*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.129$
$S = 0.860$
10 834 reflections
612 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0807P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.068$
$\Delta\rho_{\max} = 0.547$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.405$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997*b*)
Extinction coefficient: 0.0047 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Si1*A*—C9*A* | 1.854 (3) | Si1*B*—C9*B* | 1.860 (2) |
| Si1*A*—C13*A* | 1.864 (3) | Si1*B*—C13*B* | 1.862 (3) |
| Si1*A*—C6*A* | 1.865 (2) | Si1*B*—C6*B* | 1.853 (3) |
| Si1*A*—C2*A* | 1.866 (3) | Si1*B*—C2*B* | 1.864 (3) |
| C2*A*—C3*A* | 1.548 (4) | C2*B*—C3*B* | 1.549 (3) |
| C3*A*—C4*A* | 1.537 (4) | C3*B*—C4*B* | 1.532 (4) |
| C4*A*—Si5*A* | 1.905 (3) | C4*B*—Si5*B* | 1.896 (3) |
| Si5*A*—C6*A* | 1.857 (3) | Si5*B*—C6*B* | 1.861 (2) |
| Si5*A*—C16*A* | 1.861 (3) | Si5*B*—C16*B* | 1.851 (4) |
| Si5*A*—C17*A* | 1.865 (3) | Si5*B*—C17*B* | 1.880 (4) |
| C6*A*—C7*A* | 1.355 (4) | C6*B*—C7*B* | 1.358 (3) |
| C7*A*—C8*A* | 1.520 (3) | C7*B*—C8*B* | 1.518 (3) |
| C8*A*—C9*A* | 1.360 (3) | C8*B*—C9*B* | 1.352 (4) |
| C9*A*—Si10*A* | 1.862 (2) | C9*B*—Si10*B* | 1.860 (2) |
| Si10*A*—C20*A* | 1.854 (3) | Si10*B*—C20*B* | 1.869 (3) |
| Si10*A*—C21*A* | 1.864 (4) | Si10*B*—C21*B* | 1.853 (3) |
| Si10*A*—C11*A* | 1.906 (3) | Si10*B*—C11*B* | 1.898 (3) |
| C11*A*—C12*A* | 1.532 (4) | C11*B*—C12*B* | 1.556 (4) |
| C12*A*—C13*A* | 1.543 (3) | C12*B*—C13*B* | 1.549 (4) |
| C9*A*—Si1*A*—C6*A* | 94.23 (11) | C6*B*—Si1*B*—C9*B* | 94.06 (11) |
| C13*A*—Si1*A*—C6*A* | 121.76 (11) | C6*B*—Si1*B*—C13*B* | 120.20 (12) |
| C9*A*—Si1*A*—C13*A* | 106.88 (12) | C9*B*—Si1*B*—C13*B* | 105.71 (11) |
| C6*A*—Si1*A*—C2*A* | 105.45 (11) | C6*B*—Si1*B*—C2*B* | 106.24 (11) |
| C9*A*—Si1*A*—C2*A* | 119.63 (11) | C9*B*—Si1*B*—C2*B* | 121.55 (11) |
| C13*A*—Si1*A*—C2*A* | 109.14 (13) | C13*B*—Si1*B*—C2*B* | 109.33 (13) |
| C3*A*—C2*A*—Si1*A* | 113.24 (16) | C3*B*—C2*B*—Si1*B* | 112.82 (18) |
| C4*A*—C3*A*—C2*A* | 113.0 (2) | C4*B*—C3*B*—C2*B* | 113.0 (2) |
| C3*A*—C4*A*—Si5*A* | 118.04 (18) | C3*B*—C4*B*—Si5*B* | 119.26 (18) |
| C16*A*—Si5*A*—C17*A* | 109.71 (19) | C16*B*—Si5*B*—C17*B* | 112.2 (2) |
| C6*A*—Si5*A*—C4*A* | 105.89 (11) | C6*B*—Si5*B*—C4*B* | 106.92 (11) |
| C7*A*—C6*A*—Si1*A* | 106.31 (16) | C7*B*—C6*B*—Si1*B* | 106.98 (16) |
| C7*A*—C6*A*—Si5*A* | 132.98 (19) | C7*B*—C6*B*—Si5*B* | 131.8 (2) |
| Si5*A*—C6*A*—Si1*A* | 117.25 (14) | Si1*B*—C6*B*—Si5*B* | 118.13 (14) |
| C6*A*—C7*A*—C8*A* | 116.5 (2) | C6*B*—C7*B*—C8*B* | 115.7 (2) |
| C9*A*—C8*A*—C7*A* | 116.1 (2) | C9*B*—C8*B*—C7*B* | 116.8 (2) |
| C8*A*—C9*A*—Si10*A* | 132.3 (2) | C8*B*—C9*B*—Si10*B* | 133.16 (18) |
| C8*A*—C9*A*—Si1*A* | 106.72 (17) | C8*B*—C9*B*—Si1*B* | 106.38 (16) |
| Si1*A*—C9*A*—Si10*A* | 118.12 (14) | Si10*B*—C9*B*—Si1*B* | 117.28 (15) |
| C20*A*—Si10*A*—C21*A* | 111.6 (2) | C21*B*—Si10*B*—C20*B* | 110.13 (19) |
| C9*A*—Si10*A*—C11*A* | 106.59 (11) | C9*B*—Si10*B*—C11*B* | 106.02 (11) |
| C12*A*—C11*A*—Si10*A* | 119.34 (19) | C12*B*—C11*B*—Si10*B* | 118.10 (17) |
| C11*A*—C12*A*—C13*A* | 113.9 (2) | C13*B*—C12*B*—C11*B* | 112.9 (2) |
| C12*A*—C13*A*—Si1*A* | 113.05 (17) | C12*B*—C13*B*—Si1*B* | 113.25 (18) |

The two independent molecules (*A* and *B*) in the asymmetric unit not only possess pseudo-twofold symmetry but are also related by a pseudo-twofold screw axis. A thorough search for a suitable monoclinic cell, using the programs *LEPAGE* (Spek, 1988) and *DELOS* (Burzlaff & Zimmerman, 1985), for example, gave no satisfactory result. H atoms were included in calculated positions and treated as riding atoms.

Data collection: *EXPOSE* (Stoe & Cie, 1996). Cell refinement: *CELL* (Stoe & Cie, 1996). Data reduction: *INTEGRATE* (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *Xtal_GX* (Hall & du Boulay, 1997). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1538). Services for accessing these data are described at the back of the journal.

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# 4-Cyano-4′-octylbiphenyl

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## Abstract

The title compound, 4′-octylbiphenyl-4-carbonitrile, $C_{21}H_{25}N$, has the phase sequence crystal–smectic A ($S_A$)–nematic–isotropic. In the crystal structure, infinite chains with a close arrangement of CN groups are found.

## Comment

The title compound and its homologues, 4′-alkyl-4-cyanobiphenyl (*n*CB), have been widely studied as key examples of liquid crystalline behaviour, because of the accessibility of their liquid crystalline phases (low melting points), their stable properties and their simple molecular structures (Gray, 1998).

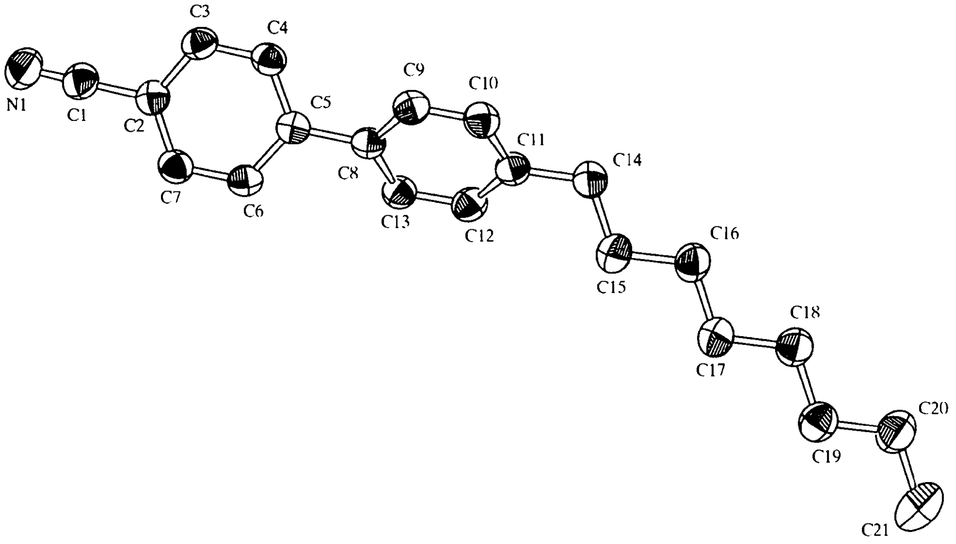
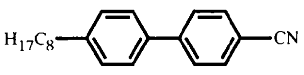


Fig. 1. The molecular structure of 8CB with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Crystal structures have been determined for the lower ($n \leq 5$) (Haase *et al.*, 1983, 1992; Vani, 1983; Hanemann *et al.*, 1995) and higher ($n$ = 9, 10, 11) (Manisekaran *et al.*, 1995, 1997) homologues, while those of the intermediate chain-length homologues have not been determined. Cell parameters were estimated for crystals of 8CB, as well as 9CB, obtained from the melts (the $S_A$ phase). However, the density values derived from the parameters seem to be too low, *i.e.* 0.87 and 0.84 Mg m$^{-3}$ for 8CB and 9CB, respectively (Chu *et al.*, 1988). The liquid crystalline phase sequences change from crystal–nematic–isotropic ($n$ = 6, 7) to crystal–smectic A–nematic–isotropic ($n$ = 8). Therefore, we have tried a systematic crystal structure determination of the intermediate homologues. This paper describes the crystal structure of 8CB, whose cell parameters are totally different from those estimated previously.



8CB

The molecular structure of 8CB with the atomic numbering scheme is shown in Fig. 1. The C4—C5—C6, C9—C8—C13 and C10—C11—C12 bond angles are slightly smaller than 120°, as was also observed in the higher homologues (Manisekaran *et al.*, 1995, 1997). The dihedral angle between the rings of the biphenyl moiety is 39.12 (5)°. The alkyl chain has an all-*trans* conformation and the dihedral angle between the plane of the C—C—C backbone of the alkyl chain and its attached benzene ring (C8–C13) is 34.92 (8)°.

The crystal structure viewed along the *b* axis is shown in Fig. 2. The cyano groups are closely arranged, with C···N distances of 3.336 (3) for C1···N1 ($-x+\frac{1}{2}$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$) and 3.283 (3) Å for C1···N1 ($-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$). Thus, they form an infinite chain with a close arrangement of CN groups along the *b* axis. A similar arrangement of CN groups was observed for 4′-pentyloxy-4-cyanobiphenyl (Mandal & Paul, 1985). In both crystals, smectic-like layer structures are not remarkable.

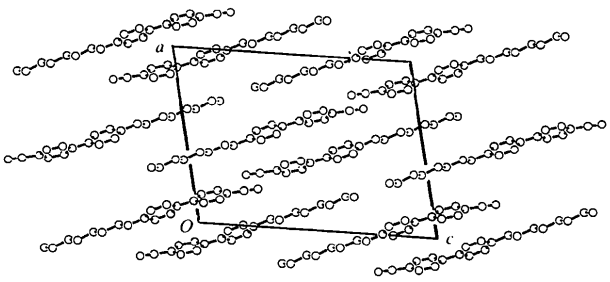


Fig. 2. The crystal structure of 8CB viewed along the *b* axis.

The crystal structure of 8CB is quite different from those of 9CB and 11CB, where the CN group is close to a ring of the biphenyl moiety of an adjacent molecule in the smectic-like layer structures. On the other hand, 8CB and 10CB have similar modes of packing, with CN···CN interactions.

## Experimental

A sample of 8CB was purchased from BDH. Single crystals were obtained from an ethanol/ethyl acetate solution kept in a refrigerator.

*Crystal data*

$C_{21}H_{25}N$
$M_r = 291.42$
Monoclinic
$P2_1/n$
$a = 14.939\,(3)$ Å
$b = 6.078\,(4)$ Å
$c = 19.740\,(2)$ Å
$\beta = 102.345\,(12)°$
$V = 1750.9\,(11)$ Å$^3$
$Z = 4$
$D_x = 1.106$ Mg m$^{-3}$
$D_m$ not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 27–29°$
$\mu = 0.475$ mm$^{-1}$
$T = 240$ K
Plate
0.50 × 0.40 × 0.05 mm
Colourless

*Data collection*

Rigaku AFC-7*R* diffractometer
$2\theta-\omega$ scans
Absorption correction: none
2706 measured reflections
2595 independent reflections
2224 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.086$
$\theta_{\rm max} = 60°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 6$
$l = -22 \rightarrow 21$
3 standard reflections every 150 reflections intensity decay: −0.22%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.153$
$S = 1.041$
2595 reflections
200 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.1034P)^2 + 0.2489P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.062$
$\Delta\rho_{\rm max} = 0.192$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.184$ e Å$^{-3}$
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0028 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N1—C1 | 1.144 (2) | C1—C2 | 1.443 (2) |
| C4—C5—C6 | 117.67 (14) | C10—C11—C12 | 116.91 (14) |
| C9—C8—C13 | 117.32 (14) | | |

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1062). Services for accessing these data are described at the back of the journal.

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# Complex of (−)-Morphine with *β*-Phenylhydracrylic Acid†

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## Abstract

The crystal structure of the complex of (−)-morphine with (*S*)-*β*-phenylhydracrylic acid, $C_{17}H_{20}NO_3^+.C_9H_9O_3^-$, is reported. There are no major differences in the conformation of the piperidine ring of morphine compared with other protonated morphines. The staggered conformation of the central bond in the free form of *β*-phenylhydracrylic acid changes to another staggered conformation in the morphine complex. This conformational change is induced by intermolecular hydrogen bonds.

## Comment

Morphine is the most important component of *papaver somniferum* extracts, which have been used as pain-alleviating medicine since ancient times. From a chemical point of view, morphine would be an interesting agent for resolving stereoisomers, but its

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† Systematic names: (5*α*,6*α*)-7,8-didehydro-4,5-epoxy-17-methylmorphinan-3,6-diol (CAS-No. 57-27-2) and (*S*)-3-hydroxy-3-phenylpropanoic acid (CAS-No. 36567-72-3).