

The Crystal and Molecular Structure of 2*H*-Nonafluorobiphenyl

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Crystals of the title compound are monoclinic, space group $P2_1/c$, with $a = 6.14$ (1), $b = 26.405$ (15), $c = 7.47$ (1) Å, $\beta = 114.42$ (5)°, $Z = 4$. The structure was determined by direct methods from X-ray counter data and refined by least-squares calculations to $R = 4.6\%$ for 1264 observed amplitudes. The molecules pack in a disordered manner, so that the H atom and the three *ortho* F atoms are distributed (unequally) over the four *ortho* positions. The angle between the phenyl rings is 59.5° and the length of the inter-ring bond is 1.486 Å (uncorrected for thermal libration). Estimated standard deviations average 0.005 Å for bond lengths and 0.3° for bond angles.

Introduction

The hydrocarbon biphenyl has been extensively studied by X-ray crystallography (Trotter, 1961; Robertson, 1961; Hargreaves & Rizvi, 1962; Charbonneau & Delugeard, 1976, 1977) and recently the crystal structure of perfluorobiphenyl has been determined (Gleason & Britton, 1976). We now report the crystal structure analysis of 2*H*-nonafluorobiphenyl (Callander, Coe & Tatlow, 1966) as part of a programme of structural studies of highly fluorinated organic molecules.

Experimental

A crystal 0.7 × 0.5 × 0.2 mm was mounted inside a Pantak capillary tube. After preliminary examination by photographic methods, intensities were measured with a Stoe computer-controlled two-circle diffractometer and graphite-monochromated Mo $K\alpha$ radiation, by the ω -scan technique. 2882 reflexions were scanned in the range $0.10 < \sin \theta/\lambda < 0.65$ Å⁻¹, of which 1264, with $I > 2.5\sigma(I)$, were considered to be observed. Three reflexions on the zero layer were remeasured after each layer of data collection to monitor the stability of the system. Intensities were converted to structure amplitudes in the usual way but absorption corrections were not applied.

Crystal data

$C_{12}HF_9$, $M_r = 316.1$, monoclinic, $a = 6.14$ (1), $b = 26.405$ (15), $c = 7.47$ (1) Å, $\beta = 114.42$ (5)°, $U = 1102.7$ Å³, $Z = 4$, $D_c = 1.90$ g cm⁻³, $F(000) = 616$. Systematic absences: $h0l$, l odd; $0k0$, k odd, space group $P2_1/c$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å; $\mu(\text{Mo } K\alpha) = 1.6$ cm⁻¹.

Structure determination

The structure was solved by direct methods (Karle & Karle, 1966; Germain & Woolfson, 1968) with *SHELX* (Sheldrick, 1975). All the atoms could be located from the *E* map, including, it appeared, the H atom at the 2-position. Refinement of positional and isotropic thermal parameters by least squares yielded reasonable results for all the atoms except H(2), for which the temperature factor became negative and the C(2)–H(2) bond length took up the rather unlikely value of 1.27 Å. H(2) was therefore left out of the calculations and after three further cycles of least-squares calculations a difference synthesis showed a peak 1.30 Å from C(2) with a height which corresponded approximately to half a F atom. The possibility was now considered that the structure may show some form of disorder. The atom at the 2-position was assigned F atomic scattering factors and a site-occupation factor of 0.5 and the least-squares refinement continued with the inclusion of the site-occupation factors of the F atoms as variables, first with isotropic and finally with anisotropic thermal parameters. The calculations were terminated when the calculated shifts were all less than 0.1σ and R was 4.6% for the 1264 observed amplitudes.* The weighting scheme was $w = 1/[\sigma^2(F) + 0.00032F^2]$, where $\sigma(F)$ is the standard deviation in the observed amplitudes based on counting statistics.

The site-occupation factors had refined to near unity for all the F atoms except those in the four *ortho* positions which had refined to the following values: F(2) 0.44 (1), F(6) 0.87 (1), F(2') 0.77 (1) and F(6')

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33065 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

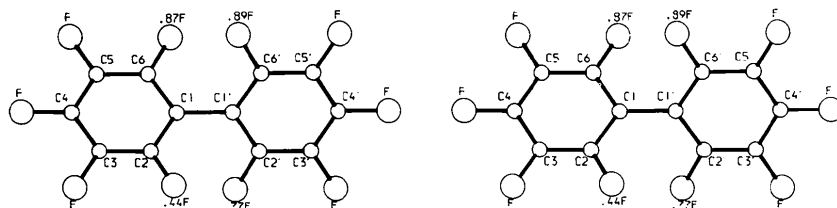


Fig. 1. Stereoscopic view of the molecule showing the numbering of the ring atoms. Substituents are assigned the number of the C atom to which they are bonded. Decimal numbers are site-occupation factors for the four *ortho* substituents considered as F atoms (see text).

Table 1. Fractional atomic coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	5294 (5)	3943 (1)	-4393 (4)
C(2)	3473 (6)	4285 (1)	-4685 (5)
C(3)	2640 (6)	4599 (1)	-6296 (5)
C(4)	3605 (7)	4585 (1)	-7653 (5)
C(5)	5403 (7)	4247 (1)	-7387 (5)
C(6)	6245 (6)	3932 (1)	-5779 (5)
C(1')	6213 (5)	3599 (1)	-2666 (4)
C(2')	4735 (5)	3254 (1)	-2314 (5)
C(3')	5578 (6)	2934 (1)	-720 (5)
C(4')	7944 (6)	2953 (1)	577 (5)
C(5')	9433 (6)	3288 (1)	276 (5)
C(6')	8574 (5)	3605 (1)	-1320 (5)
H(2)*	2632 (8)	4339 (2)	-3454 (7)
F(3)	911 (5)	4934 (1)	-6554 (3)
F(4)	2820 (5)	4896 (1)	-9201 (3)
F(5)	6338 (5)	4221 (1)	-8720 (3)
F(6)*	7917 (4)	3601 (1)	-5629 (3)
F(2')*	2459 (4)	3212 (1)	-3550 (4)
F(3')	4109 (4)	2599 (1)	-439 (4)
F(4')	8769 (4)	2638 (1)	2133 (3)
F(5')	11753 (4)	3307 (1)	1556 (3)
F(6')*	10091 (4)	3934 (1)	-1530 (3)

* These atoms are affected by disorder (see text and Fig. 1). Site-occupation factors are (2) 0.56H, 0.44F; (6) 0.87F, 0.13H; (2') 0.77F, 0.23H; (6') 0.89F, 0.11H. All F values ± 0.01 ; H values by difference.

0.89 (1). The sum of the occupation factors is 2.97, not greatly different from the expected value of $3\frac{1}{2}$. No trace was found of the hydrogen atom in difference maps, but it is assumed that it is distributed over the four *ortho* positions as follows: (2) 0.56, (6) 0.13, (2') 0.23 and (6') 0.11. The molecule therefore appears to pack in the crystal in such a way as to take up four different orientations in a random manner, but with the one in which the H atom is in the position designated as (2) predominating. The C atoms and the remaining F atoms do not seem to be greatly affected by the disorder and the thermal parameters are unexceptional.

Computations were carried out largely on the CDC 7600 computer at the University of Manchester Regional Computer Centre with *SHELX* (Sheldrick, 1975).

Results and discussion

The conformation of the molecule and the atomic labelling are shown in Fig. 1. Atomic coordinates are in Table 1 and molecular dimensions are in Table 2. Bond lengths corrected for the effect of rigid-body thermal motion (Cruickshank, 1956; Schomaker & Trueblood, 1968) are listed with superscript *c*. For the purpose of

Table 2. Molecular dimensions

(a) Bond lengths (Å). Superscript *c* denotes lengths corrected for thermal motion. Standard deviations are 0.004–0.005 Å for the uncorrected values.

C(1)–C(1')	1.486				
C(1)–C(2)	1.383	1.395 ^c	C(1')–C(2')	1.386	1.397 ^c
C(2)–C(3)	1.375	1.383 ^c	C(2')–C(3')	1.373	1.382 ^c
C(3)–C(4)	1.370	1.382 ^c	C(3')–C(4')	1.374	1.385 ^c
C(4)–C(5)	1.367	1.379 ^c	C(4')–C(5')	1.357	1.369 ^c
C(5)–C(6)	1.375	1.383 ^c	C(5')–C(6')	1.370	1.378 ^c
C(6)–C(1)	1.383	1.395 ^c	C(6')–C(1')	1.381	1.392 ^c
C(2)–H(2)	1.236		C(2')–F(2')	1.323	
C(3)–F(3)	1.333	1.345 ^c	C(3')–F(3')	1.340	1.351 ^c
C(4)–F(4)	1.336	1.344 ^c	C(4')–F(4')	1.346	1.354 ^c
C(5)–F(5)	1.341	1.353 ^c	C(5')–F(5')	1.349	1.360 ^c
C(6)–F(6)	1.317		C(6')–F(6')	1.331	

(b) Non-bonded distances (Å)

H(2)⋯F(2')	2.978	F(6)⋯F(6')	2.924
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(c) Bond angles (°); all standard deviations 0.3°

C(2)–C(1)–C(6)	117.3	C(2')–C(1')–C(6')	116.2
C(2)–C(1)–C(1')	121.9	C(2')–C(1')–C(1)	121.6
C(6)–C(1)–C(1')	120.7	C(6')–C(1')–C(1)	122.2
C(1)–C(2)–C(3)	121.1	C(1')–C(2')–C(3')	121.8
C(1)–C(2)–H(2)	121.2	C(1')–C(2')–F(2')	120.5
C(3)–C(2)–H(2)	117.6	C(3')–C(2')–F(2')	117.7
C(2)–C(3)–C(4)	120.8	C(2')–C(3')–C(4')	119.9
C(2)–C(3)–F(3)	120.8	C(2')–C(3')–F(3')	120.3
C(4)–C(3)–F(3)	118.3	C(4')–C(3')–F(3')	119.8
C(3)–C(4)–C(5)	118.7	C(3')–C(4')–C(5')	119.6
C(3)–C(4)–F(4)	120.8	C(3')–C(4')–F(4')	119.9
C(5)–C(4)–F(4)	120.5	C(5')–C(4')–F(4')	120.5
C(4)–C(5)–C(6)	120.7	C(4')–C(5')–C(6')	119.9
C(4)–C(5)–F(5)	119.5	C(4')–C(5')–F(5')	119.5
C(6)–C(5)–F(5)	119.8	C(6')–C(5')–F(5')	120.6
C(5)–C(6)–C(1)	121.3	C(5')–C(6')–C(1')	122.5
C(5)–C(6)–F(6)	118.3	C(5')–C(6')–F(6')	117.7
C(1)–C(6)–F(6)	120.3	C(1')–C(6')–F(6')	119.8

this correction, the phenyl rings with their F substituents, but excluding those in the *ortho* positions which are affected by the disorder, were considered as independent rigid units. The major axes of libration in the two segments are both approximately parallel to the long axis of the molecule (Table 3).

The phenyl rings are accurately planar (Table 4) but the substituents are displaced by up to 0.08 Å from their respective ring planes. The largest displacements occur at the *ortho* positions and are in such a direction as to increase the H(2)⋯F(2') and F(6)⋯F(6') separations. The exocyclic bond angles at the *ortho* C atoms are also slightly distorted so as to increase these separations. Similar distortions of bond angles occur in the crystal structures of biphenyl (Charbonneau & Delugeard, 1976) and perfluorobiphenyl (Gleason &

Table 3. Results of rigid-body-motion analysis

The eigenvectors of the libration tensor **L** and translation tensor **T** are referred, in terms of the corresponding direction cosines, to the orthogonal molecular system defined by the eigenvectors of the molecular tensor of inertia **I**. The eigenvectors of **I** are referred to the unit-cell axes. The calculation is referred to the origin which symmetrizes the screw tensor and reduces the trace of **T**.

(i) C(1)–(6), F(3)–(5)

	Eigenvalues	Eigenvectors		
I	198 at. wt Å ²	0.8597	-0.4027	-0.3143
	273	0.0058	-0.6075	0.7943
	471	-0.5108	-0.6847	-0.5199
L	145 × 10 ⁻⁴ rad ²	-0.0784	-0.9964	-0.0326
	70	0.9881	-0.0733	-0.1356
	51	0.1327	-0.0428	0.9902
T	658 × 10 ⁻⁴ Å ²	0.9222	0.3220	-0.2143
	557	0.2324	-0.9042	-0.3585
	397	-0.3092	0.2808	-0.9086

Components of the origin shift, referred to the inertial frame, from the centre of mass ($x = 0.3963$, $y = 0.4450$, $z = -0.6972$) are -0.026, 1.467, 0.025 Å.

R.m.s. discrepancy, $\langle \Delta U^2 \rangle^{1/2} = 0.0028 \text{ \AA}^2$

Mean e.s.d. in observed U_{ij} values = 0.002 Å²

(ii) C(1')–(6'), F(3')–(5')

	Eigenvalues	Eigenvectors		
I	198 at. wt Å ²	0.8708	0.3920	0.2966
	275	0.0109	-0.6186	0.7857
	473	0.4915	-0.6810	-0.5429
L	130 × 10 ⁻⁴ rad ²	0.0885	0.9950	0.0468
	82	0.9953	-0.0865	-0.0438
	44	-0.0395	0.0504	-0.9979
T	558 × 10 ⁻⁴ Å ²	0.4652	-0.8801	0.0946
	544	0.7883	0.4606	0.4079
	402	-0.4026	-0.1152	0.9081

Components of the origin shift, referred to the inertial frame, from the centre of mass ($x = 0.7579$, $y = 0.3085$, $z = -0.0095$) are 0.026, -1.409, 0.078 Å.

R.m.s. discrepancy, $\langle \Delta U^2 \rangle^{1/2} = 0.0026 \text{ \AA}^2$

Mean e.s.d. in observed U_{ij} values = 0.002 Å².

Table 4. Mean-plane calculations

Deviations (Å) of atoms from least-squares planes. Distances marked with an asterisk refer to atoms defining the plane.

(I) Phenyl ring C(1)–(6)		(II) Phenyl ring C(1')–(6')	
C(1)	-0.001*	C(1')	-0.002*
C(2)	0.001*	C(2')	0.001*
C(3)	-0.002*	C(3')	0.000*
C(4)	0.003*	C(4')	-0.002*
C(5)	-0.002*	C(5')	0.001*
C(6)	0.001*	C(6')	0.001*
C(1')	-0.002	C(1)	-0.003
H(2)	0.081	F(2')	-0.034
F(3)	0.022	F(3')	-0.018
F(4)	0.022	F(4')	-0.008
F(5)	-0.023	F(5')	0.005
F(6)	-0.054	F(6')	0.032

Equations of planes (x , y and z are fractional coordinates relative to the cell axes)

$$(I) \quad -3.098x - 18.219y - 1.972z = -7.957$$

$$(II) \quad 2.998x - 18.053y - 5.197z = -3.250$$

$$\text{Interplanar angle (I)–(II) } 59.5^\circ$$

Table 5. Intermolecular contact distances (Å)

Distances up to 3.3 Å

H(2)⋯F(6 ⁱ)	2.74	F(3')⋯C(2' ^{iv})	3.15
F(2')⋯F(6 ⁱ)	2.77	F(3')⋯F(5' ^{vii})	3.19
F(3)⋯H(2 ⁱⁱ)	2.90	F(4')⋯F(6' ^{viii})	3.20
F(5)⋯F(4 ⁱⁱⁱ)	2.96	F(3)⋯F(5 ⁱ)	3.21
F(3')⋯F(2' ^{iv})	2.96	F(5')⋯C(5' ^v)	3.22
F(3)⋯F(3 ⁱⁱ)	2.99	F(4')⋯C(4' ^{iv})	3.22
F(4)⋯F(3 ^v)	3.08	C(6')⋯F(5' ^{viii})	3.24
F(3')⋯F(5' ^{vi})	3.10	F(6')⋯F(3 ^{ix})	3.26
F(5')⋯C(6 ^{vi})	3.12	F(6')⋯C(4' ^{vi})	3.29
F(2')⋯F(6 ^{vi})	3.14	F(4')⋯C(5' ^{iv})	3.30
F(6')⋯F(4 ^{vi})	3.14		

Symmetry code

(i)	-1 + x,	y,	z	(vi)	1 + x,	y,	1 + z
(ii)	-x,	1 - y,	-1 - z	(vii)	-1 + x,	$\frac{1}{2} - y,$	$-\frac{1}{2} + z$
(iii)	1 - x,	1 - y,	-2 - z	(viii)	x,	y,	1 + z
(iv)	x,	$\frac{1}{2} - y,$	$\frac{1}{2} + z$	(ix)	1 - x,	1 - y,	-1 - z
(v)	-x,	1 - y,	-2 - z				

Britton, 1976). The dihedral angle between the rings is 59.5°, virtually the same as in perfluorobiphenyl but differs from biphenyl which is planar, or at least nearly so, in the solid state.

The aromatic C–C bonds range from 1.369 to 1.397 Å, mean 1.385 Å (corrected). The corresponding values for perfluorobiphenyl and biphenyl are 1.366–1.395 Å (mean 1.381 Å) and 1.379–1.399 Å (mean 1.390 Å) respectively. Thus the characteristic slight shortening of the C–C bonds relative to hydrocarbon systems noted previously in fluorinated tropones (Guy, Hamor & Jenkins, 1975; Hamor & Hamor, 1976) also occurs here, although to a somewhat smaller extent. As in the other biphenyls the longest ring bonds are those

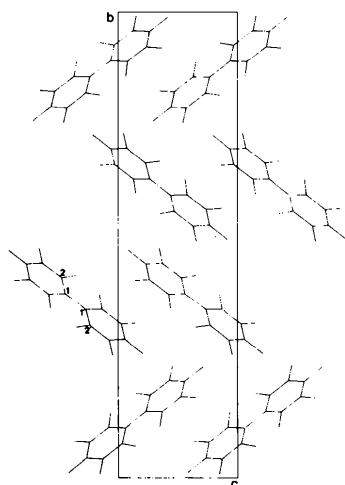


Fig. 2. Projection of the contents of the unit cell along a^* .

adjacent to the central C(1)–C(1') bond. However, owing to the disorder in the crystal structure further discussion of the dimensions of the rings does not seem worth while.

The central bond has a length of 1.486 Å, uncorrected for thermal motion. This compares with uncorrected lengths of 1.486 Å in perfluorobiphenyl and 1.494 Å in biphenyl (Robertson, 1961).^{*} Therefore, compared with biphenyl, this bond is slightly shortened, presumably by the effect of the electronegative F substituents, rather than lengthened by the effect of the 60° interplanar angle in inhibiting any π -electron delocalization which might be operative in (coplanar) biphenyl. This result would appear to lead to the conclusion that electron delocalization between the rings in biphenyls can only be very slight.[†]

^{*} Our method of treating the rigid-body thermal motion does not give a corrected length for C(1)–C(1'). The same approach was used for perfluorobiphenyl (Gleason & Britton, 1976) and only the uncorrected length is listed. Charbonneau & Delugeard (1976, 1977) give only the corrected value for this bond in biphenyl and the best uncorrected length available for comparison purposes appears to be that determined by Robertson (1961).

[†] Rather difficult to explain, however, is that UV spectroscopy (Suzuki, 1959) and Raman spectroscopy (Schmid & Brosa, 1972) of biphenyl in solution indicate significant inter-ring conjugation.

The C–F bonds (excluding those affected by the disorder) range from 1.344 to 1.360 Å. The mean length is 1.351 Å, similar to the mean lengths in perfluorobiphenyl (1.344 Å), hexafluorotroponone (1.343 Å) (Guy, Hamor & Jenkins, 1975) and 3-methoxyperfluorotroponone (1.355 Å) (Hamor & Hamor, 1976).

Intermolecular distances are listed in Table 5 and the packing arrangement is illustrated in Fig. 2. Although many close contacts occur, none of these is substantially shorter than the sum of the van der Waals radii of the atoms concerned.

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