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Influence of Directions of Two Ester Linkages on Crystal Structures of Isomeric Mesogens

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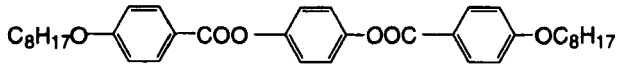
In order to make clear the influence of two or more polar groups on packing modes of molecules, crystal structures have been determined for isomeric mesogens with different directions of two ester linkages, $C_8H_{17}O$-C_6H_4-X-C_6H_4-Y-C_6H_4-OC_8H_{17}, where X=COO and Y=OOC for **I** and X=OOC and Y=COO for **II**. In crystal **I**, molecules are arranged so that moieties conjugated from C=O to an alkoxyl O atom via a benzene ring have an antiparallel arrangement, resulting in an imbricated structure. Crystal **II** has a lamellar structure with a small tilt, in which ester linkages of adjacent molecules come close each other. The crystal structures are closely related to the phase sequences, crystal-SmC-nematic-isotropic for **I** and crystal-SmC-SmA-nematic-isotropic for **II**.

Keywords: crystal structure; mesophase sequence; ester linkage

INTRODUCTION

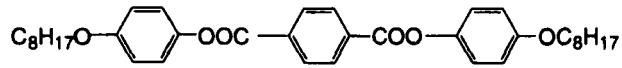
Different arrangements of two or more polar groups have a significant influence on the packing modes of molecules, and hence liquid crystalline behavior. The following compounds have different phase sequences due to the different directions of two ester groups.[1]

4-(4-octyloxybenzoyloxy)4-octyloxybenzoyloxyxylene (**I**)



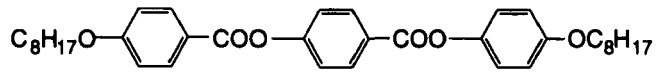
Cryst. $\overset{122}{}$ SmC $\overset{126}{}$ N $\overset{194}{}$ Iso (in °C)

4-octyloxyphenyl 4-(4-octyloxyphenoxycarbonyl) benzoate (**II**)



Cryst. $\overset{144}{}$ SmC $\overset{180}{}$ SmA $\overset{183}{}$ N $\overset{191}{}$ Iso

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



Cryst. $\overset{84}{}$ SmC $\overset{141}{}$ SmA $\overset{163}{}$ N $\overset{188}{}$ Iso

Compounds **I** shows predominantly the nematic phase rather than the smectic. On the other hand, compounds **II** and **III** have smectic phases in wider range than the nematic, although the melting points are quite different.

In order to investigate the influence of intra- and intermolecular interaction of the two ester groups on the packing modes of molecules, crystal structure determination has been attempted for the isomers. Preliminary results for **I** and **II** are described in this paper.

EXPERIMENTAL

Both compounds were synthesized in a conventional way[1]. Single crystals were obtained by slow evaporation from an ethyl acetate-methanol solution for **I** and a chloroform-methanol solution for **II** at room temperature. The structures were solved by using SHELXS86[2] and

refined by full-matrix least squares using SHELXL93[3]. Detailed experimental conditions, crystal data and final results of the refinements are summarized in Table I .

Table I. Experimental details, crystal data, and final results of refinements.

	I	II
Formula	$C_{36}H_{46}O_6$	
Formula weight	574.73	
Crystal shape	needle	plate
Crystal size / mm	0.6×0.4×0.05	0.5×0.4×0.02
X-ray source	CuKα (1.54184 Å)	
Diffractometer	AFC-7R	
l.s. for cell const	25 (56 < 2θ< 57°)	21 (56 < 2θ<57°)
Crystal system	monoclinic	triclinic
Space group	$P2_1/a$	$P\bar{1}$
a/Å	26.788(7)	7.699(3)
b/Å	4.195(11)	38.61 (2)
c/Å	14.733(12)	5.544(3)
α/°	90	91.42(4)
β/°	99.77(3)	90.66(4)
γ/°	90	93.44(4)
V/Å^3	1632(5)	1644.5(13)
Z	2	2
d_X/Mg m^{-3}	1.170	1.161
μ/mm^{-1}	0.624	0.619
No. of unique reflections	2423	4897
No. of reflections (>4σ(Fo))	1547	3740
R_1	0.0624	0.0779
R_{W2}	0.1708	0.2799
S	1.100	0.844

RESULTS and DISCUSSION

In both crystals, molecules have an inversion center on the center of the central benzene ring. A half of the molecule is crystallographically independent for **I**, while there are two crystallographically independent half-molecules, A and B for **II**.

In crystal **I**, a terminal ring is coplanar with the attached ester linkage, with the dihedral angle of 4.2(4)°. As can be seen in Fig. 1(a),

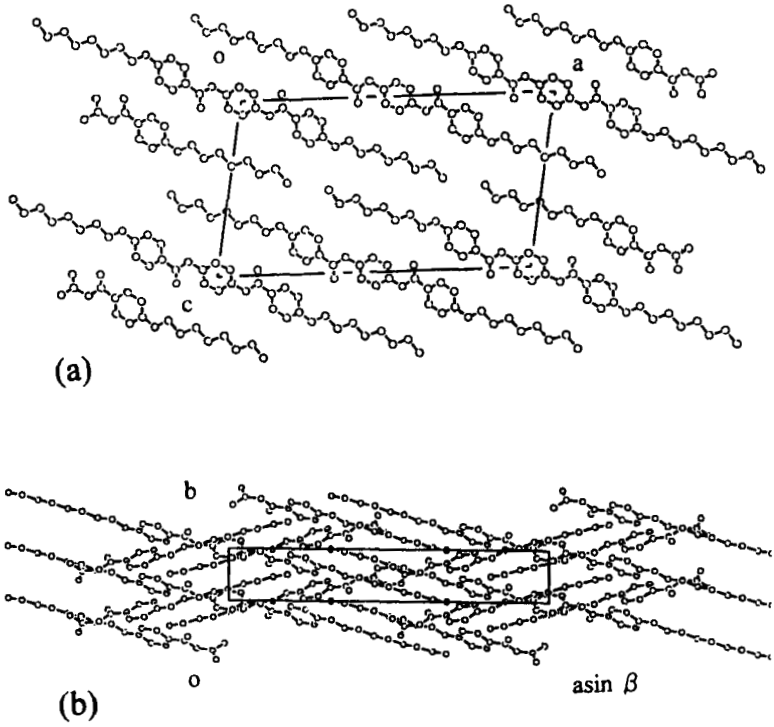


FIGURE 1. Crystal packing of **I** viewed along the b axis (a) and the c axis (b).

molecules are arranged so that the conjugated moieties from C=O to an alkoxyl O atom via a benzene ring have an antiparallel arrangement between adjacent molecules. Here, one of the oppositely directed moieties in a molecule is close to an adjacent molecule, while the other to another molecule, resulting in an imbricated structure. Figure 1(b) shows that adjacent molecules form not a parallel but a zigzag packing.

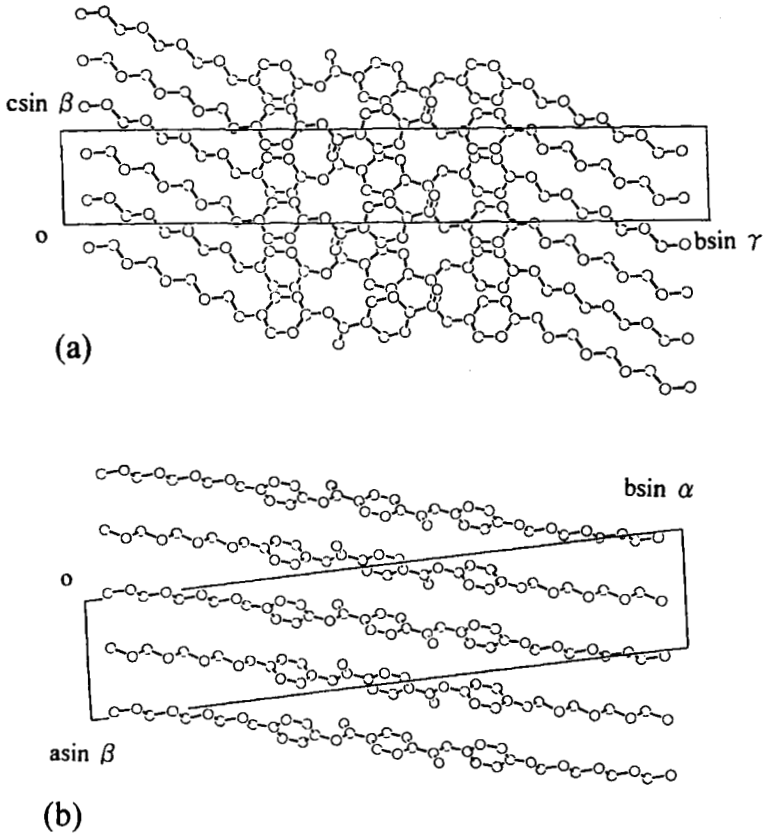


FIGURE 2. Crystal packing of **II** viewed along the a axis (a) and the c axis (b).

These features are closely related to the fact that the nematic phase predominantly exists in wider range than the smectic.

In crystal **II**, both of the ester linkages are coplanar with the central benzene ring, with the dihedral angle of 3.0(5)° and 1.6(6)° for molecules A and B, respectively. The molecular configuration allows no conjugation from C=O to an alkoxyl O atom via a benzene ring. Figure 2(a) shows that ester linkages come close each other between adjacent molecules; one of the ester linkages of a molecule comes close to that of the upper adjacent molecule, while the other comes close to that of the lower one (C=O...C; 3.2 Å), as is schematically shown in Fig. 3. In Fig. 2(b), ester linkages stack in two rows along the a axis. The directions are opposite each other as shown by arrows. In addition, core moieties and alkyl chains aggregate seperately, resulting in a distinct lamellar structure. Thus, the structure has a good correlation with the fact that crystal **II** exhibits SmC and SmA in a wider temperature range above the crystal on heating.

It is concluded that the two symmetrical molecules in which dipole moments are cancelled as a whole have quite different crystal packings, showing the significance of the local interaction of polar groups.

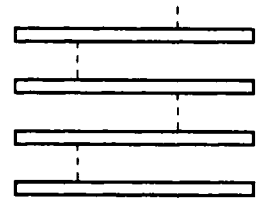


FIGURE 3 Dipole-dipole interaction (- - -) in crystal **II**.

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