Sawzik, P. & Craven, B. M. (1979). *Liquid Crystals*, edited by S. Chandrasekhar, pp. 171–178. London: Heyden.
Sawzik, P. & Craven, B. M. (1980). *Acta Cryst.* B**36**, 215–218.
Socci, E. P., Farmer, B. L., Chabinyc, M. L., Fratini, A. V., Bunning, T. J. & Adams, W. W. (1995). *Acta Cryst.* C**51**, 888–891.

Acta Cryst. (1995). C**51**, 1447–1452

A Crystalline Inclusion Compound and Two Host Structures Containing Chiral Molecules Derived from Lactic Acid

Antonio L. Llamas-Saiz and Concepción Foces-Foces*

Departamento de Cristalografía, Instituto de Química-Física 'Rocasolano', CSIC, Serrano 119, E-28006 Madrid, Spain

Edwin Weber and Claus Wimmer

Institut für Organische Chemie der Technischen Universität Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg/Sa, Germany

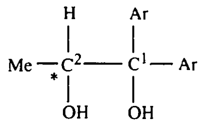
(*Received* 5 *October* 1994; *accepted* 17 *January* 1995)

Abstract

The X-ray crystal structures of an inclusion compound with 3-picoline and two free host structures, all based on lactic acid but having different aryl substitution and optical resolution states (*S* or *RS*), are reported. They are the 2:1 complex of (*S*)-1,1-bis(*p-tert*-butylphenyl)-1,2-propanediol with 3-picoline, (5) [(*S*)-1,1-bis(*p-tert*-butylphenyl)-1,2-propanediol–3-methylpyridine (2/1), $2C_{23}H_{32}O_2.C_6H_7N$], (*S*)-1,1-bis(*p*-methylphenyl)-1,2-propanediol, (6), $C_{17}H_{20}O_2$, and (*RS*)-1,1-bis(1-naphthyl)-1,2-propanediol, (7), $C_{23}H_{20}O_2$. The main structural differences between the host molecules in the three compounds are in the conformation of the phenyl or naphthyl rings. The influence of these rings is reflected in the elongation of the C(1)—C(2) bond in the propanediol moiety [up to 1.560 (5) Å] and in the angular distortion of the tetrahedral angles around C(2). The hydroxyl groups play an important role in the crystal packing in all three. Significant differences between these structures and those of the corresponding unsubstituted phenyl host and inclusion compounds are observed.

Comment

The determination of the crystal and molecular structures of compounds (5), (6) and (7) has been undertaken as part of a broad project on crystalline inclusion compounds derived from natural lactic acid. Optically resolved crystalline hosts of type (I) have proved efficient in the enantioseparation of different guest compounds by co-crystallization or vapour sorption. The crystal structures previously studied are those of compounds (1)–(4) (Weber, Wimmer, Llamas-Saiz & Foces-Foces, 1992; Llamas-Saiz, Foces-Foces, Weber & Wimmer, 1993).



(I)

(1): Ar = Ph (2*RS*) (racemic)
(2): Ar = Ph (2*S*)
(3): (2)–3-picoline (2/1)
(4): (2)–3-methylcyclohexanone (2/1)
(5): [Ar = *p*-(*t*-BuPh) (2*S*)]–3-picoline (2/1)
(6): Ar = *p*-MePh (2*S*)
(7): Ar = 1-naphthyl (2*RS*) (racemic)

The most relevant geometrical parameters are given in Table 4 according to the atom-numbering systems shown in Fig. 1. All seven compounds studied show similar features, that is, a *gauche* conformation for the hydroxyl groups, an angular distortion of the tetrahedral angles at C(1) [105.9 (2)–114.1 (2)° in (7); see Table 4] and an opening of the *ipso* angle in the phenyl derivatives as a consequence of the σ-withdrawing effect of the substituents (Domenicano & Vaciago, 1979). The naphthalene moiety displays the same pattern of bond distances and angles as naphthalene itself (Brock & Dunitz, 1982).

The packing of (5) presents a pattern of hydrogen bonds similar to (3). Both hydroxy groups of molecule *B* are involved in strong hydrogen bonds which link the two independent molecules *A* and *B* (both with the configuration *S*) and the 3-picoline molecule. H(5)*A* is involved in an intermolecular hydrogen bond, which results in chains along the *c* axis, while the interaction of H(4)*A* is weaker than the corresponding interaction in (3) [3.543 (4) in (5) *versus* 2.805 (9) Å in (3); see Table 5 and Fig. 1*a*] probably as a result of the bulky substituents. The chains of host–guest complexes along the *c* axis are connected by methyl–phenyl interactions with the methyl H atoms pointing towards the phenyl rings. There is a sinusoidal appearance of the phenyl-ring packing along **b** and the *tert*-butyl group packing along **a** (Fig. 2). This resembles the packing in (3) but with the phenyl–phenyl interactions replaced by methyl–phenyl interactions.

In (6), the two independent molecules and those related by a twofold axis parallel to **c** are linked to form tetramers (Table 5). The crystal comprises these tetrameric units, linked together by weak phenyl–phenyl *T*-type interactions (Fig. 3). H(5)*B* appears to be disordered between two sites [H(51) and H(52), Fig. 1*b*], one involved in a strong hydrogen bond [O(5)*B*···O(5)*B*(1 − *x*, 1 − *y*, *z*) 2.792 (6) Å] and the other leaving this atom free from interaction (Fig. 3).

The secondary structure in (7) is mainly due to hydroxyl–naphthalene interactions linking molecules along the [001] direction (Table 5). The shortest H···C distances are those involving C(14), C(15) and C(16)

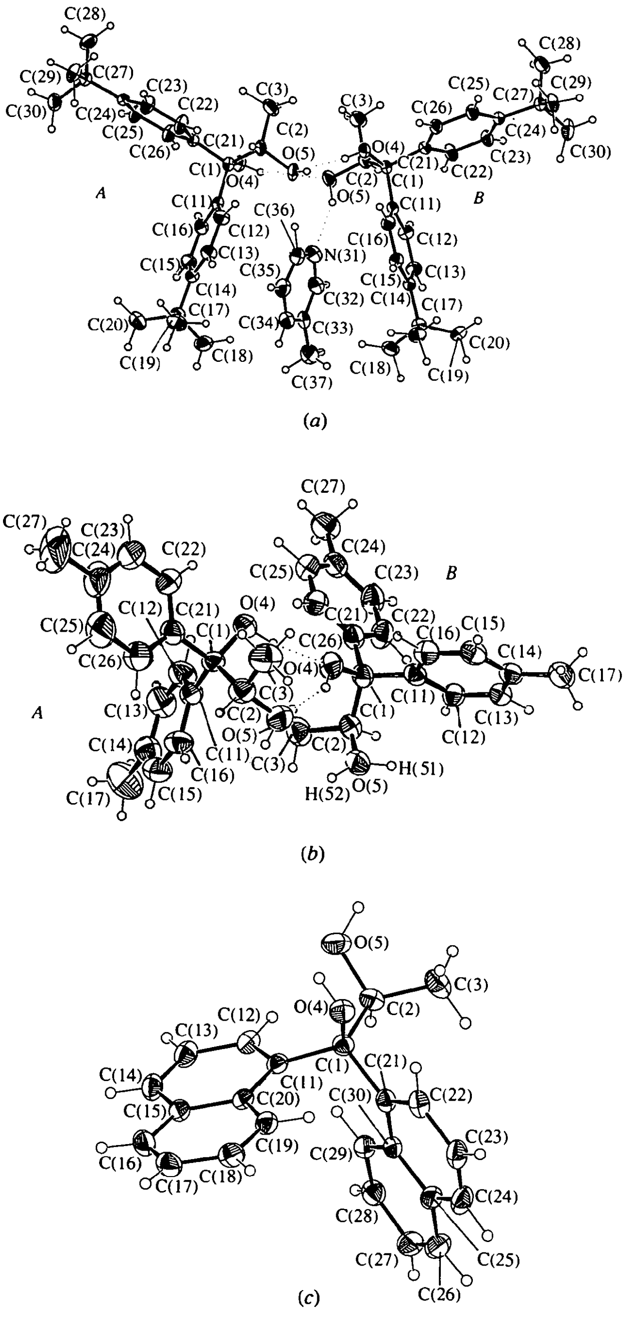


Fig. 1. Molecular structure and atomic numbering for (*a*) (5), (*b*) (6) and (*c*) (7). Displacement ellipsoids are drawn at the 30% probability level.

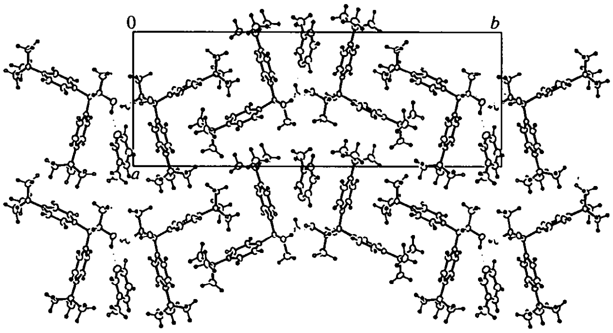


Fig. 2. Crystal packing of (5) projected along the *c* axis. Dotted lines represent hydrogen bonds.

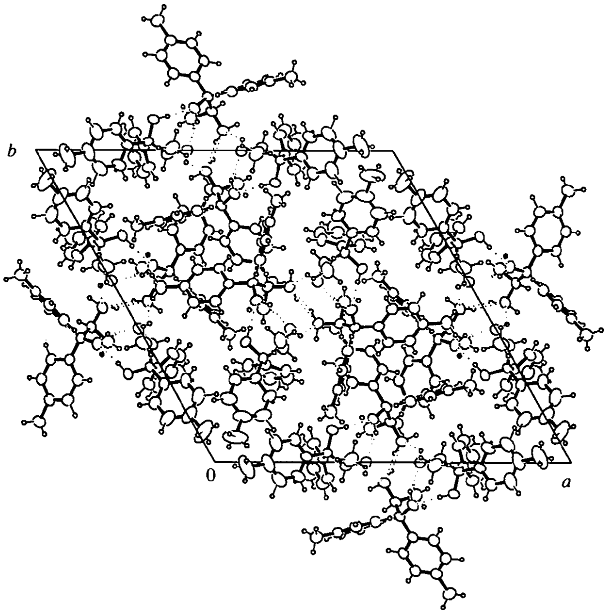


Fig. 3. Crystal packing of (6) projected along the *c* axis. Dotted lines represent hydrogen bonds.

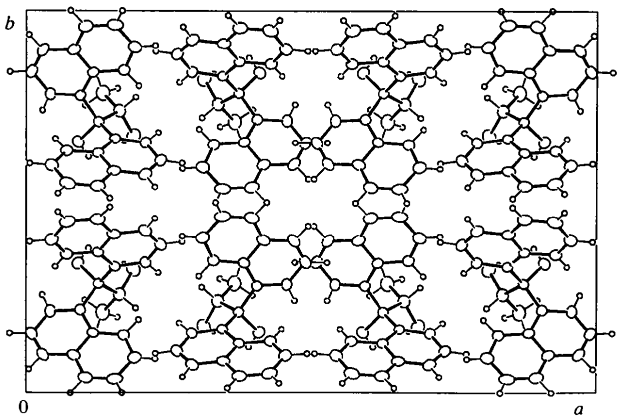


Fig. 4. Crystal packing of (7) projected along the *c* axis.

[2.67 (9), 2.36 (10) and 2.52 (8) Å, respectively]. These chains form sheets by means of weak C—H-naphthyl interactions (Fig. 4).

The location and characterization of cavities in the crystals was carried out using a model of interpenetrating spheres of van der Waals radii. The resulting surface was smoothed by rolling a sphere of radius 1.4 Å over it (Cano & Martínez-Ripoll, 1992). The guest molecules in (5) were located in channels along the *c* axis. The total packing coefficients [$C_k^{\rm all} = (V_{\rm host} + V_{\rm guest})/V_{\rm cell}$] are 0.67, 0.62 and 0.70 for compounds (5), (6) and(7), respectively, and the local packing coefficient ($C_k^{\rm l} = V_{\rm guest}/V_{\rm hole}$) in (5) is 0.55. The lower $C_k^{\rm all}$ value in (6) may be due to the presence of an almost spherical void left by the host matrix (average radius 1.9 Å).

Experimental

The host compounds in (5), (6) and (7) were synthesized as described by Weber, Wimmer, Llamas-Saiz & Foces-Foces (1992) and Weber & Wimmer (1993). Single crystals of (6) and (7) were obtained by slowly cooling toluene solutions of each. Crystals of the inclusion compound (5) were prepared by slowly cooling a solution of the relevant host compound in 3-picoline.

Compound (5)

Crystal data

$2C_{23}H_{32}O_2.C_6H_7N$
$M_r = 774.14$
Monoclinic
$P2_1$
$a = 11.6039\ (5)$ Å
$b = 31.6071\ (19)$ Å
$c = 6.2398\ (2)$ Å
$\beta = 102.220\ (3)^\circ$
$V = 2236.7\ (2)$ Å^3
$Z = 2$
$D_x = 1.149$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 74 reflections
$\theta = 2$–45°
$\mu = 0.515$ mm^{-1}
$T = 295$ K
Plate
0.38 × 0.23 × 0.17 mm
Colourless

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4303 measured reflections
3881 independent reflections
3464 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.010$
$\theta_{\rm max} = 65^\circ$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 37$
$l = 0 \rightarrow 8$
2 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F
$R = 0.049$
$wR = 0.056$
$S = 1.15$
3464 reflections
792 parameters
$(\Delta/\sigma)_{\rm max} = 0.16$

$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (5)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)*A*	0.4641 (3)	0.5589 (1)	0.3555 (5)	0.036 (1)
C(2)*A*	0.5129 (3)	0.5235 (1)	0.5200 (7)	0.043 (1)
C(3)*A*	0.6440 (4)	0.5158 (2)	0.5360 (10)	0.067 (2)
O(4)*A*	0.4854 (2)	0.5475 (1)	0.1444 (4)	0.043 (1)
O(5)*A*	0.4482 (3)	0.4858 (1)	0.4454 (5)	0.053 (1)
C(11)*A*	0.3325 (3)	0.5673 (1)	0.3364 (5)	0.036 (1)
C(12)*A*	0.2742 (3)	0.5612 (1)	0.5081 (6)	0.048 (1)
C(13)*A*	0.1565 (4)	0.5726 (1)	0.4868 (7)	0.051 (1)
C(14)*A*	0.0912 (3)	0.5898 (1)	0.2972 (6)	0.041 (1)
C(15)*A*	0.1491 (3)	0.5955 (1)	0.1259 (6)	0.048 (1)
C(16)*A*	0.2665 (3)	0.5846 (1)	0.1434 (6)	0.044 (1)
C(17)*A*	−0.0394 (3)	0.6022 (1)	0.2689 (7)	0.052 (1)
C(18)*A*	−0.1153 (4)	0.5715 (2)	0.1074 (10)	0.075 (2)
C(19)*A*	−0.0799 (4)	0.6019 (2)	0.4844 (8)	0.070 (2)
C(20)*A*	−0.0598 (5)	0.6470 (2)	0.1728 (8)	0.068 (2)
C(21)*A*	0.5288 (3)	0.6005 (1)	0.4186 (5)	0.035 (1)
C(22)*A*	0.5584 (4)	0.6140 (1)	0.6370 (6)	0.054 (1)
C(23)*A*	0.6092 (4)	0.6531 (1)	0.6931 (6)	0.052 (1)
C(24)*A*	0.6330 (3)	0.6811 (1)	0.5381 (5)	0.034 (1)
C(25)*A*	0.6056 (4)	0.6670 (1)	0.3222 (6)	0.049 (1)
C(26)*A*	0.5557 (4)	0.6278 (1)	0.2642 (6)	0.048 (1)
C(27)*A*	0.6863 (3)	0.7250 (1)	0.5941 (6)	0.037 (1)
C(28)*A*	0.8121 (4)	0.7257 (2)	0.5608 (9)	0.067 (2)
C(29)*A*	0.6852 (4)	0.7376 (1)	0.8304 (7)	0.059 (1)
C(30)*A*	0.6144 (5)	0.7583 (1)	0.4453 (8)	0.065 (2)
C(1)*B*	0.5113 (3)	0.3829 (1)	0.1257 (6)	0.041 (1)
C(2)*B*	0.5415 (3)	0.4083	−0.0669 (7)	0.051 (1)
C(3)*B*	0.6699 (4)	0.4191 (2)	−0.0349 (11)	0.079 (2)
O(4)*B*	0.5448 (2)	0.4079 (1)	0.3204 (5)	0.050 (1)
O(5)*B*	0.4762 (3)	0.4464 (1)	−0.1037 (6)	0.069 (1)
C(11)*B*	0.3799 (3)	0.3721 (1)	0.0849 (5)	0.037 (1)
C(12)*B*	0.3185 (3)	0.3559 (1)	−0.1163 (6)	0.044 (1)
C(13)*B*	0.2035 (3)	0.3437 (1)	−0.1470 (6)	0.046 (1)
C(14)*B*	0.1391 (3)	0.3467 (1)	0.0180 (6)	0.038 (1)
C(15)*B*	0.1996 (3)	0.3627 (1)	0.2159 (6)	0.045 (1)
C(16)*B*	0.3175 (3)	0.3753 (1)	0.2504 (6)	0.043 (1)
C(17)*B*	0.0103 (3)	0.3325 (1)	−0.0250 (7)	0.049 (1)
C(18)*B*	−0.0632 (4)	0.3628 (2)	−0.1916 (10)	0.067 (2)
C(19)*B*	−0.0392 (4)	0.3326 (2)	0.1847 (8)	0.064 (2)
C(20)*B*	−0.0013 (4)	0.2877 (1)	−0.1180 (9)	0.064 (2)
C(21)*B*	0.5803 (3)	0.3412 (1)	0.1702 (6)	0.038 (1)
C(22)*B*	0.5841 (4)	0.3122 (1)	0.0052 (6)	0.049 (1)
C(23)*B*	0.6352 (3)	0.2728 (1)	0.0524 (6)	0.046 (1)
C(24)*B*	0.6862 (3)	0.2605 (1)	0.2628 (6)	0.036 (1)
C(25)*B*	0.6865 (4)	0.2904 (1)	0.4269 (6)	0.046 (1)
C(26)*B*	0.6349 (3)	0.3299 (1)	0.3805 (6)	0.044 (1)
C(27)*B*	0.7392 (3)	0.2161 (1)	0.3147 (6)	0.039 (1)
C(28)*B*	0.8686 (4)	0.2173 (2)	0.3037 (11)	0.079 (2)
C(29)*B*	0.7285 (4)	0.2013 (1)	0.5444 (7)	0.057 (1)
C(30)*B*	0.6755 (5)	0.1833 (1)	0.1535 (8)	0.067 (2)
N(31)	0.2323 (4)	0.4577 (2)	−0.2157 (11)	0.090 (2)
C(32)	0.1421 (5)	0.4526 (2)	−0.3860 (11)	0.078 (2)
C(33)	0.0260 (4)	0.4634 (1)	−0.3879 (10)	0.070 (2)
C(34)	0.0065 (5)	0.4818 (2)	−0.1994 (11)	0.074 (2)
C(35)	0.0980 (5)	0.4885 (2)	−0.0227 (11)	0.081 (2)
C(36)	0.2074 (5)	0.4751 (2)	−0.0361 (12)	0.086 (2)
C(37)	−0.0725 (7)	0.4545 (2)	−0.5797 (15)	0.096 (3)

Compound (6)

Crystal data

$C_{17}H_{20}O_2$
$M_r = 256.34$
Hexagonal
$P6_2$
$a = 21.8247\ (7)$ Å
$c = 11.1964\ (4)$ Å

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 97 reflections
$\theta = 2$–45°
$\mu = 0.527$ mm^{-1}

$V = 4618.6$ (3) Å^3
$Z = 12$
$D_x = 1.106$ Mg m^{-3}
$T = 295$ K
Cube
0.37 × 0.37 × 0.37 mm
Colourless

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6014 measured reflections
6014 independent reflections
4622 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 65°$
$h = -23 \rightarrow 23$
$k = -23 \rightarrow 23$
$l = -14 \rightarrow 14$
2 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F
$R = 0.055$
$wR = 0.074$
$S = 1.05$
4622 reflections
503 parameters
$(\Delta/\sigma)_{\max} = 0.18$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (6)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)*A*	0.3000 (2)	0.3303 (2)	0.2500	0.069 (2)
C(2)*A*	0.3748 (2)	0.3627 (2)	0.3044 (4)	0.087 (2)
C(3)*A*	0.3775 (4)	0.3877 (4)	0.4320 (6)	0.124 (4)
O(4)*A*	0.2776 (1)	0.3815 (1)	0.2589 (3)	0.083 (1)
O(5)*A*	0.4236 (2)	0.4232 (2)	0.2342 (3)	0.096 (1)
C(11)*A*	0.2977 (2)	0.3088 (2)	0.1196 (4)	0.072 (2)
C(12)*A*	0.3436 (2)	0.2891 (2)	0.0722 (5)	0.089 (2)
C(13)*A*	0.3379 (3)	0.2675 (3)	−0.0447 (5)	0.101 (3)
C(14)*A*	0.2872 (3)	0.2655 (3)	−0.1203 (5)	0.102 (3)
C(15)*A*	0.2421 (3)	0.2866 (3)	−0.0720 (5)	0.113 (3)
C(16)*A*	0.2471 (3)	0.3074 (3)	0.0451 (5)	0.096 (3)
C(17)*A*	0.2807 (7)	0.2425 (7)	−0.2498 (8)	0.155 (7)
C(21)*A*	0.2471 (2)	0.2660 (2)	0.3207 (4)	0.080 (2)
C(22)*A*	0.2572 (3)	0.2093 (3)	0.3354 (6)	0.115 (3)
C(23)*A*	0.2096 (4)	0.1508 (3)	0.4001 (7)	0.142 (4)
C(24)*A*	0.1511 (4)	0.1460 (3)	0.4488 (6)	0.147 (4)
C(25)*A*	0.1401 (4)	0.2018 (4)	0.4311 (8)	0.162 (4)
C(26)*A*	0.1880 (3)	0.2611 (3)	0.3697 (6)	0.119 (3)
C(27)*A*	0.0986 (6)	0.0813 (4)	0.5200 (9)	0.247 (7)
C(1)*B*	0.3923 (2)	0.5704 (2)	0.0873 (3)	0.068 (2)
C(2)*B*	0.4276 (2)	0.5578 (2)	−0.0220 (4)	0.076 (2)
C(3)*B*	0.3805 (3)	0.4883 (3)	−0.0854 (6)	0.096 (3)
O(4)*B*	0.3739 (2)	0.5146 (1)	0.1709 (3)	0.084 (1)
O(5)*B*	0.4904 (2)	0.5586 (2)	0.0172 (3)	0.091 (2)
C(11)*B*	0.4432 (2)	0.6409 (2)	0.1466 (3)	0.066 (2)
C(12)*B*	0.4845 (2)	0.7027 (2)	0.0831 (4)	0.070 (2)
C(13)*B*	0.5315 (2)	0.7658 (2)	0.1391 (4)	0.074 (2)
C(14)*B*	0.5399 (2)	0.7696 (2)	0.2615 (4)	0.073 (2)
C(15)*B*	0.4983 (2)	0.7090 (2)	0.3259 (4)	0.081 (2)
C(16)*B*	0.4505 (2)	0.6459 (2)	0.2718 (4)	0.078 (2)
C(17)*B*	0.5929 (3)	0.8369 (3)	0.3215 (6)	0.099 (3)
C(21)*B*	0.3229 (2)	0.5669 (2)	0.0495 (4)	0.070 (2)
C(22)*B*	0.3228 (2)	0.6179 (2)	−0.0233 (5)	0.084 (2)
C(23)*B*	0.2606 (2)	0.6136 (2)	−0.0614 (5)	0.087 (2)
C(24)*B*	0.1959 (2)	0.5589 (2)	−0.0251 (4)	0.078 (2)
C(25)*B*	0.1958 (2)	0.5084 (2)	0.0475 (4)	0.086 (2)
C(26)*B*	0.2580 (2)	0.5117 (2)	0.0848 (4)	0.083 (2)
C(27)*B*	0.1286 (3)	0.5552 (4)	−0.0665 (7)	0.105 (3)

Compound (7)

Crystal data

$C_{23}H_{20}O_2$
$M_r = 328.41$
Orthorhombic
*Iba*2
$a = 25.5347$ (33) Å
$b = 17.3004$ (14) Å
$c = 7.6486$ (3) Å
$V = 3378.9$ (5) Å^3
$Z = 8$
$D_x = 1.291$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 61 reflections
$\theta = 2$–$45°$
$\mu = 0.600$ mm^{-1}
$T = 295$ K
Prism
0.50 × 0.13 × 0.13 mm
Colourless

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1565 measured reflections
1565 independent reflections
1414 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 65°$
$h = 0 \rightarrow 31$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 9$
2 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F
$R = 0.035$
$wR = 0.039$
$S = 1.15$
1414 reflections
305 parameters
All H-atom parameters refined
$(\Delta/\sigma)_{\max} = 0.12$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (7)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	0.3729 (1)	0.2127 (2)	−0.1199 (5)	0.038 (1)
C(2)	0.3363 (1)	0.2412 (2)	−0.2698 (5)	0.046 (1)
C(3)	0.3653 (1)	0.2875 (3)	−0.4071 (6)	0.064 (1)
O(4)	0.4092 (1)	0.1594 (1)	−0.2000	0.047 (1)
O(5)	0.3120 (1)	0.1750 (1)	−0.3486 (5)	0.062 (1)
C(11)	0.3444 (1)	0.1678 (1)	0.0261 (4)	0.036 (1)
C(12)	0.2907 (1)	0.1572 (2)	0.0198 (5)	0.045 (1)
C(13)	0.2645 (1)	0.1106 (2)	0.1430 (6)	0.052 (1)
C(14)	0.2915 (1)	0.0743 (2)	0.2718 (6)	0.054 (1)
C(15)	0.3461 (1)	0.0834 (2)	0.2858 (5)	0.044 (1)
C(16)	0.3746 (1)	0.0437 (2)	0.4174 (6)	0.056 (1)
C(17)	0.4273 (2)	0.0503 (2)	0.4308 (6)	0.060 (1)
C(18)	0.4549 (1)	0.0978 (2)	0.3134 (5)	0.055 (1)
C(19)	0.4290 (1)	0.1359 (2)	0.1832 (5)	0.045 (1)
C(20)	0.3738 (1)	0.1306 (1)	0.1625 (5)	0.039 (1)
C(21)	0.4052 (1)	0.2812 (2)	−0.0506 (5)	0.038 (1)
C(22)	0.4574 (1)	0.2847 (2)	−0.0944 (5)	0.047 (1)
C(23)	0.4901 (1)	0.3435 (2)	−0.0298 (6)	0.054 (1)
C(24)	0.4702 (1)	0.3990 (2)	0.0757 (6)	0.057 (1)
C(25)	0.4163 (1)	0.4005 (2)	0.1181 (5)	0.048 (1)
C(26)	0.3958 (1)	0.4599 (2)	0.2253 (6)	0.060 (1)
C(27)	0.3411 (2)	0.4636 (2)	0.2629 (6)	0.061 (1)
C(28)	0.3100 (1)	0.4072 (2)	0.1969 (5)	0.051 (1)
C(29)	0.3287 (1)	0.3477 (2)	0.0965 (5)	0.042 (1)
C(30)	0.3827 (1)	0.3414 (1)	0.0539 (5)	0.038 (1)

Table 4. *Selected geometric parameters* (Å,°)

Host molecules

	(5)		(6)		
	Molecule *A*	Molecule *B*	Molecule *A*	Molecule *B*	(7)
C(1)—C(2)	1.542 (5)	1.545 (6)	1.543 (5)	1.542 (6)	1.560 (5)
C(1)—O(4)	1.437 (4)	1.431 (4)	1.430 (6)	1.426 (5)	1.444 (3)
C(1)—C(11)	1.530 (5)	1.531 (5)	1.526 (4)	1.527 (4)	1.542 (4)
C(1)—C(21)	1.525 (5)	1.536 (5)	1.521 (4)	1.537 (6)	1.536 (4)
C(2)—C(3)	1.523 (6)	1.500 (6)	1.520 (9)	1.517 (6)	1.513 (6)
C(2)—O(5)	1.434 (4)	1.415 (4)	1.446 (5)	1.432 (6)	1.435 (4)
C(11)—C(1)—C(21)	107.4 (3)	107.5 (3)	108.8 (2)	112.0 (3)	113.0 (3)
O(4)—C(1)—C(21)	106.4 (3)	106.3 (3)	106.7 (2)	106.8 (3)	107.2 (2)
O(4)—C(1)—C(11)	109.6 (3)	110.2 (3)	109.5 (2)	109.1 (3)	106.7 (2)
C(2)—C(1)—C(21)	111.3 (3)	113.0 (3)	111.0 (2)	109.9 (3)	109.3 (2)
C(2)—C(1)—C(11)	113.4 (3)	111.6 (2)	112.6 (3)	110.3 (3)	114.1 (2)
C(2)—C(1)—O(4)	108.5 (3)	108.1 (2)	108.1 (2)	108.7 (3)	105.9 (2)
C(1)—C(2)—O(5)	107.1 (3)	111.4 (2)	109.3 (4)	108.4 (4)	108.4 (3)
C(1)—C(2)—C(3)	112.4 (3)	113.4 (3)	112.2 (5)	113.7 (4)	112.6 (3)
C(3)—C(2)—O(5)	109.5 (3)	108.2 (3)	107.7 (5)	108.6 (4)	110.0 (3)
C(12)—C(11)—C(16)/C(20)	116.8 (3)	116.6 (3)	117.6 (4)	116.2 (3)	118.8 (3)
C(22)—C(21)—C(26)/C(30)	116.4 (3)	117.0 (3)	117.3 (5)	117.3 (4)	119.4 (3)
C(1)—C(11)—C(12)	123.7 (3)	122.0 (3)	123.1 (4)	123.3 (3)	120.6 (3)
C(1)—C(21)—C(22)	121.4 (3)	122.1 (3)	120.3 (4)	121.3 (4)	118.0 (3)
C(2)—C(1)—C(21)—C(22)	−41.5 (4)	−51.2 (4)	−58.1 (6)	−68.1 (5)	−106.2 (3)
C(2)—C(1)—C(11)—C(12)	29.9 (5)	46.2 (4)	28.3 (5)	44.0 (5)	−1.6 (4)
O(4)—C(1)—C(2)—O(5)	−62.4 (4)	−62.9 (4)	−63.8 (4)	−61.1 (4)	56.9 (3)
O(4)—C(1)—C(2)—C(3)	58.0 (4)	59.4 (4)	55.6 (5)	59.7 (5)	−65.0 (3)
C(11)—C(1)—C(2)—O(5)	59.7 (4)	58.4 (4)	57.4 (4)	58.5 (4)	−60.2 (3)
C(11)—C(1)—C(2)—C(3)	180.0 (3)	−179.2 (3)	176.8 (4)	179.3 (4)	177.9 (3)
C(21)—C(1)—C(2)—O(5)	−179.1 (3)	179.8 (3)	179.5 (3)	−177.6 (3)	172.1 (3)
C(21)—C(1)—C(2)—C(3)	−58.8 (4)	−57.9 (4)	−61.1 (5)	−56.8 (5)	50.2 (4)

3-Picoline

N(31)—C(32)	1.335 (8)	N(31)—C(36)	1.334 (15)
C(32)—C(33)	1.387 (8)	C(33)—C(34)	1.373 (9)
C(34)—C(35)	1.376 (8)	C(35)—C(36)	1.357 (9)
C(33)—C(37)	1.496 (9)		
C(32)—N(31)—C(36)	116.5 (5)	N(31)—C(32)—C(33)	125.0 (6)
C(32)—C(33)—C(37)	122.5 (6)	C(32)—C(33)—C(34)	115.7 (6)
C(34)—C(33)—C(37)	121.9 (6)	C(33)—C(34)—C(35)	120.8 (6)
C(34)—C(35)—C(36)	118.4 (6)	N(31)—C(36)—C(35)	123.5 (7)

Table 5. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(5)				
O(4)*A*—H(4)*A*···O(5)*B*	0.81 (6)	2.83 (6)	3.543 (4)	147 (5)
O(5)*A*—H(5)*A*···O(5)*B*$^{\text{i}}$	1.03 (11)	2.03 (11)	3.031 (5)	163 (9)
O(4)*B*—H(4)*B*···O(5)*A*	0.79 (8)	2.10 (9)	2.880 (4)	169 (7)
O(5)*B*—H(5)*B*···N(31)	0.91 (7)	1.98 (7)	2.790 (5)	148 (6)
O(4)*A*—H(4)*A*···O(5)*A*	0.81 (6)	2.36 (5)	2.804 (4)	115 (4)
Symmetry code: (i) $x, y, 1 + z$.				
(6)				
O(4)*A*—H(4)*A*···O(4)*B*	0.88 (5)	1.94 (4)	2.779 (3)	159 (5)
O(4)*B*—H(4)*B*···O(5)*A*	0.83 (6)	2.10 (6)	2.796 (6)	141 (4)
O(5)*A*—H(5)*A*···O(5)*B*$^{\text{i}}$	0.84 (11)	2.59 (9)	2.974 (5)	109 (7)
O(5)*B*—H(52)*B*···O(5)*B*$^{\text{i}}$	0.86 (9)	1.96 (10)	2.792 (6)	163 (7)
Symmetry code: (i) $1 - x, 1 - y, z$.				
(7)				
O(4)—H(4)···O(5)	0.89 (5)	2.36 (5)	2.742 (3)	106 (4)
O(5)—H(5)···C(11–20$^{\text{i}}$)	1.04 (10)	3.00 (11)	3.941 (4)	151 (5)
O(5)—H(5)···C(15–29$^{\text{i}}$)	1.04 (10)	2.84 (9)	3.817 (3)	155 (6)
Symmetry code: (i) $x, y, z - 1$.				

The structures were solved by direct methods (*SIR*92; Altomare *et al.*, 1994). Friedel pairs of reflections were measured for (6) in order to check the absolute configuration. η unsuccessful refinements (Rogers, 1981) gave $\eta = 0.432\ (14)$, so the proposed chirality (known from the synthesis) was assumed to be correct. All H atoms were located in difference Fourier syntheses. In (5) all the parameters for H(4)*A* and the displacement factor for H(5)*B* were kept fixed during the last cycles of refinement. In (6) H(5)*B* was disordered over two equally populated sites [H(51) and H(52); Fig. 1*b*] and all the parameters for H(273)*A* and the displacement factors for H(271)*A*, H(272)*A* and H(33)*A* were kept fixed. All parameters for all other H atoms in the three structures were refined. Although the displacement factors for the phenyl-ring atoms C(21)*A*–C(26)*A* in (6) were high, no model for disorder could be established. Final atomic coordinates for the non-H atoms are given in Tables 1–3. Weighting schemes were chosen so as to give no trends in plots of $\langle w\Delta^2F\rangle$ *versus* $\langle |F_{\rm obs}|\rangle$ and $\langle \sin\theta/\lambda\rangle$.

Data processing, refinement and geometrical calculations were carried out on a VAX6410 computer using the *XRAY*80 program package (Stewart *et al.*, 1980), *PESOS* (Martínez-Ripoll & Cano, 1975) and *PARST* (Nardelli, 1983). Molecular graphics were produced using *Xtal*3.2 (Hall, Flack & Stewart, 1994).

Financial support from COST (No. CIPA-CT 93-0171) is greatly acknowledged. CFF also thanks DGICYT (Spain PB93-0125) and EW thanks the Fonds der Chemischen Industrie for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1235). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Brock, C. P. & Dunitz, J. D. (1982). *Acta Cryst.* **B38**, 2218–2228.
Cano, F. H. & Martínez-Ripoll, M. (1992). *J. Mol. Struct. (Theochem.)*, **258**, 139–158.
Domenicano, A. & Vaciago, A. (1979). *Acta Cryst.* **B35**, 1382–1388.
Hall, S. R., Flack, H. D. & Stewart, J. M. (1994). *Xtal3.2 User's Manual.* Univs. of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
Llamas-Saiz, A. L., Foces-Foces, C., Weber, E. & Wimmer, C. (1993). *Supramol. Chem.* **2**, 215–223.
Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS.* Unpublished program.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Rogers, D. (1981). *Acta Cryst.* **A37**, 734–741.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1980). *The XRAY80 System.* Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
Weber, E. & Wimmer, C. (1993). *Chirality*, **5**, 315–319.
Weber, E., Wimmer, C., Llamas-Saiz, A. L. & Foces-Foces, C. (1992). *J. Chem. Soc. Chem. Commun.* pp. 733–735.

Acta Cryst. (1995). **C51**, 1452–1454

Disordered Fluorine in 2-Fluorobiphenyl

RAJNIKANT† AND DAVID WATKIN*

Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, England

GEORGE TRANTER

Department of Physical Sciences, The Wellcome Foundation Ltd, Langley Court, South Eden Park Road, Beckenham, Kent BR3 3BS, England

(*Received* 7 *November* 1994; *accepted* 13 *January* 1995)

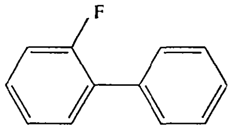
Abstract

In the title compound, $C_{12}H_9F$, the average C—C bond length in the phenyl ring is 1.384 (3) Å. Unlike the planar biphenyl, the torsion angle C2—C1—C1′—C2′ between the phenyl rings is −52.3°. The dihedral angle between the phenyl rings is 54 (3)° and the angle C4—C1—C1′—C4′ is 0.9 (2)°. The molecule lies across an axis of twofold symmetry, so the F atom is found disordered with half occupancy.

Comment

The biphenyl molecule, which is planar in the solid state (Hargreaves & Rizvi, 1962; Charbonneau & Delugeard, 1976, 1977) but shows a dihedral twist of 42° in the gas phase (Almenningen & Bastiansen, 1958; Bastiansen & Traetteberg, 1962), is a good subject for studying molecular geometry, crystal packing and thermal motion (Brock & Haller, 1984; Brock & Morelan, 1986; Brock & Minton, 1989).

As part of our research on the systematic analysis of growth conditions and morphology modifiers for the preparation of substituted biphenyls from organic solvents (Rajnikant, Watkin & Tranter, 1995), the present work reports the crystal and molecular structure of the title compound, (I). There is substantial literature on fluoro-substituted biphenyls (Jones & Brown, 1986; Lemée, Toupet, Délugeard, Messager & Cailleau, 1987; Wasicki *et al.*, 1988; Gleason, Brostrom, Etter & Johnson, 1991).



(I)

Since the molecule lies across a twofold axis, the F atom on C2 must be disordered at 1:1 with the H atom on C2′. The bond-length distribution in the fluoro-substituted phenyl ring agrees well with the literature values (Krausse & Dunken, 1966; Young, Tollin & Sutherland, 1968; Sutherland & Rawas, 1983), but the C—F bond length [1.319 (4) Å] is significantly shorter. The biphenyl bond [C1—C1′ 1.483 (4) Å] is shorter than the value found in biphenyl (1.506 Å).

As in other biphenyl derivatives, the internal ring bond angle at C1 is reduced [117.2 (2)°] and the adjacent angles are enlarged [121.2 (2), 122.4 (2)°]. The distribution of bond angles around the C atom bonded to the F atom is similar to that found in 4-acetyl-2′-fluorobiphenyl (Young *et al.*, 1968). In many of the 2′- and 3′-halogen-substituted biphenyls, the halogen atom has been found to be displaced out of the ring plane

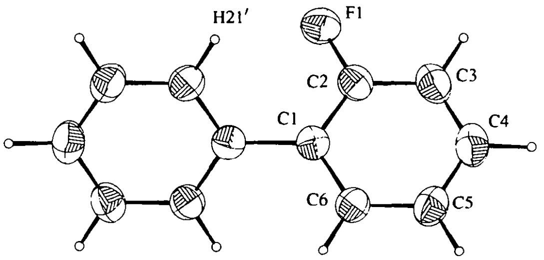


Fig. 1. Projection of 2-fluorobiphenyl onto the best plane through the molecule. Displacement ellipsoids are drawn at the 50% probability level. Note that the molecule lies across a twofold axis, so that F1 and H21′ are disordered with each other, with occupancies of 0.50.

---

† Permanent address: Post-graduate Department of Physics, University of Jammu, Canal Road, Jammu Tawi 180 001, India.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995