

4'-Octyloxybiphenyl-4-carbonitrile
polymorph IIIRoger J. Davey, Amy L. Gillon, Michael J. Quayle* and
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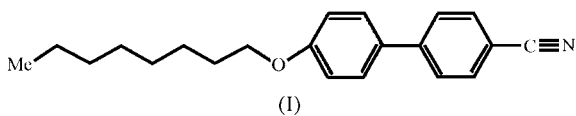
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The title compound, $C_{21}H_{25}NO$, is a member of a well known family of liquid crystals (4-oxy-4'-cyanobiphenyls, OCBs) and packs in lamellar-type bilayers in the solid state, through $CN\cdots H$ hydrogen bonds. This packing type is analogous to that found of other members of the *n*-OCB homologous series, *viz.* 7-OCB and 9-OCB.

Comment

The OCB family of compounds (4-*n*-alkoxy-4'-cyano-biphenyls) are well known and well utilized for their thermotropic (melt) liquid crystal behaviour, with the members in the range $n = 5-8$ forming both smectic A and nematic phases. Since these molecules readily order themselves to some degree in the liquid crystal phases, we were interested in probing structural mechanisms during the crystallization



event. On cooling the systems from the higher-temperature melt through the different liquid crystal stages, through to crystallization, the long-range *d*-spacing was tracked by *in situ* powder diffraction. The aim was to understand the molecular-molecular associations, through the various stages of assembly, before the system crystallizes. During the course of

this work, a number of new crystal structures were encountered, as identified by X-ray powder diffraction patterns. To exploit as much structural information as possible, attempts at growing single crystals with diffraction patterns matching those of the unknown crystalline phases were made.

The title compound, (I), is the third identified polymorph of 8-OCB (4-octyloxy-4'-cyanobiphenyl polymorph), and packs in the same arrangement as polymorphs of 7-OCB (Hori, Koma *et al.*, 1996) and 9-OCB (Hori & Wu, 1999). The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The two rings of the biphenyl group are rotated by $\sim 42^\circ$, and the $C15-C14-O1-C11$ torsion angle is $168.7(2)^\circ$. The aliphatic chain is in a rigid conformation, apparently to aid efficient packing. The molecular packing, which is rich in $CN\cdots H$ hydrogen bonds, is shown in Fig. 2. A number of notable features are apparent from the packing arrangement. Molecules pack head-to-head, forming bilayers (*ca* 36 Å in length) extending along the *a* axis. Each molecule forms four hydrogen bonds (two symmetry unique) with two head-on molecules. Pairs of hydrogen bonds (centrosymmetric dimers) in turn form catemeric chains along the *b* axis. The head-to-head packing of molecules in the *a* direction has a lateral displacement of 1.9 Å relative to the mean planes of the pairs of terminal arene groups. A second, identical, set of catemeric chains (not shown in Fig. 2) extends in the *b* direction but at *ca* 45° to the first set.

The two unique $CN\cdots H$ hydrogen bonds are $N1\cdots H7$ and $N1\cdots H3$ (Table 2), as shown in Fig. 2, with $C1-N1\cdots H7$ and $C1-N1\cdots H3$ angles of 135 and 131° . The $C1-C2$ bond is unusually long for a Csp^2-Csp bond [$1.455(4)$ Å], possibly as a result of the π -electron withdrawing cyano group and its associated hydrogen bonds.

Polymorphs of 7-OCB (Hori, Koma *et al.*, 1996) and 9-OCB (Hori & Wu, 1999) also display this packing configuration, with $CN\cdots H$ hydrogen-bond lengths over the narrow range 2.68–2.76 Å. Another polymorph of 8-OCB (Hori, Kurosaki *et al.*, 1996; Rajnikant *et al.*, 2000) also has layered-type packing, but in this configuration dimers are again formed through $CN\cdots H$ interactions, which extend only to tetramers. In this form, the direction of adjacent pairs of molecules at the interface is different from that in (I), *i.e.* chains in the *a* direction are antiparallel. In a final type of polymorph displayed by 7-OCB (Hori *et al.*, 1995) and 8-OCB (Hori, Kurosaki *et al.*, 1996), another mixed bilayer structure is

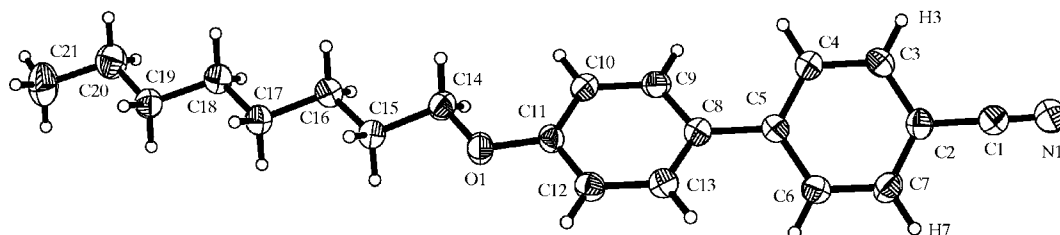
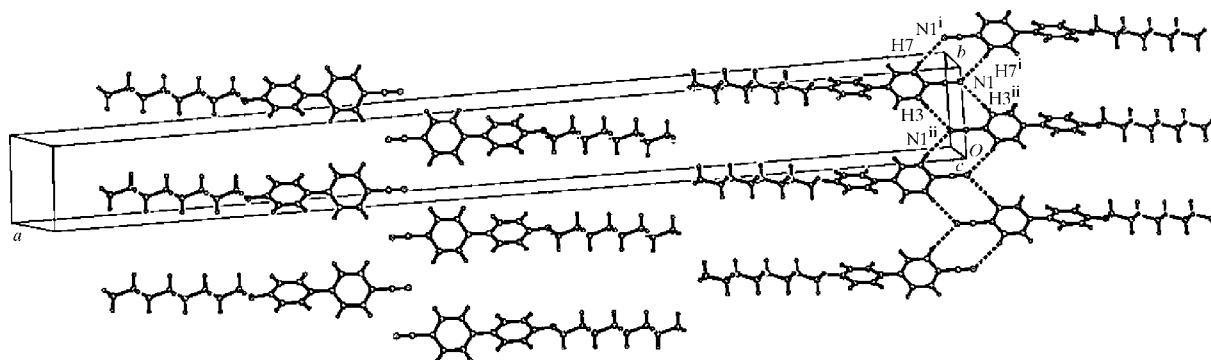


Figure 1

A view of (I), showing 50% probability displacement ellipsoids.


Figure 2

A packing diagram of (I), viewed along the *a* axis. [Symmetry codes: (i) $-x, 2 - y, 1 - z$, (ii) $-x, 1 - y, 1 - z$.]

formed, but notably in this case the $\text{CN} \cdots \text{H}$ dimer is absent; a CN group is close not to another CN group but to the biphenyl moiety. The O atom is utilized forming $\text{O} \cdots \text{H}$ hydrogen bonds along with $\text{CN} \cdots \text{H}$ hydrogen bonds.

The number and structural variety of polymorphs (at least five known) exhibited by the *n*-OCB series of compounds (the structural identity of some is still unknown) is typical of compounds that exhibit liquid crystalline behaviour. The apparent ease at which one form might be crystallized over another is caused by weak and competing intermolecular interactions.

Experimental

Crystals of 8-OCB form III were grown from propan-2-ol (0.1 g ml⁻¹) at 278 K, yielding transparent crystals with a plate morphology.

Crystal data

$\text{C}_{21}\text{H}_{25}\text{NO}$	Mo $K\alpha$ radiation
$M_r = 307.42$	Cell parameters from 865 reflections
Monoclinic, $C2/c$	$\theta = 5\text{--}50^\circ$
$a = 73.814$ (15) Å	$\mu = 0.07 \text{ mm}^{-1}$
$b = 7.0080$ (14) Å	$T = 293$ (2) K
$c = 6.8710$ (14) Å	Plate, transparent
$\beta = 94.98$ (3)°	$0.20 \times 0.20 \times 0.05 \text{ mm}$
$V = 3540.9$ (12) Å ³	
$Z = 8$	
$D_x = 1.153 \text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD diffractometer	1551 reflections with $I > 2\sigma(I)$
φ or ω scans	$R_{\text{int}} = 0.032$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$\theta_{\text{max}} = 25.0^\circ$
$T_{\text{min}} = 0.976$, $T_{\text{max}} = 0.996$	$h = -87 \rightarrow 88$
6626 measured reflections	$k = -8 \rightarrow 8$
3073 independent reflections	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.159$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.99$	$\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{Å}^{-3}$
3073 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{Å}^{-3}$
210 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0017 (4)

H atoms were constrained to idealized geometries and assigned $U_{\text{iso}}(\text{H})$ values of 1.2 times U_{eq} of their attached C atom for aromatic H atoms and $1.5U_{\text{eq}}$ for all others.

Table 1

Selected geometric parameters (Å, °).

C1—N1	1.132 (3)	C11—O1	1.377 (3)
C1—C2	1.455 (4)	C14—O1	1.443 (3)
C5—C8	1.487 (3)		
N1—C1—C2	178.8 (3)	O1—C14—C15	107.5 (2)
O1—C11—C10	124.1 (2)	C11—O1—C14	117.2 (2)
O1—C11—C12	116.0 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
$\text{C7}^i\text{—H7}^i \cdots \text{N1}$	0.93	2.74	3.400 (4)	129
$\text{C3}^{ii}\text{—H3}^{ii} \cdots \text{N1}$	0.93	2.68	3.420 (3)	137

Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.

Data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXL97; software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1183). Services for accessing these data are described at the back of the journal.

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