Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Intermolecular Interactions Studied by Crystal Structure Analysis I. Biphenyl-ester Liquid Crystals

Kayako Hori [a], Noriko Seo-Hayashi [a], Sachiko Ueno [a] & Sanae Watanabe [a]

[a] Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo, Japan

Version of record first published: 31 Aug 2006

To cite this article: Kayako Hori, Noriko Seo-Hayashi, Sachiko Ueno & Sanae Watanabe (2005): Intermolecular Interactions Studied by Crystal Structure Analysis I. Biphenyl-ester Liquid Crystals, Molecular Crystals and Liquid Crystals, 437:1, 311/[1555]-319/[1563]

To link to this article: http://dx.doi.org/10.1080/15421400590955136

Mol. Cryst. Liq. Cryst., Vol. 437, pp. 311/[1555]–319/[1563], 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590955136

Intermolecular Interactions Studied by Crystal Structure Analysis I. Biphenyl-ester Liquid Crystals

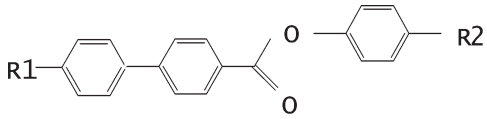
Kayako Hori
Noriko Seo-Hayashi
Sachiko Ueno
Sanae Watanabe
Department of Chemistry, Ochanomizu University,
Bunkyo-ku, Tokyo, Japan

*4-Substituted phenyl 4′-substituted biphenyl-4-carboxylates with methyl and/or methoxy groups have been synthesized and proved to be enantiotropic nematogens. Crystal structures have been determined for 4-methylphenyl 4′-methylbiphenyl-4-calboxylate (***1-1***), 4-octylphenyl 4′-methoxybiphenyl-4-calboxylate (***1O-8***), and 4-octylphenyl 4′-methylbiphenyl-4-calboxylate (***1-8***). **1O-8** has a packing mode with one-dimensional chains of close arrangements of ester linkages, as previously found for many biphenyl esters with at least one alkoxy chain. **1-8** and **1-1** have a similar packing of core moieties with ester linkages far from each other, but different from **8-8** and **8-1** (4-octylphenyl and 4-methylphenyl 4-octylbiphenyl-4′-carboxylates), suggesting the dominant role of a chain attached to a biphenyl moiety in intermolecular interactions.*

Keywords: biphenyl esters; crystal structures; intermolecular interaction

INTRODUCTION

A biphenyl ester with a phenyl ring is a fundamental core for liquid crystalline materials. Variation of chains leads to a variety of liquid crystalline phases including ferro- and antiferroelectric ones. In order to obtain intermolecular interactions controlling the mesophase behavior, crystal structures were determined for,



Address correspondence to K. Hori, Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo 112–8610, Japan. E-mail: khori@cc.ocha.ac.jp

where abbreviation **n(O)-(O)m** is used for a compound with $R_1 = C_nH_{2n+1}(O)-$ and $R_2 = C_mH_{2m+1}(O)-$, and classified into several packing modes according to the structures of chains; alkyl or alkoxy, normal or branched [1].

Figure 1 shows the representative packing modes of molecules with both the chains are octyl and/or octyloxy chains. **8O-O8** and **8O-8** are in the same packing mode, despite the different molecular shapes as a whole. A layer is composed of parallel molecules with one-dimensional chains of close arrangements of ester linkages (3.2–3.5 Å) with distances of C···O < distances of O···O. **8O-O1** [2], **1O-O8**, **1-O8** are in this group (designated as mode III in ref. 1). **8-O8** has a similar

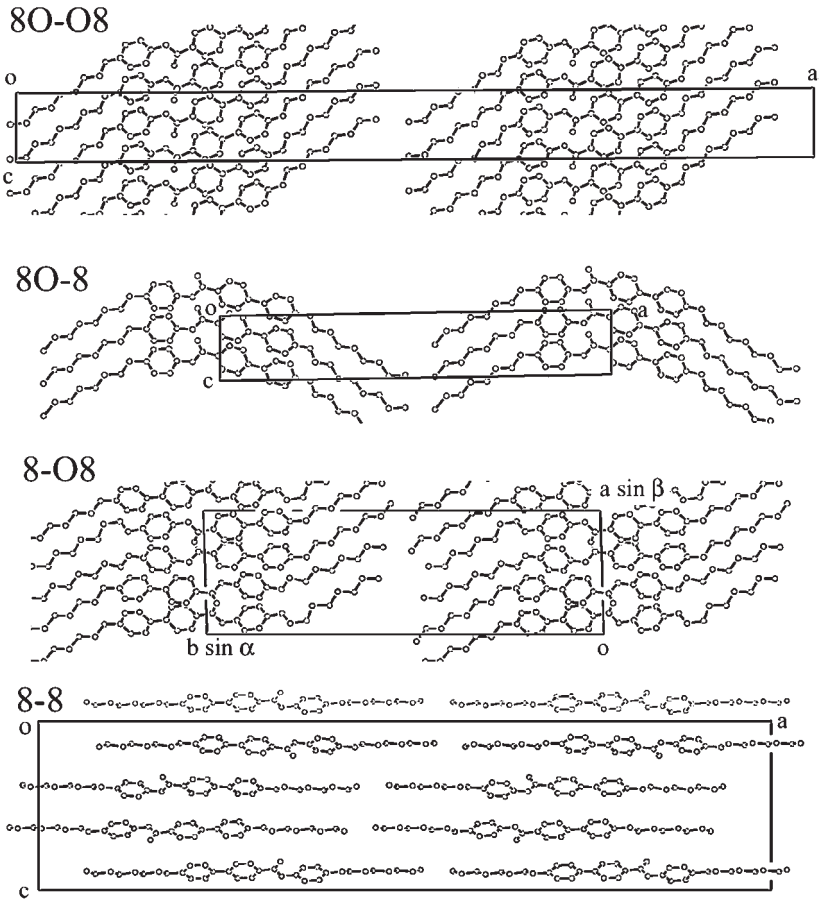


FIGURE 1 Representative packing modes previously found (from Ref. 1).

TABLE 1 Crystal Data, Experimental Details, and Results of Refinements

	1O-8	**1-8**	**1-1**
Formula	$C_{28}H_{32}O_3$	$C_{28}H_{32}O_2$	$C_{21}H_{18}O_2$
F. W.	416.56	400.56	302.35
Crystal shape	plate	plate	needle
Solvent	Ethyl acetate	Et_2O /EtOH	Ethyl acetate
Crystal size	0.3, 0.3, 0.01	0.3, 0.2, 0.01	0.6, 0.5, 0.07
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$Pca2_1$	$P2_1/c$	$P2_1/n$
a/Å	7.397(4)	5.97(2)	34.535(11)
b/Å	53.207(4)	7.96(2)	7.6564(12)
c/Å	5.658(6)	49.084(13)	6.077(2)
α/°	90	90	90
β/°	90	92.84(12)	90.96(2)
γ/°	90	90	90
V/Å^3	2227(2)	2331(10)	1606.7(7)
Z	4	4	4
d_X/g cm^{-3}	1.19	1.14	1.25
μ/mm^{-1}	0.593	0.541	0.624
No. of refl. measd.	2319	4641	4048
No. of unique refl.	2319	3222	2932
R_{int}	—	0.0238	0.0795
No. of refl. ($>2\sigma$(I))	830	2003	2414
$R1$ for $I>2\sigma(I)$	0.1230	0.1072	0.0577
Rw2 for $I>2\sigma(I)$	0.3668	0.1907	0.1723
S	0.949	1.132	1.019
$(\Delta/\sigma)_{max}$	0.129	0.048	0.003
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e A^{-3}	0.427, −0.395	0.201, −0.277	0.307, −0.199

arrangement but with distances of C···O > distances of O···O. **8O-1** belongs to the group (mode IV). On the other hand, **8-8** has a quite different packing from those mentioned above: units composed of parallel molecules are further arranged in an antiparallel way in every two columns. Distances between ester linkages are rather long (O···O > 3.8 Å). **8-1** belongs to this group (mode V).

In order to make clearer the different effect between alkyl and alkoxy chains, the simplest compounds having both the chains to be methyl and/or mthoxy groups, i.e., **1O-O1**, **1O-1**, **1-O1**, and **1-1**, have been synthesized. All the compounds are enantiotropic nematogens. It is noteworthy that a compound with methyl groups in both the terminal groups, which lacks the conformational change produces the enantiotropic nematic phase. This paper describes the crystal structures of **1-1**, **1-8**, and **1O-8** and relationships between molecular structures and mesophase behavior for these compounds.

EXPERIMENTAL

All the compounds were synthesized and purified similarly as described previously [1]. 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 diffraction was measured on a conventional diffractometer (Rigaku) with a heating stage.

X-ray diffraction data for single crystals were collected on an AFC-7R at room temperature using CuKα radiation monochromated by graphite ($\lambda = 1.5418$ Å). Absorption correction was made based on Ψ scan for **1-8** and **1-1**, but not for **1O-8** because of the absence of

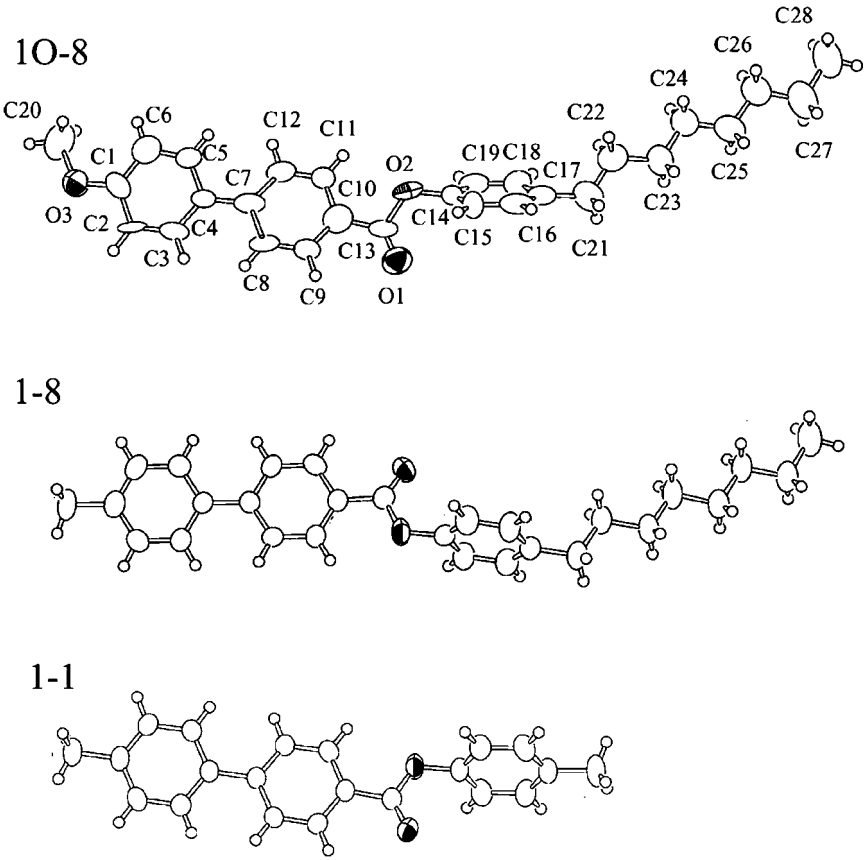


FIGURE 2 Molecular structures of **1O-8**, **1-8**, and **1-1**. Displacement ellipsoids are at 50% level. All molecules are numbered in the same scheme.

appropriate reflections for Ψ scan. Structures were solved and refined by using SHELXS86 [3] and SHELXL93 [4], respectively. Crystal data and results of the final refinements are summarized in Table 1. The large R-values of **1O-8** are attributable to weak intensities due to the small crystal size and poor crystallinity, despite the repeated attempts of crystallization. Final atomic coordinates and related materials were deposited at Cambridge Structural Database (No. 241544-241546).

RESULTS AND DISCUSSION

Molecular Structures

Figure 2 shows the molecular structures of **1O-8**, **1-8**, and **1-1**. Dihedral angles of biphenyl moieties are 8.6(7), 12.8(5), and 10.8(1)°, respectively. Dihedral angles between the phenyl ring and the octyl

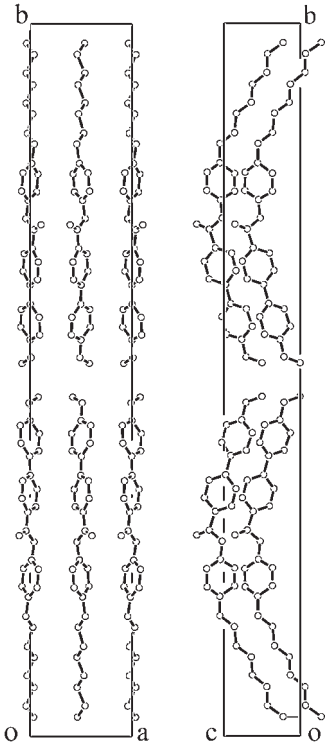


FIGURE 3 Crystal structure of **1O-8** viewed along the *c* (upper) and *a* (lower) axes. Hydrogen atoms are omitted for simplicity.

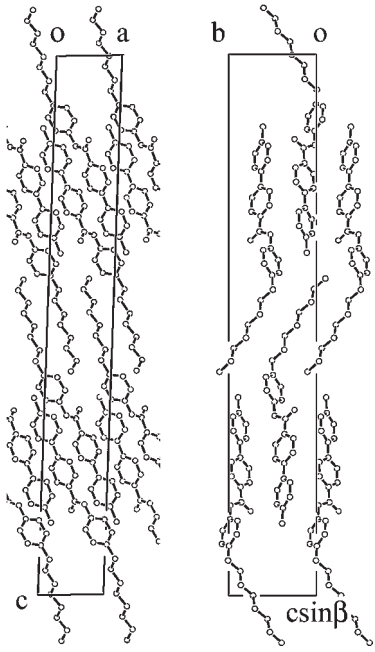


FIGURE 4 Crystal structure of **1-8** viewed along the *a* (upper) and *b* (lower) axes. Hydrogen atoms are omitted for simplicity.

chain (C−C−C plane) are 65.1 and 83.0° for **1O-8** and **1-8**, respectively. The bent shape of **1O-8** is very similar to that of **8O-8**. The dihedral angle between the phenyl ring and the octyl chain of **8O-8** is 63.2(7)° [1]. Semi-empirical MO calculations using AM1 and PM3 methods showed that the dihedral angles between the phenyl ring and the octyloxy or octyl chains determine the different molecular shapes of **8O-O8** (extended) and **8O-8** (bent), which are one of the most stable conformers [5].

Packing Modes

Figure 3 shows the crystal structure of **1O-8** viewed along the *c* and *a* axes. The packing mode is also very similar to that of **8O-8**. Here again molecules with an alkoxy chain and a long chain have arrangements in which ester linkages are close: 3.19 and 3.37 Å for C···O and O···O, respectively. Figure 4 shows the crystal structure of **1-8** viewed along the *a* and *b* axes. The packing mode is very different from the modes mentioned above in respect that ester linkages are

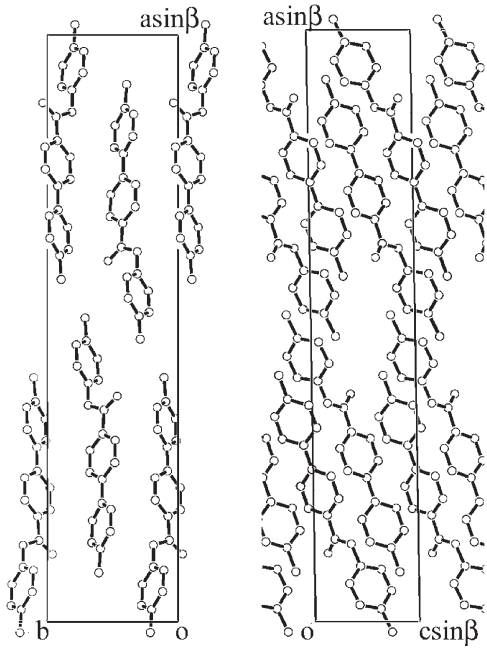


FIGURE 5 Crystal structure of **1-1** viewed along the *c* (upper) and *b* (lower) axes. Hydrogen atoms are omitted for simplicity.

far from each other between adjacent molecules. Core moieties aggregate and chain moieties are interdigitated. Figure 5 shows the crystal structure of **1-1** viewed along the *c* and *b* axes. The packing mode of core moieties is almost the same as that of **1-8**, but different from those of **8-8** and **8-1**. Thus the packing mode is designated as mode VI.

Mesophase Behaviour

The mesophase temperature ranges are shown in Figure 6 with the crystalline packing modes in parentheses. Liquid crystalline phases were characterized for **8O-O8**, **8O-8**, **8-O8**, and **8-8** [6], and for **8O-O1** and **8O-1** [7]. Those for others were identified by DSC results and microscope observation. X-ray diffraction showed the layer thickness of **8-O1** and **8-1** to be 28.3 (at 100°C) and 26.4 Å (at 107°C), respectively. These values are comparable with the molecular length of **8-1** derived from the X-ray structure (28.6 Å). It is noteworthy that **8(O)-(O)1** series has Sm A in addition to nematic, while **1(O)-(O)8** series has only nematic. Furthermore, **1(O)-(O)1** series also has

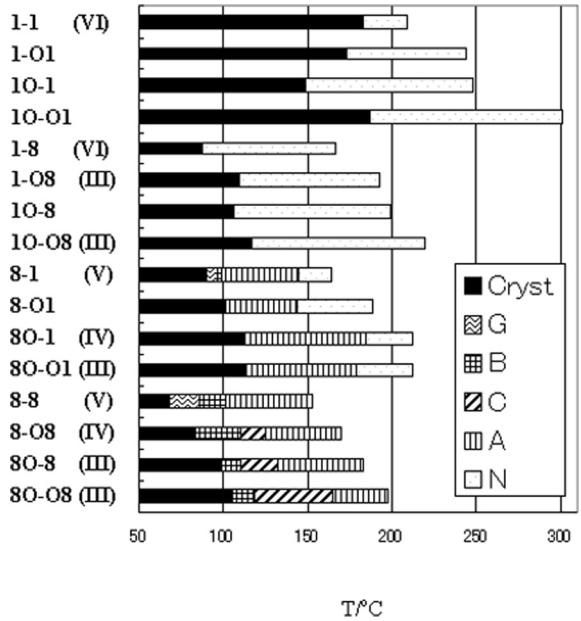


FIGURE 6 Phase sequences. Packing modes in crystal structures are shown in parentheses. For **8-1**, the G and B phases were tentatively assigned from the DSC results and the analogy of **8-8**.

nematic, despite the lack of flexible chains. In each series, clearing temperatures rise in the order of alkyl-alkyl, alkyl-alkoxy, alkoxy-alkyl, and alkoxy-alkoxy compounds. Liquid crystal phases are more stable for an alkoxy-alkyl compound than for an alkyl-alkoxy one in each series. This fact also shows the more dominant role of the chain attached to the biphenyl moiety.

CONCLUSIONS

1) Compounds with only methyl and/or methoxy groups have been synthesized and proved to be enantiotropic nematogens.
2) **1O-8** has a packing mode with one-dimensional chains of close arrangements of ester linkages in the crystal, as previously found for many biphenyl esters with at least one alkoxy chain.
3) **1-8** and **1-1** have very similar arrangements of core moieties with ester linkages far from each other in the crystals.
4) Clearing temperatures are higher for alkoxy-alkyl derivatives than for alkyl-alkoxy one in each series with the same number of carbon atoms.

These facts suggest the importance of alkoxyl O atom in crystal packing and more dominant role of the chain attached to a biphenyl moiety than that attached to a phenyl one.

REFERENCES

[1] Seo, N. & Hori, K. (2001). *Liq. Cryst*., *28*, 77–88 and references cited therein.
[2] Oki, M. & Hori, K. (1998). *Bull. Chem. Soc. Jpn*., *71*, 543.
[3] Sheldrick, G. M. 1986, SHELXS86. Program for the Solution of Crystal Structures. University of Göttingen, Germany.
[4] Sheldrick, G. M. 1993, SHELXS86. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
[5] Yoshida, M., Seo, N., Hori, K., & Toriumi, H. (2001). *Mol. Cryst. Liq. Cryst*., *365*, 813.
[6] Goodby, J. W., Gray, G. W., & McDonnell, D. C. (1976). *Mol. Cryst. Liq. Cryst*., *34*, 183.
[7] Takeda, H., Sakurai, Y., Takenaka, S., Miyake, H., Doi, T., & Kusabayashi, S. (1990). *J. Chem. Soc., Faraday Trans*., *86*, 3429.