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.

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

Disordered Fluorine in 2-Fluorobiphenyl

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

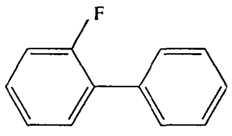
Abstract

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

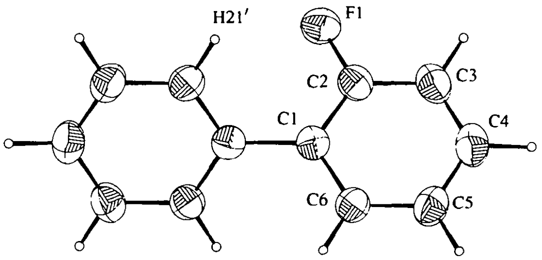


Fig. 1. Projection of 2-fluorobiphenyl onto the best plane through the molecule. Displacement ellipsoids are drawn at the 50% probability level. Note that the molecule lies across a twofold axis, so that F1 and H21′ are disordered with each other, with occupancies of 0.50.

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Acta Crystallographica Section C
ISSN 0108-2701 ©1995

(Sutherland & Rawas, 1983); the F atom in the present structure is displaced by 0.104 (3) Å. The distance between the F atom and an H atom geometrically placed on C2′ is 2.78 Å (there is a shorter non-bonded contact of 2.63 Å to H31 on an adjacent molecule in the cell) indicating no great torsional strain, and the dihedral angle [54 (3)°] is close to that found in flurbiprofen (Flippen & Gilardi, 1975). The molecules in the unit cell adopt a herringbone configuration.

Experimental

The material was supplied by Aldrich and crystallization from various solvents was carried out to produce good quality crystals. Crystals of 2-fluorobiphenyl were obtained from toluene, chloroform and dimethylformamide at room temperature by the slow evaporation technique. Adjoined tabular crystals were obtained from the latter two solvents. Toluene yielded a single very thick and large crystal (approximate dimensions 3.5 × 2.0 × 1.5 mm). X-ray photographic surveys of crystals from all these solvents (oscillation and Weissenberg) revealed that all crystallization of this material yield the same unit cell. Therefore, a rectangular-shaped piece of the title compound (grown from toluene) was cleaved and chosen for data collection.

Crystal data

$C_{12}H_9F$
$M_r = 172.2$
Orthorhombic
*F*2*dd*
$a = 5.894\,(3)$ Å
$b = 12.954\,(1)$ Å
$c = 23.602\,(2)$ Å
$V = 1802.0\,(9)$ Å^3
$Z = 8$
$D_x = 1.269$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 0\text{–}40°$
$\mu = 0.673$ mm^{-1}
$T = 293$ K
Thick rectangular plate
0.60 × 0.30 × 0.20 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1827 measured reflections
480 independent reflections
451 observed reflections $[I > 3\sigma(I)]$
$R_{\text{int}} = 0.0405$

$\theta_{\text{max}} = 72°$
$h = -7 \rightarrow 6$
$k = -6 \rightarrow 15$
$l = -10 \rightarrow 29$
3 intensity standard reflections monitored every 60 min of exposure time
intensity decay: none

Refinement

Refinement on F
$R = 0.04534$
$wR = 0.06006$
$S = 0.85$
451 reflections
65 parameters
H-atom parameters not refined
$w = [\text{weight}][1-(\delta F/6\times\sigma F)^2]^2$, weighting coefficients 14.6, 8.40 and 10.6

$(\Delta/\sigma)_{\text{max}} = 0.13$
$\Delta\rho_{\text{max}} = 0.952$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.185$ e Å^{-3}
Extinction correction: secondary (Larson, 1969)
Extinction coefficient: 177.5
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)

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

	x	y	z	U_{eq}
C1	0.0373 (3)	0.0471 (1)	0.48219 (9)	0.0526
C2	−0.1400 (4)	0.0695 (2)	0.4455 (1)	0.0619
C3	−0.1397 (5)	0.1551 (2)	0.4111 (1)	0.0722
C4	0.0410 (5)	0.2228 (2)	0.4131 (1)	0.0731
C5	0.2202 (5)	0.2032 (2)	0.4497 (1)	0.0705
C6	0.2185 (4)	0.1160 (2)	0.4834 (1)	0.0612
F1†	−0.3067 (4)	0.0026 (3)	0.4392 (1)	0.0777

† Occupancy 0.50.

Table 2. *Geometric parameters* (Å, °)

C1—C1	1.483 (4)	C2—F1	1.319 (4)
C1—C2	1.388 (3)	C3—C4	1.380 (4)
C1—C6	1.392 (3)	C4—C5	1.387 (5)
C2—C3	1.374 (4)	C5—C6	1.382 (4)
C1—C1—C2	121.7 (2)	C3—C2—F1	117.7 (2)
C1—C1—C6	121.1 (2)	C2—C3—C4	119.6 (2)
C2—C1—C6	117.2 (2)	C3—C4—C5	119.5 (2)
C1—C2—C3	122.4 (2)	C4—C5—C6	120.1 (3)
C1—C2—F1	119.6 (2)	C1—C6—C5	121.2 (2)

The structure was solved using *SHELXS*86 (Sheldrick, 1985) and refined using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Isotropic refinement of the structure by least squares was followed by anisotropic refinement of all the non-H atoms. All H atoms (except H21′) were located from the difference Fourier map. H21′ was included only in the geometry calculations. The space group *F*2*dd* is a non-standard setting of *Fdd*2. The equivalent positions are x, y, z; $x, -y, -z$; $\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z$; $\frac{1}{4}+x, \frac{1}{4}+y, \frac{1}{4}-z$, in addition to the *F* centrings. Molecular graphics: *CAMERON* (Pearce, Watkin & Prout, 1992). Preparation of material for publication: *CRYSTALS*.

One of us (R) wishes to acknowledge the Department of Science and Technology (DST), Ministry of Science and Technology, Government of India, for the award of BOYSCAST Fellowship (DST ref. SR/BY/P-04/93) and the University of Jammu, Jammu Tawi, India, for granting a year's deputation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1225). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1454–1457

2,2′-Oxybispyridine and 2,2′-Selenobispyridine

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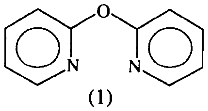
(*Received* 15 *October* 1994; *accepted* 3 *January* 1995)

Abstract

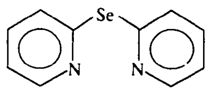
The oxy structure ($C_{10}H_8N_2O$) adopts a skew conformation with the skew angle 69.9 (4)°; the angle at the O atom is 120.3 (3)° and the O—C distances are 1.378 (6) and 1.395 (6) Å. The seleno structure ($C_{10}H_8N_2Se$) adopts a twist conformation with the twist angle 52.5 (3)°; the angle at the Se atom is 101.9 (2)° and the Se—C distances are 1.920 (4) and 1.940 (4) Å.

Comment

Studies investigating the gas-phase and solution structures of the diphenyl and dipyridyl chalcogenides have led to a variety of conclusions regarding the stereochemistry of these systems (Higgasi & Uyeo, 1939; Rolla & Sanesi, 1962; Fong, 1964; Cumper, Read & Vogel, 1965; Anderson & Smyth, 1965; Pappalardo & Pistara, 1972; Montaudo, Finocchiaro & Caccamese, 1973). More recently, NMR data have indicated substantially non-planar equilibrium structures for diphenyl ethers with interplanar angles in the range 20–50° (Krivdin & Kalabin, 1982). Photoelectron studies by Dunne, Summers & von Nagy-Felsobuki (1991, 1992*a*,*b*, 1993) on the chalcogenobispyridines have now provided evidence for the existence of a range of conformers in the gas phase, but were best modelled at the *ab initio* level using the skew conformer. The scarcity of structural data on the parent compounds has made the accuracy of these earlier studies difficult to determine. To complement our earlier theoretical and photoelectron spectroscopic studies on the chalcogenobispyridines, we now report the crystal structures of the title compounds.



(1)



(2)

2,2′-Oxybispyridine, (1), adopts a skew conformation as defined by the torsional angles C2′—O1—C2—N1 and C2—O1—C2′—C3′ of 0.0 (6) and −73.3 (6)°, respectively, with the lone pair on N1 in the proximal position and that on N1′ in the distal position.* The dihedral angle between the pyridine rings of 69.9 (4)°, the C—O—C angle of 120.3 (3)° and the C—O bond lengths of 1.378 (6) and 1.395 (6) Å lie close to comparable values reported for bis(phenyl) ethers; *cf.* 73.2 (3), 119.6 (3)°, 1.374 (3) and 1.383 (3) Å in bis(3,4-dichlorophenyl) ether (Singh & McKinney, 1980), 64.5 (3), 119.9 (2)°, 1.379 (2) and 1.398 (2) Å in 2,2′-bis(tosylmethylphenyl) ether (Stepien, Wajsman, Grabowski, Glinka & Lecocq, 1987), and 68.4 (8), 120.6 (6)°, 1.376 (8) Å in bis(2,4-dichlorophenyl) ether (Rissanen, Valkonen & Virkki, 1988).

2,2′-Selenobispyridine, (2), on the other hand, adopts a twist conformation defined by the torsional angles C2—Se1—C2′—N1′ of 42.2 (3)° and C2′—Se1—C2—C3 of 25.3 (3)°. The lone pair on N1 occupies the distal position whilst on N1′ it is proximal.* The dihedral angle between the pyridine ring planes is 52.5 (3)° and the C—Se1—C angle is 101.9 (2)°, compared with the analogous values of 55 and 106 (2)° in di-*p*-tolylselenide (Blackmore & Abrahams, 1955). The more acute C—Se1—C angle of 101.9 (2)° in (2) and 106 (2)° in the tolylselenide compared with the C—O—C angle in (1) may restrict the adoption of a skew conformation, as observed in the latter despite the longer Se1—C bonds of 1.920 (4) and 1.940 (4) Å in (2) and 1.92 (5) and 1.93 (5) Å in the tolylselenide. These distances are also similar to those of 1.93 (5) Å found in diphenyl-

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* Refer to the convention of van der Heijden, Griffith, Chandler & Robertson (1975).

Acta Crystallographica Section C
ISSN 0108-2701 ©1995