (b).

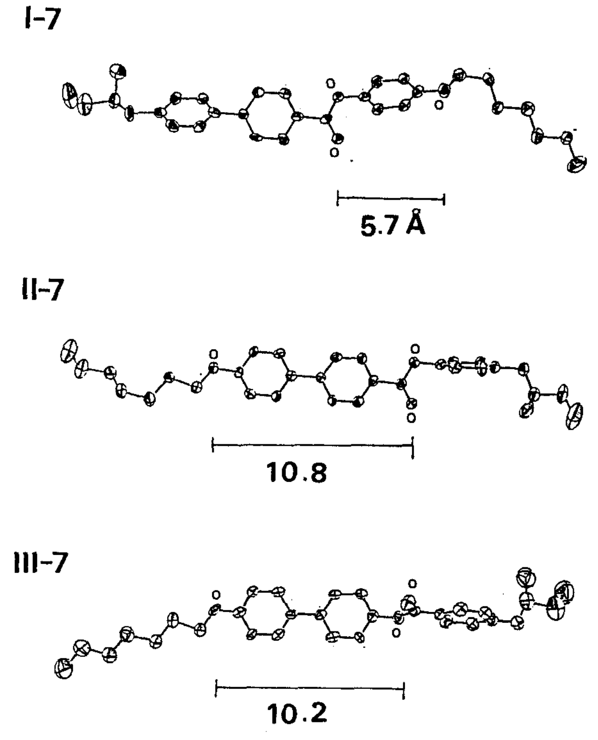


FIGURE 4 Lengths of the moieties sandwiched by polar groups.

is found in the series II but not for the series III, would enhance the effect of the small difference in the molecular geometry. The competition is interpreted to be responsible to the complicated behavior of the third series.

In order to confirm the relationship between crystal structures and mesophase behavior, we extended crystal structure determination to the biphenyl esters with 1-methylheptyloxy group, whose isomers have various liquid crystal phases.[5] Figure 5 shows the crystal structure of 4-octylphenyl 4′-[(S)-1-methylheptyloxy]biphenyl-4-carboxylate, which has a phase sequence of cryst-Sm*C-Sm A-chol. Crystal data: $P2_1$, a = 33.818(3), b = 8.2140(9), c = 5.7128(5) Å, β = 98.733(9)°, V = 1568.5(3)

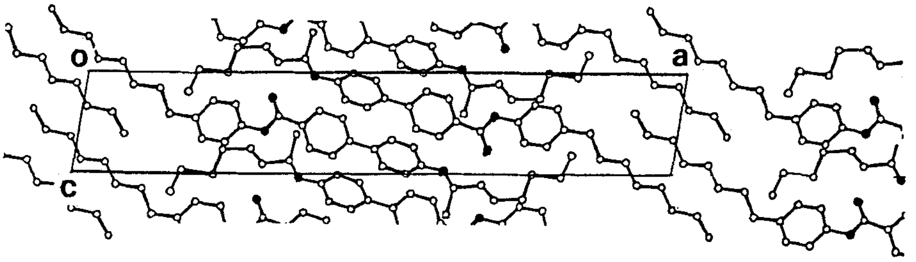


FIGURE 5 Crystal structure of 4-octylphenyl 4′-[(S)-1-methylheptyloxy]biphenyl-4-carboxylate.

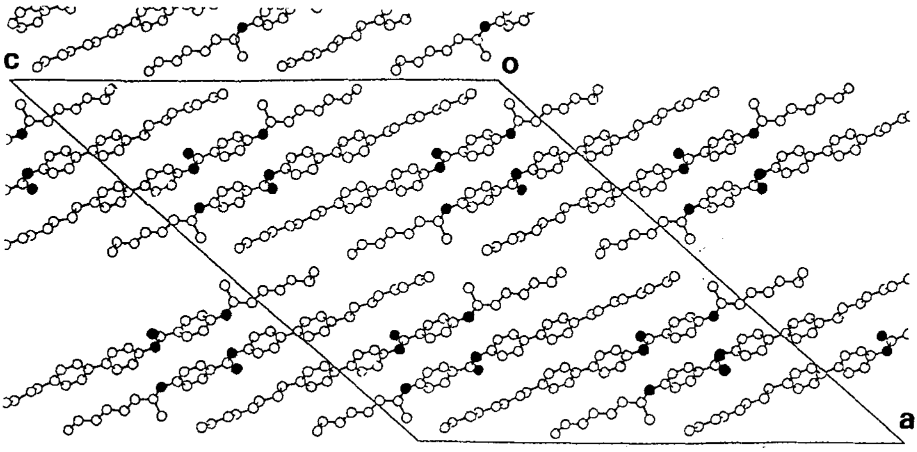


FIGURE 6 Crystal structure of 4′-octyl-4-biphenylyl 4-[(S)-1-methylheptyloxy]benzoate.

Å^3, Z = 2. The crystal has a smectic-like layer structure, in which molecules are related by 2-fold screw axis. A twisted chain, although of the chiral group, is concerned in the molecular overlapping within a layer, leading to a small tilt (about 10°). These features are similar to those of the series II. On the other hand, a difference is found in the normal paraffin chain, which has an all-trans conformation between layers. This aspect seems to be a resemblance to that of the series I. The inter-chain distances (>4.4 Å), however, are not so short as those in the series I.

Figure 6 shows the crystal structure of 4′-octyl-4-biphenylyl 4-[(S)-1-methylheptyloxy]benzoate, which has a phase sequence of cryst-Sm*C-chol. Crystal data: C2, a = 44.09(1), b = 5.494(3), c = 39.52(2) Å, β = 139.02(1)°, V = 6278(4) Å^3, Z = 8. A smectic-like layer structure is composed of two crystallographically independent molecules, whose tilt angle is large (65°). These features are similar to those of the series I. However, polar groups are arranged in the mode 2 in this crystal. In the crystal of the biphenyl-carboxylate shown in Figure 5, the ester and ether groups are in short distances. Similar modes lead to the large overlapping in the biphenyl-carboxylate crystal and the small one in the crystal of the benzoate.

It is concluded that a molecular packing in a smectic-like layer of a crystal, which is closely related to the liquid crystal behavior, is subject to a mode of arrangements of the polar groups.

Acknowledgment

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