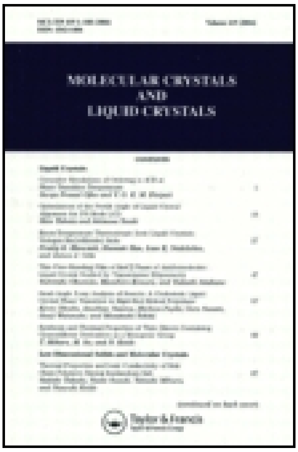

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Crystal Structures of 6OCB and 7OCB

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Crystal Structures of 6OCB and 7OCB

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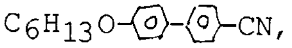
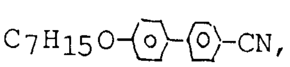
Crystal structures of title compounds have been determined by single crystal x-ray analysis. Crystal data. 4′-Hexyloxy-4-cyanobiphenyl (6OCB),



M_r = 279.37, monoclinic, $P2_1/a$, T = 298 K, a = 26.76(1), b = 7.609(3), c = 16.636(7) Å, β = 105.52(3)°, V = 3263(2) Å^3, Z = 8, d_x = 1.142 g cm^{-3}, μ(Mo Kα) = 0.37 cm^{-1}, $F(000)$ = 1200; 4′-Heptyloxy-4-cyanobiphenyl (7OCB),



M_r = 293.39, triclinic, $P\bar{1}$, T = 298 K, a = 12.6556(8), b = 19.044(2), c = 7.3495(5) Å, α = 94.142(8), β = 100.108(5), γ = 91.036(7)°, V = 1738.4(2) Å^3, Z = 4, d_x = 1.125 g cm^{-3}, μ(Cu Kα) = 4.58 cm^{-1}, $F(000)$ = 632. Molecular structures in both crystals are very similar with twisted biphenyl moieties and fully extended paraffin chains. Dimers are formed by close contacts of CN groups between neighboring molecules (C—N: 3.56 and 3.40 Å for 6OCB and 3.55 and 3.39 Å for 7OCB). The neighboring dimers in 6OCB are overlapped half-and-half, while those in 7OCB are arranged in a smectic-like layer structure.

INTRODUCTION

Good correlations between crystal structures and liquid crystalline phase behavior have been found by systematic single crystal x-ray analyses for chiral smectogenic biphenyl esters with various mesophase sequences.[1] On the other hand, 4′-alkoxy-4-cyanobiphenyls (nOCB) have relatively simple molecular structures with a systematic change of phase sequences according to the chain length: monotropic nematics for n = 1 ~ 4, nematics for n = 5 ~ 7, nematics and smectics A for n = 8 and 9, and only smectics A for n = 10 ~ 12.[2] Crystal structures, however, have been determined only for short-chain members ($n = 1 \sim 4$,[3] and 5[4]). In order to elucidate the intermolecular interaction controlling the systematic change of the phase sequences, we extended the crystal structure determination to longer-chain members. Here, we describe the crystal structures of 6OCB and one of the polymorphs of 7OCB (needle crystal).

EXPERIMENTAL

Single crystals were grown from an acetone-water solution of commercially available 6OCB or 7OCB (BDH Chemicals Ltd.) at about 5°C. Transparent plate-like crystals were obtained for 6OCB, while transparent plate-like and needle crystals were obtained for 7OCB. The former crystals of 7OCB degradated too rapidly to obtain the reflection data.

Procedures of data collection and final results of refinements are summarized in Table I. The structures were solved by using the program MULTAN78[5] for 6OCB and SHELX86[6] for 7OCB and refined by full-matrix least squares in two blocks using SHELX76.[7] The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = (\sigma(|F_o|)^2 + 0.004|F_o|^2)^{-1}$. Atomic scattering factors were taken from International Tables

TABLE I

Experimental details

	6OCB	7OCB
crystal habit	plate	needle
crystal size/mm	0.45x0.45x0.1	0.15x0.15x0.5
X-ray source	Mo Kα(0.71069 Å)	Cu Kα(1.54184 Å)
monochrometer	graphite	
diffractometer	off-centered AFC-5	AFC-4
l.s.for cell const.	17(15<2 θ<23°)	19(45<2θ<59°)
scan mode	2 θ−ω	
scan width/°	ω=(1.0+0.35tanθ)	ω=(1.0+0.15tanθ)
scan rate/° min^{-1} (2θ)	4	
background	5 s at both ends of a scan	
standard refl.	3 after every 50 refl.	
intensity variation	not significant	
total No. of refl	5745	5546
No.of refl.(>3σ)	4646	4140
correction	Lorentz and polarization	
Δ/σ	0.462	0.160
Δρ/e Å^{-3}	0.192	0.200
R	0.082	0.077
R$_w$	0.079	0.092

TABLE II

Final atomic coordinates with their estimated standard deviations, multiplied by 10^4, of 4'-hexyloxy-4-cyanobiphenyl (6OCB)

Atom	x	y	z	$B_{eq}/\text{Å}^2$
O (A)	1702(1)	5052(3)	442(1)	5.9
N (A)	5920(1)	3787(5)	3094(2)	7.8
C (1A)	4075(1)	3880(4)	2484(2)	5.5
C (2A)	5490(1)	3847(4)	2750(2)	6.0
C (3A)	4752(1)	4331(4)	1510(2)	5.5
C (4A)	4223(1)	4485(4)	1160(2)	5.4
C (5A)	3874(1)	4302(3)	1648(1)	4.8
C (6A)	4598(1)	3711(4)	2840(2)	5.7
C (7A)	4942(1)	3964(4)	2353(2)	5.1
C (8A)	3306(1)	4525(3)	1292(1)	4.7
C (9A)	3048(1)	3999(3)	484(2)	4.8
C(10A)	2519(1)	4150(4)	178(2)	4.9
C(11A)	2227(1)	4867(3)	669(2)	4.9
C(12A)	2478(1)	5452(4)	1468(2)	5.4
C(13A)	3002(1)	5272(4)	1771(2)	5.3
C(14A)	1413(1)	4475(5)	-363(2)	5.6
C(15A)	849(1)	4696(4)	-416(2)	6.0
C(16A)	501(1)	4370(5)	-1287(2)	5.7
C(17A)	-70(1)	4447(4)	-1318(2)	6.6
C(18A)	-427(1)	4119(6)	-2176(2)	7.5
C(19A)	-991(1)	4328(6)	-2204(2)	10.9
O (B)	9935(1)	7469(3)	4939(1)	6.3
N (B)	6016(1)	4326(4)	1012(2)	9.2
C (1B)	6419(1)	4546(4)	1449(2)	6.7
C (2B)	6931(1)	4861(3)	1989(2)	5.4
C (3B)	7000(1)	5788(4)	2729(2)	5.7
C (4B)	7491(1)	6172(3)	3206(2)	5.4
C (5B)	7933(1)	5634(3)	2983(1)	4.8
C (6B)	7854(1)	4653(4)	2248(2)	5.6
C (7B)	7367(1)	4280(4)	1763(2)	5.9
C (8B)	8462(1)	6096(3)	3487(2)	4.7
C (9B)	8572(1)	6450(3)	4342(1)	5.3
C(10B)	9063(1)	6882(3)	4807(2)	5.6
C(11B)	9465(1)	7015(3)	4425(2)	5.3
C(12B)	9363(1)	6677(4)	3586(2)	6.0
C(13B)	8874(1)	6238(4)	3129(2)	5.8
C(14B)	10366(1)	7600(4)	4583(2)	6.0
C(15B)	10838(1)	8069(5)	5267(2)	5.8
C(16B)	11325(1)	8198(4)	4985(2)	6.3
C(17B)	11801(1)	8592(5)	5702(2)	5.9
C(18B)	12303(1)	8609(5)	5465(3)	7.5
C(19B)	12775(1)	8909(8)	6190(4)	8.0

$$B_{eq}=(8\pi^2/3)\ \sum_i \sum_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

for X-ray Crystallography.[8] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms found in the difference Fourier maps and calculated geometrically (C—H, 1.0 Å) were refined isotropically. Computations were carried out on an IBM 4381-R24 computer at the Information Processing Center of Ochanomizu University. Final atomic coordinates are shown in Tables II and III.

TABLE III

Final atomic coordinates with their estimated standard deviations, multiplied by 10^4, of 4′-heptyloxy-4-cyanobiphenyl (7OCB)

Atom	x	y	z	$B_{eq}/\text{Å}^2$
O (A)	6835(2)	6923(1)	-9862(3)	6.1
N (A)	6966(3)	3319(2)	1235(5)	7.4
C (1A)	7044(3)	3689(2)	120(5)	5.9
C (2A)	7072(2)	4163(2)	-1320(5)	5.1
C (3A)	7480(3)	4848(2)	-924(5)	5.4
C (4A)	7439(3)	5291(2)	-2336(5)	5.4
C (5A)	6998(2)	5074(2)	-4159(4)	4.7
C (6A)	6616(3)	4380(2)	-4531(5)	5.6
C (7A)	6653(3)	3929(2)	-3138(5)	5.5
C (8A)	6921(2)	5565(2)	-5667(4)	5.0
C (9A)	7742(2)	6061(2)	-5691(5)	5.5
C(10A)	7679(3)	6508(2)	-7094(5)	5.5
C(11A)	6800(3)	6470(2)	-8517(4)	5.1
C(12A)	5982(3)	5981(2)	-8514(5)	5.5
C(13A)	6039(3)	5536(2)	-7107(5)	5.5
C(14A)	5971(3)	6903(2)	-11430(5)	5.8
C(15A)	6253(3)	7435(2)	-12674(6)	6.1
C(16A)	5411(3)	7463(2)	-14417(5)	5.9
C(17A)	5655(4)	8015(2)	-15651(6)	6.5
C(18A)	4821(4)	8067(3)	-17391(5)	6.5
C(19A)	5094(4)	8613(3)	-18618(7)	8.4
C(20A)	4274(6)	8694(4)	-20336(9)	9.8
O (B)	10046(2)	1171(1)	14963(3)	6.3
N (B)	9172(3)	4459(2)	3117(4)	6.8
C (1B)	9191(3)	4125(2)	4338(5)	5.4
C (2B)	9253(2)	3702(2)	5922(4)	4.6
C (3B)	8849(3)	3015(2)	5646(5)	5.6
C (4B)	8957(3)	2609(2)	7166(5)	5.6
C (5B)	9468(2)	2874(2)	8913(4)	4.6
C (6B)	9843(3)	3571(2)	9146(4)	4.9
C (7B)	9737(3)	3982(2)	7659(4)	5.0
C (8B)	9633(3)	2425(2)	10509(4)	4.8
C (9B)	8840(3)	1942(2)	10781(5)	5.3
C(10B)	9014(3)	1535(2)	12279(4)	5.4
C(11B)	9978(3)	1595(2)	13539(5)	5.2
C(12B)	10765(3)	2067(2)	13266(5)	5.7
C(13B)	10587(2)	2480(2)	11783(5)	5.6
C(14B)	10978(3)	1255(2)	16386(6)	5.9
C(15B)	10835(4)	755(2)	17839(6)	6.1
C(16B)	11793(3)	770(2)	19396(6)	6.2
C(17B)	11638(4)	268(2)	20833(6)	6.3
C(18B)	12574(4)	239(3)	22388(7)	7.2
C(19B)	12417(5)	-334(4)	23709(7)	8.7
C(20B)	13338(7)	-365(5)	25297(10)	11.5

$$B_{eq}=(8\pi^2/3)\sum_i \sum_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

RESULTS AND DISCUSSION

Molecular Conformation

There are two crystallographically independent molecules, A and B in an asymmetric unit of both crystals. The bond lengths and angles are compatible with other

TABLE IV

Torsion angles (°) of paraffin chains

	6OCB		7OCB	
	A	B	A	B
O-C(14)-C(15)-C(16)	171.9	178.2	-179.1	-177.7
C(14)-C(15)-C(16)-C(17)	175.2	-177.3	-177.5	180.0
C(15)-C(16)-C(17)-C(18)	179.7	175.8	179.0	-178.1
C(16)-C(17)-C(18)-C(19)	-175.9	-177.1	178.9	174.4
C(17)-C(18)-C(19)-C(20)			178.6	179.1

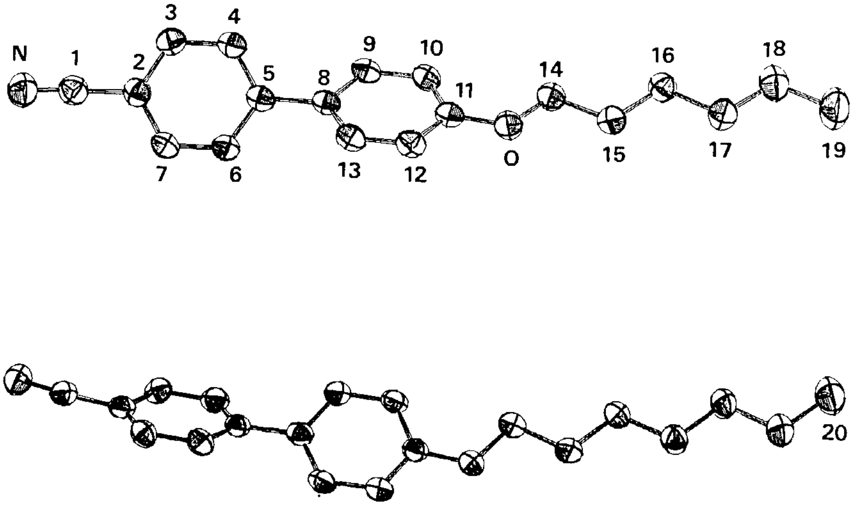


FIGURE 1 ORTEP drawings of the molecules A of 6OCB (upper) and 7OCB (lower), with 50% probability ellipsoids. Numbering schemes are the same for all the molecules.

mesogens.[3,4] The phenyl rings are planar within the experimental errors. All the molecules have similar conformations: twisted biphenyl moieties (36° (A) and 26° (B) for 6OCB and 37° (A) and 40° (B) for 7OCB) and almost all-trans zig-zag chains as shown in Table IV. Figure 1 shows ORTEP drawings[10] with numbering scheme of the molecules A of 6OCB (upper) and 7OCB (lower). In contrary, a highly planar biphenyl moiety (0.82°) and a twisted O—C—C—C chain were found in 5OCB.[4]

Crystal Packing

Figure 2 shows the crystal structure of 6OCB. Molecules are arranged in a parallel way and stacked along the *b* axis, being related by a 2-fold screw axis for A and by an inversion for B. Close contacts of CN groups are found between the un-

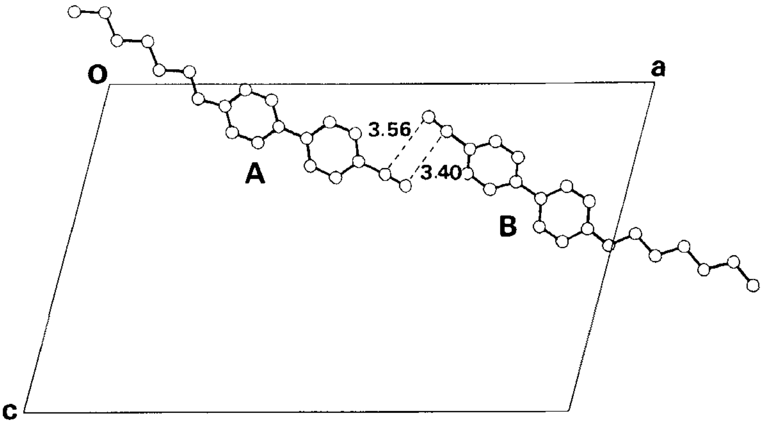


FIGURE 2 Crystal structure of 6OCB viewed along the *b* axis. Close contact of CN—CN are shown by broken lines with distance (Å).

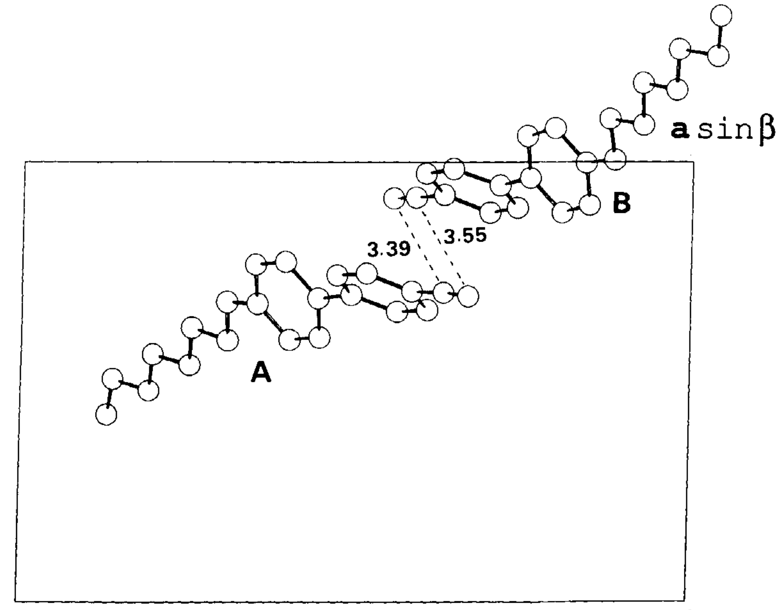


FIGURE 3 Crystal structure of 7OCB viewed along the *c* axis. Close contact of CN—CN are shown by broken lines with distance (Å).

equivalent molecules A and B: 3.57 (N(A)—N(B)), 3.40 (N(A)—C(B)) and 3.56 Å (C(A)—N(B)). In addition, a short O—O distance (3.87 Å) is found between the inversion-related B molecules. Thus the molecules A and B are in rather different environment from each other.

Figure 3 shows the crystal structure of 7OCB. Here again, close contacts of CN groups are found between molecules A and B: 3.52 (N(A)—N(B)), 3.39

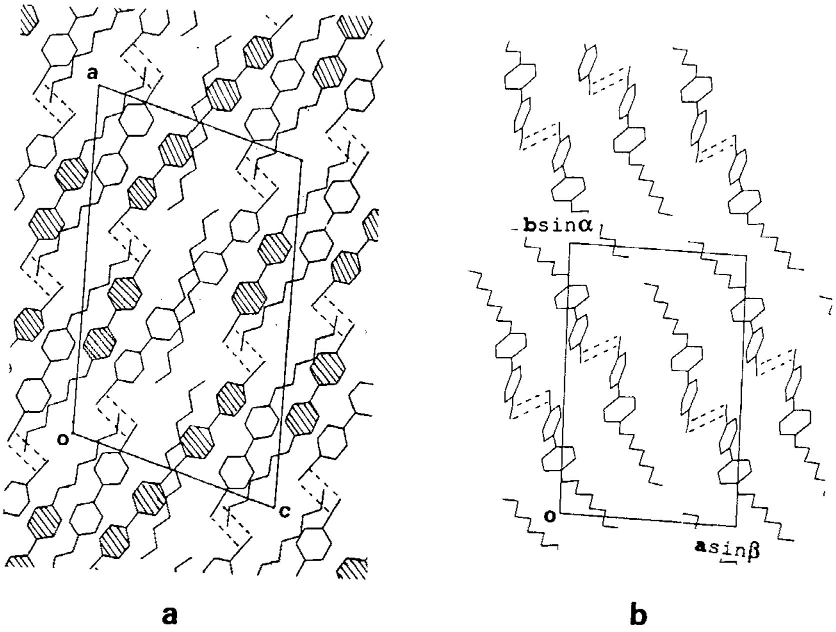


FIGURE 4 Schematic diagrams of crystal packings of 6OCB (a) and 7OCB (b). In (a), shadowed and unshadowed molecules denote those at different height along the *b* axis (about 0.5 and 0.0, respectively, although the molecules have slight tilts with ac plane). Close contacts of CN groups are denoted by broken lines.

(N(A)—C(B)) and 3.55 Å (C(A)—N(B)). In 5OCB crystal, an infinite chain of close contacts of CN groups (C—N, 3.338 and 3.304 Å with the two neighboring molecules) was found along the *b* axis. Therefore, a tendency of dimer formation is clearer in the present crystals than in 5OCB.

In spite of these similarities of 6OCB and 7OCB in molecular conformations and dimer formations, the crystal packings are quite different, as schematically shown in Figure 4. In 6OCB, neighboring dimers shift each other by a molecular length; a half of a dimer is overlapped with a half of a neighboring dimer and another half with a half of another neighbor. This feature of a half-and-half overlapping is closely related to a nematic structure.

On the other hand, dimers in 7OCB are arranged in a smectic-like layer structure, whose layer plane is the ac plane. The tilt angle is estimated to be 64° from the layer thickness and the length of the dimer (a sum of the distance between the terminal C(20A) and C(20B) atoms of the dimer and twice of van der Waals radius of methyl group (2.0 Å)).

Relationship Between the Crystal Structures and Liquid Crystalline Behavior

Repeat distances of about 1.4 molecular lengths have been observed in both nematics and smectics A of nCB and nOCB series by X-ray diffraction studies[11–14] and interpreted to be due to largely overlapped dimer formed by CN and phenyl contacts.[11,13] In the present crystals, however, dimers are formed by CN—CN end group contacts. This indicates that packing efficiency is more important in the crystalline states than in the fluid liquid crystalline states. Relaxation to the more overlapped structure would be caused at the crystal-mesophase transition.

In spite of the same phase sequence of 6OCB and 7OCB, i.e., cryst.-nem.-isotropic, crystal packings are quite different; the crystal structure of the former is closely related to a nematic, while the latter to a smectic. This is interpreted as follows; the tendency that a smectic structure is stable above $n = 8$ appears already in 7OCB in the crystalline state, although the layer struture is not stable enough in the liquid crystalline phase with large thermal motions.

Polymorphism and phase transition behavior of 7OCB will be described elsewhere.

Acknowledgment

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Supplementary Material

Bond distances (Å) and angles (○) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. 90263. Copies may be obtained through Customer Services, The British Library, Document Supply Centre, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, UK.

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