

## Structures of Polyfluoroaromatic Compounds.

### V.\* Crystal Structure of Perfluorodiphenylacetylene

BY N. GOODHAND AND T. A. HAMOR

*Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England*

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#### Abstract

$C_{14}F_{10}$  is orthorhombic, space group *Pbca*, with  $a = 9.59$  (1),  $b = 9.59$  (1),  $c = 27.34$  (2) Å,  $Z = 8$ . The structure was refined to  $R = 5.25\%$  for 1202 counter amplitudes [ $I > 2.5\sigma(I)$ ]. The molecule is essentially planar, but its long axis is slightly bent so that the aromatic rings make an in-plane angle of  $4^\circ$  with one another. The C–C triple-bond length is 1.198 Å and the two C(sp)–C(sp<sup>2</sup>) lengths average 1.419 Å (uncorrected for thermal libration). E.s.d.'s are 0.004–0.006 Å for bond lengths and 0.4–0.5° for bond angles.

#### Introduction

The crystal structure of diphenylacetylene (tolan) was determined by Robertson & Woodward (1938) from projection data and later refined with three-dimensional photographic data (Samarskaya, Myasnikova & Kitaigorodskii, 1969). We now report the crystal structure of perfluorodiphenylacetylene (Callander, 1966; Birchall, Bowden, Haszeldine & Lever, 1967; Callander, Coe, Tatlow & Terrell, 1971) as part of a continuing study of highly fluorinated organic molecules.

#### Experimental

Suitable crystals were obtained from  $CCl_4$ . A crystal  $0.7 \times 0.6 \times 0.2$  mm was sealed in a Pantak capillary tube and aligned about **a**. The intensities and cell dimensions were measured on a Stoe computer-controlled two-circle diffractometer operating in the  $\omega$ -scan mode with graphite-monochromated Mo  $K\alpha$  radiation. For layers  $0kl$ – $2kl$ , 140 counts of 1 s at intervals of  $0.01^\circ$  were taken for each reflexion. For the higher layers a variable scan range was used (Hamor & Hamor, 1978). Backgrounds were measured for 30 s at each end of the scan. Reflexions were scanned within

the range  $0.1 < \sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$  and 1214 having  $I > 2.5\sigma(I)$  were used in the analysis. Four zero-layer reflexions were remeasured after each layer of data collection to check the stability of the system. There was no systematic variation of their intensities. No absorption corrections were made.

#### Crystal data

$C_{14}F_{10}$ ,  $M_r = 358.1$ , orthorhombic,  $a = 9.59$  (1),  $b = 9.59$  (1),  $c = 27.34$  (2) Å,  $U = 2514 \text{ \AA}^3$ ,  $Z = 8$ ,  $D_c = 1.892 \text{ Mg m}^{-3}$ ,  $F(000) = 1392$ . Systematic absences:  $0kl$ ,  $k$  odd;  $h0l$ ,  $l$  odd;  $hk0$ ,  $h$  odd; space group *Pbca*. Mo  $K\alpha$  radiation,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu(\text{Mo } K\alpha) = 0.157 \text{ mm}^{-1}$ .

#### Structure determination

The structure was solved by direct methods with *SHELX* (Sheldrick, 1975). Full-matrix least-squares

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(A)	1146 (4)	–1186 (4)	3348 (2)
C(B)	1127 (4)	–1203 (4)	2910 (2)
C(1)	1178 (4)	–1155 (4)	3868 (1)
C(2)	2204 (4)	–406 (4)	4117 (1)
C(3)	2262 (5)	–369 (5)	4621 (2)
C(4)	1317 (5)	–1106 (5)	4887 (2)
C(5)	281 (4)	–1849 (4)	4662 (2)
C(6)	210 (4)	–1882 (5)	4158 (2)
C(1')	1142 (4)	–1181 (4)	2392 (1)
C(2')	2118 (4)	–404 (5)	2132 (2)
C(3')	2116 (5)	–353 (5)	1628 (2)
C(4')	1169 (5)	–1120 (5)	1375 (2)
C(5')	210 (5)	–1911 (5)	1612 (2)
C(6')	178 (4)	–1940 (5)	2114 (2)
F(2)	3129 (2)	315 (3)	3859 (1)
F(3)	3249 (3)	371 (3)	4843 (1)
F(4)	1373 (3)	–1081 (3)	5379 (1)
F(5)	–646 (3)	–2538 (3)	4925 (1)
F(6)	–760 (3)	–2619 (3)	3935 (1)
F(2')	3080 (2)	333 (2)	2379 (1)
F(3')	3098 (3)	401 (3)	1394 (1)
F(4')	1170 (3)	–1080 (3)	881 (1)
F(5')	–753 (3)	–2645 (3)	1358 (1)
F(6')	–783 (2)	–2711 (3)	2347 (1)

\* Part IV: Hamor & Hamor (1978).

calculations varying coordinates and isotropic temperature factors reduced  $R$  from an initial value of 40% to 11.4%. With the introduction of anisotropic temperature factors  $R$  was reduced to a final value of 5.25%. Four very intense low-order reflexions which appeared to be affected by extinction were removed from the final cycles, as were eight small reflexions for which  $F_o/F_c > 3$  or  $< \frac{1}{3}$ . 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 amplitudes based on counting statistics. Complex neutral-atom scattering factors were employed.

Computations were carried out on the CDC 7600 computer at the University of Manchester Regional Computer Centre and on the Birmingham University ICL 1906A.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34114 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular dimensions*

(a) Bond lengths (Å) with e.s.d.'s in parentheses. Values in the second column are corrected for thermal libration.

C(A)—C(B)	1.198 (5)				
C(1)—C(A)	1.422 (6)	C(1')—C(B)	1.415 (6)		
C(1)—C(2)	1.396 (6)	1.406	C(1')—C(2')	1.393 (5)	1.402
C(2)—C(3)	1.381 (5)	1.391	C(2')—C(3')	1.376 (5)	1.385
C(3)—C(4)	1.359 (6)	1.369	C(3')—C(4')	1.359 (6)	1.367
C(4)—C(5)	1.369 (6)	1.380	C(4')—C(5')	1.357 (6)	1.366
C(5)—C(6)	1.379 (5)	1.388	C(5')—C(6')	1.373 (5)	1.382
C(6)—C(1)	1.406 (5)	1.416	C(6')—C(1')	1.401 (5)	1.410
C(2)—F(2)	1.327 (4)	1.337	C(2')—F(2')	1.345 (4)	1.353
C(3)—F(3)	1.329 (5)	1.339	C(3')—F(3')	1.350 (4)	1.359
C(4)—F(4)	1.349 (4)	1.358	C(4')—F(4')	1.352 (5)	1.360
C(5)—F(5)	1.320 (4)	1.330	C(5')—F(5')	1.354 (4)	1.362
C(6)—F(6)	1.318 (4)	1.328	C(6')—F(6')	1.343 (4)	1.352

(b) Bond angles (°) with e.s.d.'s in parentheses

C(1)—C(A)—C(B)	179.5 (4)	C(1')—C(B)—C(A)	177.7 (5)
C(2)—C(1)—C(A)	120.8 (4)	C(2')—C(1')—C(B)	121.8 (4)
C(6)—C(1)—C(A)	122.6 (4)	C(6')—C(1')—C(B)	121.9 (4)
C(6)—C(1)—C(2)	116.5 (4)	C(6')—C(1')—C(2')	116.3 (4)
C(3)—C(2)—C(1)	121.9 (4)	C(3')—C(2')—C(1')	122.0 (4)
F(2)—C(2)—C(1)	118.8 (4)	F(2')—C(2')—C(1')	119.0 (4)
F(2)—C(2)—C(3)	119.3 (5)	F(2')—C(2')—C(3')	119.0 (5)
C(4)—C(3)—C(2)	119.5 (5)	C(4')—C(3')—C(2')	119.4 (5)
F(3)—C(3)—C(2)	119.8 (5)	F(3')—C(3')—C(2')	119.6 (5)
F(3)—C(3)—C(4)	120.7 (4)	F(3')—C(3')—C(4')	121.0 (4)
C(5)—C(4)—C(3)	121.0 (4)	C(5')—C(4')—C(3')	120.8 (4)
F(4)—C(4)—C(3)	119.8 (4)	F(4')—C(4')—C(3')	119.5 (5)
F(4)—C(4)—C(5)	119.1 (4)	F(4')—C(4')—C(5')	119.6 (5)
C(6)—C(5)—C(4)	119.7 (4)	C(6')—C(5')—C(4')	120.2 (5)
F(5)—C(5)—C(4)	120.3 (4)	F(5')—C(5')—C(4')	120.5 (5)
F(5)—C(5)—C(6)	120.0 (4)	F(5')—C(5')—C(6')	119.2 (5)
C(5)—C(6)—C(1)	121.3 (4)	C(5')—C(6')—C(1')	121.2 (4)
F(6)—C(6)—C(1)	118.1 (4)	F(6')—C(6')—C(1')	118.8 (4)
F(6)—C(6)—C(5)	120.6 (4)	F(6')—C(6')—C(5')	120.0 (4)

## Results and discussion

Bond lengths and angles are listed in Table 2, and the results of mean-plane calculations in Table 3. The labelling of the atoms is shown in Fig. 1. Bond lengths corrected for the effect of rigid-body thermal motion (Cruickshank, 1956; Schomaker & Trueblood, 1968) are also listed in Table 2. In these calculations the two  $C_6F_3$  rings were treated as independent units to give the results in Table 4. Inclusion of the central ethynyl moiety led to significantly worse agreement between observed and calculated  $U_{ij}$  values and corrected lengths for this grouping would therefore not be meaningful.

The two phenyl rings are planar to within  $\pm 0.01$  Å (Table 3) and the maximum deviation of a ring substituent from the plane of its ring is 0.032 Å. The angle between the mean planes of the phenyl rings is only 2.2° and the molecule as a whole is essentially planar. Statistically significant atomic displacements of

Table 3. *Mean-plane calculations*

Deviations (Å) of atoms from least-squares planes. Distances marked with an asterisk refer to atoms defining the plane. Estimated standard deviations in the distances are 0.003–0.005 Å.

	(I)	(II)	(III)	(IV)
C(A)	−0.024	0.029	0.000*	−0.000*
C(B)	−0.042	0.012	−0.009*	−0.010*
C(1)	−0.002*	0.049	0.012*	0.012*
C(2)	−0.003*		−0.018*	−0.015*
C(3)	0.009*		−0.017*	−0.013*
C(4)	−0.009*		−0.018*	−0.016*
C(5)	0.004*		0.023*	0.023*
C(6)	0.002*		0.032*	0.031*
C(1')	−0.051	0.003*	−0.008*	−0.009*
C(2')		−0.012*	0.005*	0.005*
C(3')		0.011*	0.037*	0.037*
C(4')		−0.001*	0.008*	0.005*
C(5')		−0.008*	−0.026*	−0.031*
C(6')		0.006*	−0.022*	−0.026*
F(2)	0.013			−0.014*
F(3)	0.021			−0.026*
F(4)	−0.006			−0.022*
F(5)	0.012			0.046*
F(6)	−0.018			0.036*
F(2')		−0.032		0.005*
F(3')		−0.024		0.031*
F(4')		0.012		0.027*
F(5')		0.015		−0.029*
F(6')		0.016		−0.046*

Interplanar angles (°)

(I)—(II)	2.2	(I)—(III)	1.2	(II)—(III)	1.2
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Equations of planes ( $x$ ,  $y$  and  $z$  are fractional coordinates relative to the cell axes)

(I)	$5.722x - 7.700y - 0.336z = 1.432$
(II)	$6.016x - 7.473y - 0.328z = 1.494$
(III)	$5.870x - 7.588y - 0.145z = 1.524$
(IV)	$5.857x - 7.599y - 0.157z = 1.519$

Table 4. 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 reciprocal-cell axes.

Eigenvalues		Eigenvectors		
(i) C(1)–(6), F(2)–(6)				
<b>I</b>	332 (at. wt Å <sup>2</sup> )	0.7993	0.5992	0.0447
	483	0.0422	0.0181	0.9989
	815	0.5994	–0.8004	–0.0108
<b>L</b>	94 (× 10 <sup>–4</sup> rad <sup>2</sup> )	0.1561	–0.9058	–0.3939
	70	0.9857	0.1683	0.0038
	60	0.0628	–0.3888	0.9192
<b>T</b>	522 (× 10 <sup>–4</sup> Å <sup>2</sup> )	0.9335	–0.2710	0.2349
	503	–0.2884	–0.9566	0.0424
	308	0.2132	–0.1073	–0.9711
r.m.s. discrepancy $\langle \Delta U^2 \rangle^{1/2} = 0.004 \text{ \AA}^2$ .				
(ii) C(1')–(6'), F(2')–(6')				
<b>I</b>	331 (at. wt Å <sup>2</sup> )	0.7839	0.6206	0.0166
	490	–0.0038	–0.0218	0.9998
	821	0.6208	–0.7838	–0.0147
<b>L</b>	73 (× 10 <sup>–4</sup> rad <sup>2</sup> )	0.9930	0.3576	–0.0403
	63	–0.3566	0.9338	0.0292
	58	0.0481	–0.0129	0.9988
<b>T</b>	492 (× 10 <sup>–4</sup> Å <sup>2</sup> )	0.8383	–0.5420	–0.0593
	457	–0.5397	–0.8403	0.0505
	345	–0.0772	–0.0103	–0.9970
r.m.s. discrepancy $\langle \Delta U^2 \rangle^{1/2} = 0.004 \text{ \AA}^2$ .				

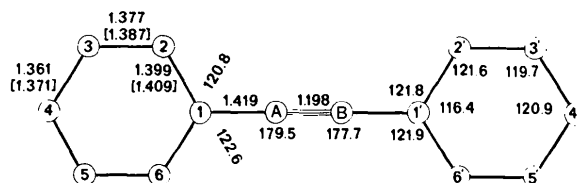


Fig. 1. Bond lengths (Å) and angles (°) for the C framework. Lengths corrected for thermal libration are in square brackets. Apart from the exocyclic angles at C(1) and C(1'), and the angles at C(A) and C(B), lengths and angles have been averaged on the basis of  $D_{2h}$  symmetry (see text).

up to  $\pm 0.046 \text{ \AA}$  from the calculated mean plane, however, occur ( $\chi^2 = 1656$  for 21 degrees of freedom). The near  $mmm$  ( $D_{2h}$ ) molecular symmetry is further distorted by an in-plane bending of the central axis of the molecule [F(4), C(4), C(1), C(A), C(B), C(1'), C(4'), F(4')]. The principal angular deviations are the unequal exocyclic angles at C(1) and the non-linear geometry at the acetylenic C(B). The phenyl rings are bent in the same direction so that C(2) and C(2') come closer together and C(6) and C(6') are farther apart [C(2)···C(2') = 5.43, C(6)···C(6') = 5.59 Å]. The angle between the rings is *ca* 4°.

The slight distortion from  $D_{2h}$  symmetry does not seem to affect the C–C lengths. Equivalent lengths

agree within experimental error ( $\chi^2 = 9.6$  for 10 degrees of freedom) and averaged values are shown in Fig. 1. Averaging seems to be justified also for bond angles, apart from the exocyclic angles at C(1) and C(1') and the acetylenic angles. Omitting these angles  $\chi^2 = 19.9$  for 23 degrees of freedom and selected averaged angles are also shown in Fig. 1.

The C–F lengths, however, do not conform to  $D_{2h}$  symmetry. For the phenyl ring C(1)–C(6), the four C–F lengths involving F(2), F(3), F(5) and F(6) are all in the range 1.328–1.339 Å [mean 1.334 Å (corrected)], while C(4)–F(4) is longer at 1.358 Å. In the other phenyl ring, all five C–F bonds are longer, ranging from 1.352 to 1.362 Å (mean 1.357 Å). The set of four short C–F bonds are comparable with the shorter than average C–F bonds in 2-nitrononafluorobiphenyl (Hamor & Hamor, 1978) where the range is 1.331–1.348 Å (mean 1.342 Å). The remaining C–F bonds are nearer in length to those found in 2,3,5,6-tetrafluorobiphenyl (Goodhand & Hamor, 1978), range 1.357–1.364 Å (mean 1.360 Å). It does not seem possible to rationalize these differences in the present structure.

The mean aromatic C–C length is 1.389 Å (corrected), slightly larger than the mean of 1.381 Å in both perfluorobiphenyl (Gleason & Britton, 1976) and 2-nitrononafluorobiphenyl, but very slightly smaller than in biphenyl itself (Charbonneau & Delugeard, 1976, 1977) where the corresponding mean is 1.391 Å. The pattern of bond-length variation (Fig. 1) is similar to that commonly found in fluorobiphenyl structures, except that the C(1)–C(2) mean length of 1.409 Å is larger by some 0.015 Å.

The C(A)–C(B) triple-bond length of 1.198 Å (uncorrected) compares well with the standard triple-bond value of 1.202 Å (Sutton, 1965). In 1,8-bis(phenylethynyl)naphthalene (Jungk & Schmidt, 1971) the triple-bond lengths are 1.189 and 1.191 Å (uncorrected), and in tetramethylverdene (Brodherr, Narayanan, Zechmeister & Hoppe, 1971) both triple bonds are 1.19 Å (uncorrected), in good agreement with our value. The four C( $sp^2$ )–C( $sp$ ) bonds in the former structure all have lengths in the range 1.439–1.443 Å and in the latter the four bonds of this type are 1.43–1.44 Å. E.s.d.'s in these bond lengths are quoted as 0.002 Å for the former and 0.003–0.005 Å for the latter structure. In the present structure the C(1)–C(A) and C(1')–C(B) lengths are 1.422 (6) and 1.415 (6) Å (uncorrected), probably significantly shorter than the bonds of similar type in 1,8-bis(phenylethynyl)naphthalene and tetramethylverdene. A possible reason for this difference is that in the two hydrocarbon molecules the aromatic systems linked by the ethynyl functions are in three cases inclined at angles of  $>40^\circ$  to one another, and in the fourth case at  $14^\circ$ , while in the perfluorodiphenylacetylene molecule the corresponding angle is  $2^\circ$ . It is possible, therefore, that there

is some conjugation between the virtually coplanar  $C_6F_5$  rings. The long C(1)–C(2) bonds (Fig. 1) are consistent with this. There does not, however, appear to be a concomitant increase in the length of the C(A)–C(B) triple bond, although a slight increase does occur. The small endocyclic angles at C(1) and C(1'), mean  $116.4^\circ$ , are consistent with some double-bond character in C(1)–C(A) and C(1')–C(B). They are, however, also explainable, as in tetrafluorobiphenyl (Goodhand & Hamor, 1978), by the presence of the electronegative F substituents.

For diphenylacetylene itself accurate molecular dimensions are not available. Like the perfluoro derivative, the molecule is essentially planar. The early work of Robertson & Woodward (1938) leads to lengths of 1.40 Å for the C( $sp^2$ )–C( $sp$ ) single bond and 1.19 Å for the C–C triple bond (averaged over two independent centrosymmetric molecules). The corresponding lengths obtained by Samarskaya, Myasnikova & Kitaigorodskii (1969) are 1.401 and 1.226 Å, with a mean C–C aromatic length of 1.401 Å. These lengths are in reasonable agreement with those found in perfluorodiphenylacetylene and also seem to indicate some conjugation between the coplanar aromatic rings. Non-linearity of the ethynyl moiety noted previously is found also in 1,8-bis(phenylethynyl)naphthalene and tetramethylverdene, with C–C≡C angles generally  $172$ – $174^\circ$ . These deviations from linearity can be

Table 5. *Intermolecular contact distances* (Å)  
(F...F < 3.0, F...C < 3.2, C...C < 3.4 Å)

Estimated standard deviations are ca 0.01 Å.

F(3')...F(4')	2.89	F(3')...C(5' <sup>IV</sup> )	3.11
F(4')...F(3')	2.97	F(5')...C(2' <sup>V</sup> )	3.18
F(5)...F(3 <sup>II</sup> )	2.99	F(2')...C(6' <sup>IV</sup> )	3.19
F(6')...F(2' <sup>III</sup> )	2.99	C(5')...F(2' <sup>V</sup> )	3.20
F(3)...C(5' <sup>IV</sup> )	3.06	C(4)...C(4' <sup>V</sup> )	3.36
F(5)...C(3 <sup>II</sup> )	3.10		

Symmetry code

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

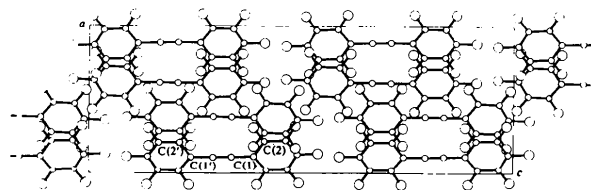


Fig. 2. Projection of the contents of the unit cell along *b*.

rationalized on steric grounds (Jungk & Schmidt, 1971; Brodherr, Narayanan, Zechmeister & Hoppe, 1971). In the present structure, the bending of the central axis of the molecule, involving a small deviation from linearity of the ethynyl moiety, is presumably due to packing forces. Diphenylacetylene, however, is essentially linear.

The packing of the molecules is illustrated in Fig. 2 which shows a view of the unit cell along *b*. The molecules lie almost parallel to *c* and are inclined at  $\pm 38^\circ$  to (010). The shorter intermolecular contact distances are listed in Table 5. None of these is substantially shorter than the sum of the van der Waals radii of the atoms concerned.

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