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# Intermolecular Interactions Studied by Crystal Structure Analysis II. Naphthyl-ester Liquid Crystals

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*Crystal structures have been determined for 4-octylphenyl 6-octyloxy-2-naphthoate (***8Onp8***) with the phase sequence of cryst–SmA – Nem–isotropic and 6-octyloxy-2-naphthylyl 4-octyloxybenzoate (***8OpnO8***) with the phase sequence of cryst–SmC – Nem–isotropic. In the former, monomolecular layers of antiparallel molecules are stacked, while in the latter, alkyl chains are interdigitated between layers. Differential scanning calorimetry (DSC) with varying heating rates showed that the crystal phase of* **8Onp8** *determined here is a metastable phase. Similarity between naphthalene derivatives and biphenyl esters with a chiral chain is found and plausibly interpreted as the effect of the widening of molecules.*

**Keywords:** crystal structures; crystalline polymorphs; intermolecular interaction; naphthyl esters



## INTRODUCTION

A biphenyl ester with a phenyl ring is a fundamental core for liquid crystalline materials. It was shown that crystal structures are classified into several packing modes according to the chain configurations [1,2]. In order to make clearer the geometrical factors, following naphthyl-esters were synthesized and characterized, considering that the naphthalene core is wider and flatter than the biphenyl one.

This paper describes the phase sequences of these compounds and the crystal structures of **8Onp8** and **8OpnO8**.

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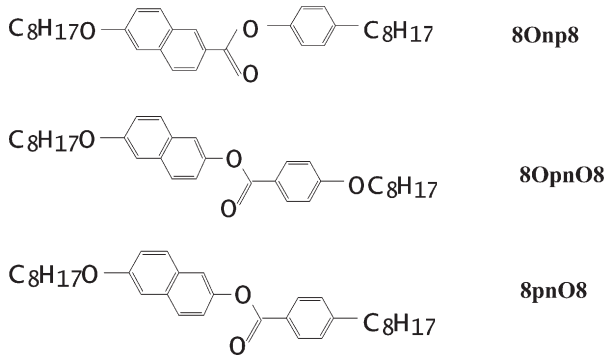




## EXPERIMENTAL

All the compounds were synthesized and purified as described previously [3]. Phase transition temperatures were determined on a DSC22C (Seiko Instruments). Microscopic observation was done on a POM microscope (Olympus) equipped with a hotstage FP82 (Mettler). X-ray powder diffraction was measured on a conventional diffractometer (Rigaku) with a heating stage.

X-ray diffraction data were collected on an AFC-7R (Rigaku) at room temperature using CuK$\alpha$ radiation monochromated by graphite. Structures were solved by using SHELXS86 [4] and refined by using SHELXL93 [5] (for **8OpnO8**) and –97 [6] (for **8Onp8**). Crystal data and results of the final refinements are summarized in Table 1. Final atomic coordinates and related materials were deposited at Cambridge Structural Database Centre (No. 242761 & 242762).

For **8pnO8**, two crystal forms were found. Crystal data: I: monoclinic, $P2_1/c$, a = 32.997(5), b = 15.398(6), c = 5.783(3) Å, $\beta = 92.17(5)^\circ$, V = 2936(4) Å$^3$, Z = 4, dx = 1.106 g cm$^{-3}$; II: monoclinic, $P2_1/c$, a = 23.821(11), b = 6.277(4), c = 20.516(11) Å, $\beta = 98.71(4)^\circ$, V = 3032(4) Å$^3$, Z = 4, dx = 1.069 g cm$^{-3}$. Unfortunately, however, only poor results were obtained for both crystals (R1 = 0.15 and 0.2, respectively). Thus, we only refer the structures briefly.

## RESULTS AND DISCUSSION

### Phase Sequences

Phase sequences were determined by microscopic observation. Phase transition temperatures (°C) [and transition entropies (J K$^{-1}$ mol$^{-1}$)] are 73.6 [88.6] (cryst–SmA), 105.2 [6.2] (SmA–Nem.), and 107.2 [5.1] (Nem.–isotropic) for **8Onp8;** 69.5 [107.5] (cryst–SmC), 84.8 [1.67]

**TABLE 1** Experimental Details and Results of Refinements

| | **8Onp8** | **8OpnO8** |
|---|---|---|
| Formula | $C_{33}H_{44}O_3$ | $C_{33}H_{44}O_4$ |
| F. W. | 488.68 | 504.68 |
| Crystal shape | plate | plate |
| Solvent | Ethyl acetate/EtOH | |
| Crystal size | 0.5, 0.2, 0.01 | 0.2, 0.2, 0.05 |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/a$ |
| a/ Å | 10.155(7) | 19.738(2) |
| b/ Å | 25.805(19) | 8.448(2) |
| c/ Å | 5.853(4) | 20.121(3) |
| $\alpha/^\circ$ | 92.79(6) | 90 |
| $\beta/^\circ$ | 103.53(5) | 116.275(9) |
| $\gamma/^\circ$ | 87.39(7) | 90 |
| V/ Å$^3$ | 1488.4(18) | 3008.4(10) |
| Z | 2 | 4 |
| $d_X$/g cm$^{-3}$ | 1.090 | 1.114 |
| $\mu$/mm$^{-1}$ | 0.525 | 0.560 |
| No. of refl. measd. | 7200 | 5600 |
| No. of unique refl. | 5342 | 5422 |
| $R_{int}$ | 0.041 | 0.023 |
| No. of refl. ($>2\sigma$(I)) | 1827 | 3958 |
| $T_{min}/T_{max}$ | — | 0.898 |
| R1 for $I>2\sigma$(I) | 0.0820 | 0.0806 |
| Rw2 for $I>2\sigma$(I) | 0.2312 | 0.2203 |
| S | 0.888 | 1.083 |
| $(\Delta/\sigma)_{max}$ | 0.017 | 0.007 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$/e A$^{-3}$ | 0.181, −0.192 | 0.186, −0.205 |

(SmC–Nem.), and 133.1 [3.98] (Nem.–isotropic) for **8OpnO8;** 74.7 [96.5] (cryst–Nem.) and 108.3 [3.85] (Nem.–isotropic) for **8pnO8**. The tilt angle of the SmC phase of **8OpnO8** was estimated to be 40° at 80°C from the layer thickness (25.7 Å) determined by X-ray diffraction and molecular length, the distance of terminal atoms in the crystal structure and van der Waals radii for methyl groups (34.2 Å). For **8OnpO8**, the phase sequence was found to be cryst–SmC – SmA–Nem.–isotropic [3]. Thus, the alkoxy O atom attached to the phenyl ring induces the SmC phase. On the other hand, the inversion of direction of ester linkage, from naphthoate to benzoate, leads to the disappearance of SmA phase. Similar relation was found between biphenyl derivatives with a chiral chain [7–9].

Both the rapidly precipitated powder sample in the purification procedure and single crystals obtained by slow evaporation of **8Onp8**

showed double peaks of melting: the extrapolated temperatures are 72.3 and 73.6°. On slow heating (0.2 K $min^{-1}$), only the higher peak appeared, while on rapid heating (10 K $min^{-1}$), the lower peak became dominant. Furthermore, a sample kept at 55°C showed only the higher-temperature peak. Thus the crystal structure determined in this work is a metastable phase, which undergoes gradual stabilization at higher temperature. The entropy change mentioned above is for the sum of the two peaks.

## Crystal Structures

Figure 1 shows the molecular structures of **8Onp8** and **8OpnO8**. Both chains have all-trans conformation in the former, while twisted at the root of the chain in the latter: twisted angles for O3-C21-C22-C23 and O4-C31-C32-C33 are 65.5(5) and 67.1(5)°, respectively. The dihedral angles between the naphthyl moiety and the ester linkage of **8Onp8** and between the phenyl and the ester linkage of **8OpnO8** are 3.1(8) and 7.1(5)°, respectively, being planar as expected.

Figure 2 shows the crystal structure of **8Onp8**. Core moieties have antiparallel packing with the tilt angle of 40° to the layer normal. Carbonyl O atoms and alkoxy O atoms are close (interatomic distance: 3.43 Å) between adjacent molecules. This packing mode has been

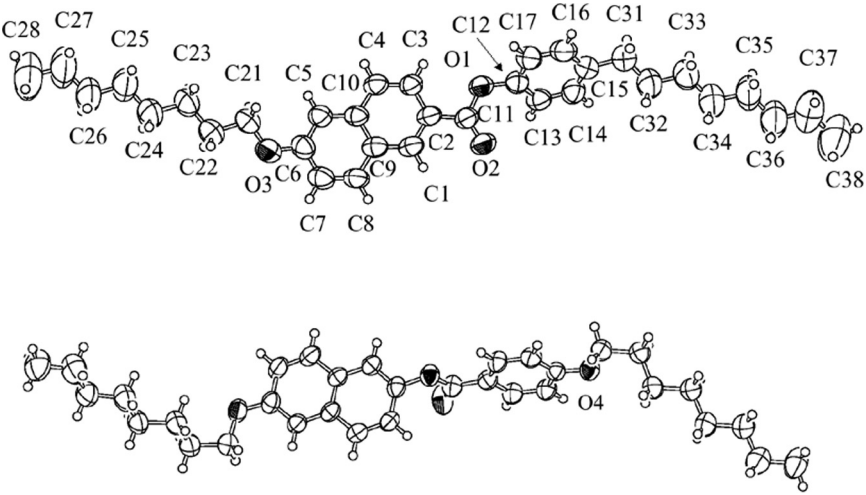


**FIGURE 1** Molecular structures with the numbering scheme. The same scheme was applied for **8OpnO8**. Displacement ellipsoids are shown at the 50% level.

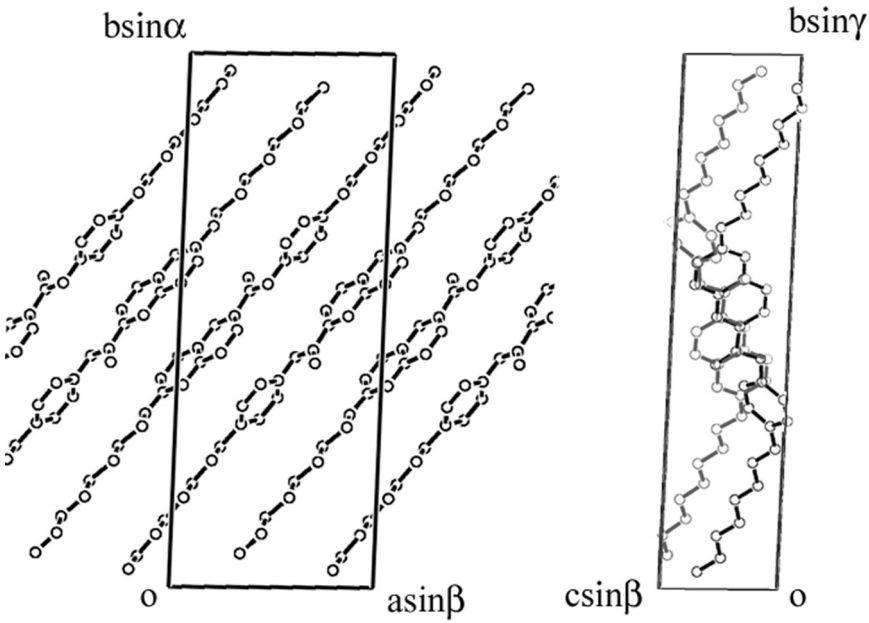


**FIGURE 2** Crystal structure of **8Onp8** viewed along the c (left) and a (right) axes. Hydrogen atoms were omitted for simplicity.

observed for biphenyl esters with a chiral chain and an alkoxy chain [10], for which predominance of SmA was also pointed out [1], as is the case here.

On the other hand, **8OpnO8** has a quite different packing mode as shown in Figure 3: a layer structure comprises largely tilted core moieties and interdigitated chains, which are twisted at the root of the chains and the extended moieties are almost perpendicular to the layer plane. No proximity is found between oxygen atoms. The association of alkyl chains between layers was found for the biphenyl derivatives having a chiral chain with the phase sequence of SmC–N [11].

As mentioned in Experimental section, two crystal forms were found for **8pnO8**. Although only poor results were obtained for both crystals, it was suggested that in the denser form (I), molecular long axes are packed in a parallel way with every two columns antiparallel, while in the other form (II) molecular long axes of neighboring molecules cross with large angle (70°). The quite different packing modes result in the different packing efficiencies: the unit cell volumes are different by 3%.

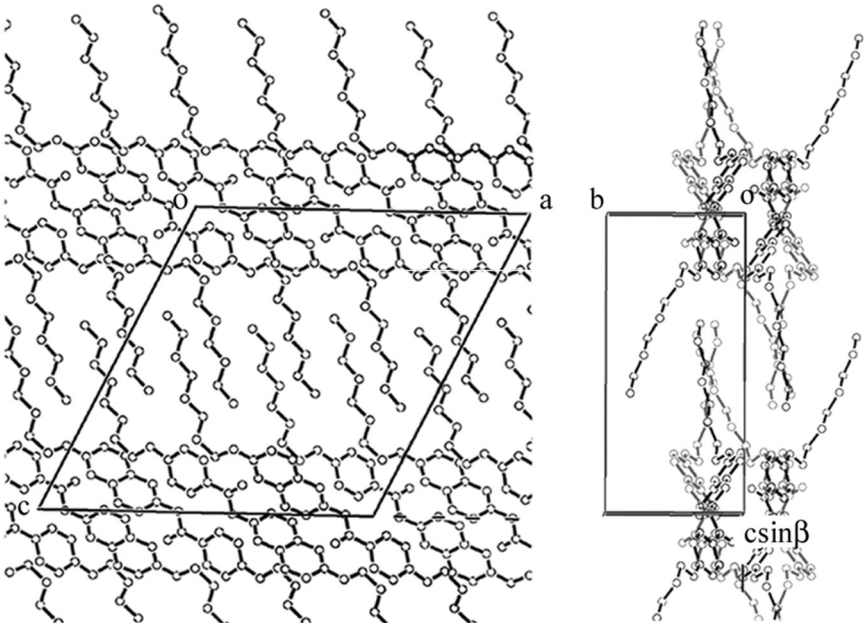


**FIGURE 3** Crystal structure of **8OpnO8** viewed along the b (left) and a (right) axes. Hydrogen atoms were omitted for simplicity. In right, molecular pairs shown black and gray, each of which is related by inversion center, are related by $2_1$ axis.

Similarities between naphthalene derivatives and biphenyl esters with a chiral chain are found in several aspects. This is plausibly interpreted that the widening of molecules, by the naphthalene moiety or bulkiness of a chiral chain, makes lateral intermolecular interaction similar, leading to the similar situations.

## CONCLUSIONS

1. Naphthalene derivatives were synthesized and characterized. The direction of ester linkage governs the appearance of SmA phase.
2. Crystal structures were determined for **8Onp8** and **8OpnO8**. In the former, monomolecular layers of antiparallel molecules are stacked, while in the latter, alkyl chains are interdigitated between layers.
3. Similarity between naphthalene derivatives and biphenyl esters with a chiral chian is found.

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