The mean P–C bond lengths for the sulphide and selenide are almost exactly the same (~1·812 Å) but are noticeably longer in the phosphine (1·835 Å). The lengths do not vary significantly from those observed in the o-tolyl derivatives and it would seem, therefore, that the position of substitution of the methyl group has no direct effect upon them. The length of the P–C bonds seems to be influenced by two factors only: the valence state of the P atom and, for individual bond lengths, the degree of intermolecular steric hindrance.

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Structures of Polyfluoroaromatic Compounds.
II.* Crystal Structure of 2,3,5,6-Tetrafluorobiphenyl

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$C_{12}H_6F_4$ is monoclinic, space group $P2_1/c$, with $a = 12·92$ (1), $b = 5·91$ (1), $c = 12·90$ (1) Å, $\beta = 104·22$ (5)°, $Z = 4$. The structure was refined to $R = 4·35\%$ for 904 counter amplitudes. The angle between the phenyl rings is 57·9° and the inter-ring bond length is 1·492 Å (uncorrected for thermal libration). Estimated standard deviations average 0·005 Å for bond lengths and 0·3° for bond angles.

Introduction

The structure of biphenyl has been investigated by X-ray crystallography, gas-phase electron diffraction and spectroscopic techniques (see references cited in part I of this series). We have now determined the crystal structure of 2,3,5,6-tetrafluorobiphenyl (Chaudhry & Stephens, 1963) as part of a continuing study of highly fluorinated molecules.

Experimental

Suitable crystals were obtained from aqueous methanol. A crystal 0·6 × 0·3 × 0·2 mm was sealed in a Pantak capillary tube and aligned about y. Initial photographs determined the space group and approximate cell dimensions. Final cell dimensions and intensities were measured with a Stoe computer-controlled two-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. The diffractometer was operated in the ω-scan mode (Goodhand & Hamor, 1978) with a scan rate of 0·6° min⁻¹ and 30 s background counts at each end of the scan. Four zero-layer reflexions were remeasured after each layer of data collection to check the stability of the system. Of 2492 unique reflexions scanned within the range $0·1 < \sin\theta/\lambda < 0·65$ Å⁻¹, 904 with $I > 2·5\sigma(I)$ were considered to be observed and were used in the analysis.

Crystal data

$C_{12}H_6F_4$, $M_r = 226·2$, monoclinic, $a = 12·92$ (1), $b = 5·91$ (1), $c = 12·90$ (1) Å, $\beta = 104·22$ (5)°, $U = 955$ Å³, $D_c = 1·57$ g cm⁻³, $Z = 4$, $F(000) = 456$; systematic absences: 0k0, k odd; h0l, l odd; space group $P2_1/c$, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å; μ(Mo $K\alpha) = 0·99$ cm⁻¹.

Structure determination

The structure was solved with *SHELX* (Sheldrick, 1975). Phases were found for 434 reflexions with $E > 1.2$ and from the E map all the atoms (apart from H atoms) could be located. At this stage R was 40.4% and full-matrix least-squares refinement of atomic coordinates and isotropic temperature factors reduced R to 11.5%. Introduction of anisotropic thermal parameters further reduced R to 6.1%. All H atoms were now located from a difference synthesis and were included in the refinement with isotropic temperature factors. The calculations were terminated when all calculated shifts were $<0.01\sigma$ and R was 4.4%. The final atomic coordinates are listed in Table 1.* The weighting scheme was $w = 1/\sigma^2(F)$, where $\sigma(F)$ is the standard deviation in the observed $|F(hkl)|$ values derived from counting statistics.

Results and discussion

The conformation of the molecule and the atom numbering are shown in Fig. 1. Bond lengths and angles are in Table 2. The thermal parameters of the atoms were analysed for rigid-body thermal motion (Schomaker & Trueblood, 1968), the two ring systems being treated separately (Table 3). For both rings the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33260 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

major axis of libration is parallel to the long axis of the molecule. Bond lengths corrected for the effect of libration (Cruickshank, 1956) are listed in Table 2 beside the uncorrected values.

The phenyl rings are planar and the angle between the rings is 57.9° (Table 4). This, somewhat surprisingly, is only slightly smaller than the inter-ring angles in perfluorobiphenyl (Gleason & Britton, 1976) and 2*H*-nonafluorobiphenyl (Hamor & Hamor, 1978) which are 59.6 and 59.5°, respectively, where F···F interactions between *ortho* substituents on the rings are involved. The inter-ring bond C(1)—C(1') has a length of 1.492 Å (uncorrected for libration), not significantly different from the corresponding lengths in perfluorobiphenyl (1.486 Å), 2*H*-nonafluorobiphenyl (1.486 Å) and biphenyl (1.494 Å) (Robertson, 1961). Unlike the fluorocarbons, biphenyl is near-planar in the solid state, so that there does not seem to be any correlation between the inter-ring angle and the inter-ring bond length. The length of this bond in all three molecules corresponds to that of a single bond between sp^2-hybridized C atoms (Cruickshank, 1962).

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *with estimated standard deviations in parentheses*

	x	y	z
C(1)	7242 (2)	2284 (5)	2955 (2)
C(2)	6497 (3)	3960 (6)	2973 (3)
C(3)	5828 (3)	3874 (6)	3650 (3)
C(4)	5877 (3)	2135 (7)	4353 (3)
C(5)	6604 (3)	459 (5)	4355 (3)
C(6)	7271 (2)	535 (5)	3672 (3)
C(1')	7956 (2)	2342 (5)	2205 (2)
C(2')	8638 (3)	4138 (6)	2201 (3)
C(3')	9302 (3)	4184 (8)	1511 (3)
C(4')	9282 (3)	2430 (7)	810 (3)
C(5')	8609 (3)	635 (7)	799 (3)
C(6')	7949 (3)	580 (6)	1500 (3)
F(2)	6396 (2)	5708 (3)	2275 (2)
F(3)	5106 (2)	5557 (4)	3601 (2)
F(5)	6684 (2)	−1297 (3)	5037 (2)
F(6)	7996 (2)	−1134 (3)	3734 (1)
H(4)	5429 (24)	2024 (48)	4823 (23)
H(2')	8662 (25)	5291 (55)	2670 (24)
H(3')	9748 (28)	5392 (58)	1525 (25)
H(4')	9727 (28)	2502 (60)	329 (27)
H(5')	8593 (26)	−482 (53)	318 (25)
H(6')	7510 (25)	−560 (51)	1462 (24)

Table 2. *Molecular dimensions*

(a) Bond lengths (Å). Values in the second column are corrected for thermal libration.

C(1)—C(1')	1.492 (4)					
C(1)—C(2)	1.386 (4)	1.394	C(1')—C(2')	1.380 (5)	1.390
C(2)—C(3)	1.372 (5)	1.378	C(2')—C(3')	1.380 (5)	1.385
C(3)—C(4)	1.363 (5)	1.371	C(3')—C(4')	1.372 (6)	1.382
C(4)—C(5)	1.365 (5)	1.373	C(4')—C(5')	1.370 (5)	1.379
C(5)—C(6)	1.375 (5)	1.382	C(5')—C(6')	1.389 (5)	1.394
C(6)—C(1)	1.382 (4)	1.391	C(6')—C(1')	1.381 (5)	1.391
C(2)—F(2)	1.355 (4)	1.364	C(2')—H(2')	0.908 (34)	
C(3)—F(3)	1.355 (4)	1.363	C(3')—H(3')	0.915 (37)	
C(4)—H(4)	0.938 (32)		C(4')—H(4')	0.944 (37)	
C(5)—F(5)	1.349 (4)	1.357	C(5')—H(5')	0.903 (34)	
C(6)—F(6)	1.350 (4)	1.358	C(6')—H(6')	0.874 (32)	

(b) Non-bonded distances (Å)

F(2)···H(2')	2.855	F(6)···H(6')	2.864

(c) Bond angles (°)

|			
C(2)—C(1)—C(6)	115.3 (3)	C(2')—C(1')—C(6')	118.6 (3)
C(2)—C(1)—C(1')	122.5 (3)	C(2')—C(1')—C(1)	121.1 (3)
C(6)—C(1)—C(1')	122.2 (3)	C(6')—C(1')—C(1)	120.3 (3)
C(1)—C(2)—C(3)	122.2 (3)	C(1')—C(2')—C(3')	121.1 (4)
C(1)—C(2)—F(2)	119.2 (3)	C(1')—C(2')—H(2')	119.5 (21)
C(3)—C(2)—F(2)	118.5 (3)	C(3')—C(2')—H(2')	119.4 (21)
C(2)—C(3)—C(4)	121.2 (3)	C(2')—C(3')—C(4')	119.7 (4)
C(2)—C(3)—F(3)	118.5 (3)	C(2')—C(3')—H(3')	119.4 (22)
C(4)—C(3)—F(3)	120.3 (3)	C(4')—C(3')—H(3')	120.9 (22)
C(3)—C(4)—C(5)	117.9 (4)	C(3')—C(4')—C(5')	120.1 (4)
C(3)—C(4)—H(4)	123.3 (20)	C(3')—C(4')—H(4')	118.9 (24)
C(5)—C(4)—H(4)	118.8 (20)	C(5')—C(4')—H(4')	121.0 (24)
C(4)—C(5)—C(6)	120.9 (3)	C(4')—C(5')—C(6')	120.1 (4)
C(4)—C(5)—F(5)	120.1 (3)	C(4')—C(5')—H(5')	118.8 (22)
C(6)—C(5)—F(5)	118.9 (3)	C(6')—C(5')—H(5')	121.1 (22)
C(5)—C(6)—C(1)	122.4 (3)	C(5')—C(6')—C(1')	120.4 (4)
C(5)—C(6)—F(6)	118.2 (3)	C(5')—C(6')—H(6')	118.3 (21)
C(1)—C(6)—F(6)	119.4 (3)	C(1')—C(6')—H(6')	121.3 (21)
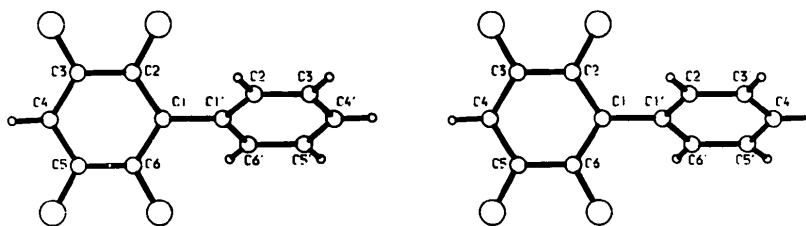
Fig. 1. Stereoscopic view of the molecule showing the atomic labelling.

The aromatic C—C bonds range from 1·371 to 1·394 Å, mean 1·384 Å (corrected for thermal motion). There is, however, a slight, but not statistically significant, difference between the bonds in the

Table 3. *Results of rigid-body-motion analysis*

The eigenvectors of the libration tensor L and translation tensor T are referred, in terms of 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.

(i) C(1)—C(6), F(2), F(3), F(5), F(6)

	Eigenvalues	Eigenvectors		
	205 (at. wt Å^2)	−0·3370	0·8600	−0·3833
I	488	−0·7860	−0·0329	0·6173
	693	0·5182	0·5093	0·6870
	93 (×10^{-4} rad^2)	−0·0254	−0·9958	−0·0881
L	55	0·8950	0·0166	−0·4458
	36	0·4454	−0·0901	0·8908
	493 (×10^{-4} Å^2)	0·8882	−0·4574	0·0430
T	388	0·4544	0·8884	0·0641
	330	−0·0676	−0·0374	0·9970

r.m.s. discrepancy $\langle \Delta U^2 \rangle^{1/2} = 0.003$ Å^2.

(ii) C(1')—C(6')

	Eigenvalues	Eigenvectors		
	68 (at. wt Å^2)	−0·7818	−0·0344	0·6226
I	77	−0·2666	−0·8841	−0·3837
	145	0·5637	−0·4660	0·6820
	130 (×10^{-4} rad^2)	0·9710	0·0163	−0·2385
L	43	0·1982	0·5026	0·8415
	30	0·1335	−0·8644	0·4848
	458 (×10^{-4} Å^2)	0·7730	0·4646	0·4320
T	410	0·6343	−0·5794	−0·5119
	350	0·0125	0·6697	−0·7425

r.m.s. discrepancy $\langle \Delta U^2 \rangle^{1/2} = 0.003$ Å^2.

two rings, the mean C—C length for the fluorinated ring [1·382 (4) Å] being slightly smaller than that for the unfluorinated ring [1·387 (2) Å]. Similar slight shortenings of C—C bonds in unsaturated fluorocarbons relative to the parent hydrocarbon have been noted previously [Hamor & Hamor, 1976 (and references therein), 1978]. The pattern of bond-angle variation in the aromatic rings is consistent with the effect of hybridization changes induced by the electronegative F substituents (Bent, 1961; Domenicano, Vaciago & Coulson, 1975). The small angles at C(1) and C(1') are possibly indicative of a slight degree of inter-ring conjugation, although the measured length of C(1)—C(1') would appear to preclude this.

The C—F bonds have lengths 1·357–1·364 Å, mean 1·360 Å (corrected), rather longer than the mean lengths in perfluorobiphenyl (1·344 Å) and 2H-nonafluorobiphenyl (1·351 Å).

The arrangement of the molecules in the unit cell is shown in Fig. 2 and the shorter intermolecular contact distances are in Table 5. The packing forces seem to
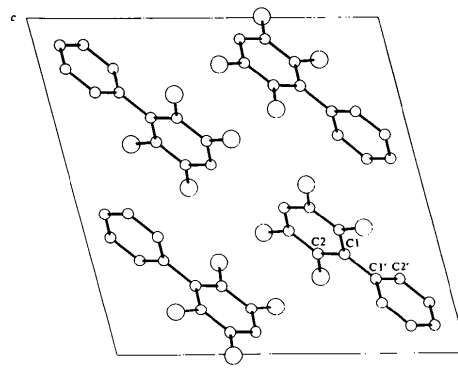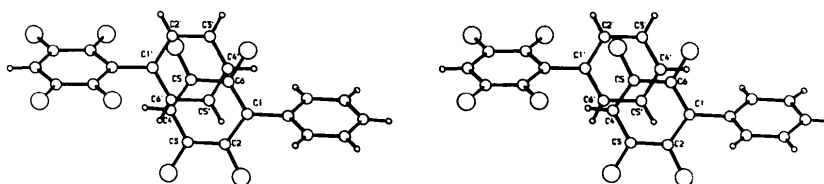

Fig. 2. Projection of the contents of the unit cell along b.

Fig. 3. Stereoscopic view of a pair of molecules related by the c glide plane.

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')	−0·001*
C(2)	0·003*	C(2')	−0·002*
C(3)	−0·005*	C(3')	0·003*
C(4)	0·003*	C(4')	0·000*
C(5)	0·000*	C(5')	−0·003*
C(6)	−0·001*	C(6')	0·004*
C(1')	−0·021	C(1)	0·001
F(2)	−0·033	H(2')	0·013
F(3)	−0·029	H(3')	0·005
H(4)	−0·007	H(4')	−0·021
F(5)	0·008	H(5')	−0·032
F(6)	0·040	H(6')	−0·027

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

$$(I) \quad -6·772x - 2·961y - 6·952z = -7·636$$
$$(II) -7·281x + 2·755y - 6·744z = -6·636$$

Interplanar angle (I)–(II) = 57·9°.

Table 5. *Intermolecular contact distances* (Å)

Listed are contacts between the heavier atoms <3·4 Å, and contacts involving one H atom <3·0 Å. All H···H contacts are >2·6 Å and are not listed.

F(3)···C(2$^{\mathrm{I}}$)	3·23	F(2)···F(6$^{\mathrm{IV}}$)	3·07
F(2)···C(4$^{\mathrm{I}}$)	3·27	H(6')···F(5$^{\mathrm{II}}$)	2·65
C(6')···F(5$^{\mathrm{II}}$)	3·34	H(4)···F(3$^{\mathrm{V}}$)	2·71
F(3)···C(1$^{\mathrm{I}}$)	3·36	H(2')···F(6$^{\mathrm{IV}}$)	2·77
F(2)···C(3$^{\mathrm{I}}$)	3·39	H(4)···F(5$^{\mathrm{VI}}$)	2·81
F(5)···F(2$^{\mathrm{III}}$)	3·02	H(5')···F(6$^{\mathrm{II}}$)	2·83
F(3)···F(5$^{\mathrm{IV}}$)	3·03	F(2)···H(6'$^{\mathrm{IV}}$)	2·96

Symmetry code

(I)	$1-x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$	(IV)	$x,$	$1+y,$	z
(II)	$x,$	$-\frac{1}{2}-y,$	$-\frac{1}{2}+z$	(V)	$1-x,$	$1-y,$	$1-z$
(III)	$x,$	$\frac{1}{2}-y,$	$\frac{1}{2}+z$	(VI)	$1-x,$	$-y,$	$1-z$

involve mainly F···H interactions. Molecules related by the c glide plane pack in such a way that fluorinated and unfluorinated rings are oriented approximately parallel (interplanar angle 3°) and overlie one another to some extent. This is illustrated in Fig. 3 which shows two such molecules viewed in the direction perpendicular to the plane of the unfluorinated ring. There do not, however, appear to be particularly strong interactions between these ring systems. The perpendicular separation between the rings averages 3·5 Å and the shortest contacts are H(4')···F(6), 3·40 Å; C(2')···F(5), 3·51 Å; C(4')···C(6), 3·51 Å; C(4')···F(6), 3·54 Å; and C(6')···C(4), 3·61 Å.*

We thank Dr P. L. Coe for supplying a sample of the title compound, Professor J. C. Tatlow and Dr R. Stephens for their interest, and the University of Birmingham for the award of a Research Studentship (to NG).

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