

Structure of 1-Bromo-3,4,5-trifluoro-2,6-bis(pentafluorophenyl)benzene*

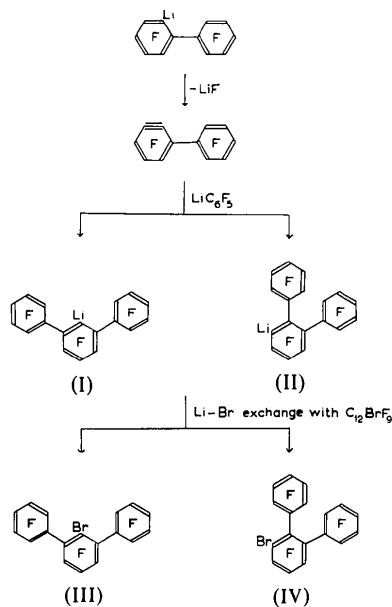
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Abstract. $C_{18}BrF_{13}$, orthorhombic, $Pnma$ (from intensity statistics and successful refinement), $a = 21.164$ (5), $b = 15.140$ (4), $c = 5.632$ (5) Å, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.56$ mm⁻¹, crystal size $0.7 \times 0.2 \times 0.1$ mm. $R = 0.069$ for 789 observed reflexions with $I > 3\sigma(I)$. The dihedral angle between the central and terminal phenyl rings is 78.3 (7)° and the inter-ring bond length is 1.47 (1) Å (uncorrected for thermal libration).

Introduction. Cohen, Tomlinson, Wiles & Massey (1968) showed that the reaction of 2-lithiononafluorobiphenyl with (pentafluorophenyl)lithium yields the perfluoroterphenyl derivatives (I) and (II), and that Li-Br exchange can occur with (I) and (II) in the presence of 2-bromononafluorobiphenyl giving the title compound (III) and its isomer (IV). The structures of (III) and (IV) were deduced from their ¹⁹F NMR spectra and an aryne mechanism was proposed (Cohen, Tomlinson, Wiles & Massey, 1968) to account for their formation from 2-lithiononafluorobiphenyl.



* Structures of Substituted Perfluoropolyphenyls. I.

Confirmation of the structures of (III) and (IV) by X-ray crystallography will strengthen the evidence for the proposed aryne mechanism. It is hoped to report subsequently on the structure of (IV).

This analysis is also part of a series of studies on the correlation between inter-ring bond lengths and dihedral angles in substituted perfluoropolyphenyls. There appears to be no such correlation in 2-substituted perfluorobiphenyls (Hamor & Hamor, 1978).

The compound was prepared by the method of Cohen, Tomlinson, Wiles & Massey (1968). Colourless crystals were obtained by vapour diffusion with methanol and a solution of $C_{18}BrF_{13}$ in toluene, and the selected crystal was mounted in a sealed Lindemann-glass capillary.

The intensities and cell dimensions were obtained from a Stoe Stadi-2 two-circle diffractometer by an ω scan with graphite-monochromated Mo $K\alpha$ radiation. Of 1538 reflexions measured, 789 had $I > 3\sigma(I)$ and were classed as observed. Reflexions were measured out to a maximum 2θ of 50°. Lp corrections were applied, but none for absorption or extinction.

The position of the Br atom on the mirror plane was found from the Patterson function. All other atoms were located from the E map phased on the Br position.

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

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)*
Br	3110 (1)	2500	3172 (5)	6.8 (2)
C(1)	3926 (7)	2500	1766 (38)	4.3 (1.8)
C(2)	4211 (5)	3308 (6)	1345 (25)	4.1 (1.3)
C(3)	4805 (5)	3281 (7)	350 (30)	5.0 (1.6)
C(4)	5116 (7)	2500	-95 (47)	6.2 (2.6)
C(5)	3916 (5)	4171 (6)	1817 (25)	4.0 (1.1)
C(6)	3478 (6)	4520 (8)	308 (30)	5.5 (1.6)
C(7)	3198 (6)	5331 (8)	690 (32)	5.9 (1.7)
C(8)	3377 (6)	5810 (7)	2602 (35)	5.9 (1.8)
C(9)	3808 (7)	5484 (8)	4163 (32)	5.9 (1.7)
C(10)	4074 (5)	4672 (7)	3735 (28)	5.0 (1.5)
F(3)	5112 (3)	4032 (4)	-112 (17)	6.3 (1.0)
F(4)	5698 (5)	2500	-996 (30)	8.1 (1.8)
F(6)	3293 (3)	4071 (5)	-1665 (18)	7.3 (1.1)
F(7)	2772 (4)	5643 (5)	-909 (21)	8.7 (1.3)
F(8)	3109 (4)	6599 (4)	3011 (23)	8.9 (1.3)
F(9)	3987 (4)	5953 (6)	6090 (20)	9.3 (1.3)
F(10)	4499 (4)	4358 (5)	5303 (17)	7.5 (1.1)

* B_{eq} is given by $\frac{1}{3}(B_{11} + B_{22} + B_{33})$.

The structure was refined by full-matrix least squares to $R = 0.069$ with calculated shifts $< 0.2\sigma$ in the final cycle. Unit weight was used for all reflexions. Scattering factors were those of Cromer & Mann (1968).*

All calculations were carried out with the XRAY system (1972) implemented at the University of Manchester Regional Computer Centre.

Final atomic coordinates are listed in Table 1, bond lengths and angles in Table 2, short intermolecular contacts in Table 3, and displacements of atoms from phenyl-ring planes in Table 4. The atom numbering is given in Fig. 1. Fig. 2 shows the cell contents projected down c .

Discussion. The confirmation of the molecular structure of 1-bromo-3,4,5-trifluoro-2,6-bis(pentafluorophenyl)benzene has strengthened the evidence for the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35587 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°)

C(1)—Br	1.90 (2)	C(7)—C(8)	1.35 (2)
C(1)—C(2)	1.38 (1)	C(8)—C(9)	1.36 (2)
C(2)—C(3)	1.38 (2)	C(9)—C(10)	1.37 (2)
C(2)—C(5)	1.47 (1)	C(10)—C(5)	1.36 (2)
C(3)—C(4)	1.38 (1)	C(6)—F(6)	1.36 (2)
C(3)—F(3)	1.34 (1)	C(7)—F(7)	1.36 (2)
C(4)—F(4)	1.33 (2)	C(8)—F(8)	1.34 (1)
C(5)—C(6)	1.36 (2)	C(9)—F(9)	1.35 (2)
C(6)—C(7)	1.38 (2)	C(10)—F(10)	1.35 (2)
C(2)—C(1)—Br	118 (1)	C(5)—C(6)—F(6)	121 (1)
C(2)—C(1)—C(2')	124 (1)	C(7)—C(6)—F(6)	117 (1)
C(1)—C(2)—C(3)	116 (1)	C(6)—C(7)—C(8)	119 (1)
C(1)—C(2)—C(5)	125 (1)	C(6)—C(7)—F(7)	119 (1)
C(3)—C(2)—C(5)	119 (1)	C(8)—C(7)—F(7)	122 (1)
C(2)—C(3)—C(4)	122 (1)	C(7)—C(8)—C(9)	121 (1)
C(2)—C(3)—F(3)	120 (1)	C(7)—C(8)—F(8)	120 (1)
C(4)—C(3)—F(3)	118 (1)	C(9)—C(8)—F(8)	120 (1)
C(3)—C(4)—F(4)	121 (1)	C(8)—C(9)—C(10)	119 (1)
C(3)—C(4)—C(3')	118 (1)	C(8)—C(9)—F(9)	121 (1)
C(2)—C(5)—C(6)	121 (1)	C(10)—C(9)—F(9)	120 (1)
C(2)—C(5)—C(10)	122 (1)	C(5)—C(10)—C(9)	122 (1)
C(6)—C(5)—C(10)	116 (1)	C(5)—C(10)—F(10)	119 (1)
C(5)—C(6)—C(7)	123 (1)	C(9)—C(10)—F(10)	118 (1)

Table 3. Intermolecular contacts < 3.30 Å

F(8)⋯F(8 ⁱ)	2.73 (1)	F(10)⋯F(6 ^v)	3.10 (1)
F(10)⋯F(10 ⁱⁱ)	2.90 (1)	F(9)⋯F(7 ^v)	3.11 (1)
F(3)⋯F(10 ⁱⁱⁱ)	2.93 (1)	F(8)⋯F(6 ^{vi})	3.14 (1)
F(3)⋯F(9 ⁱⁱ)	2.96 (1)	C(7)⋯F(7 ^{vi})	3.17 (2)
F(3)⋯F(3 ^{iv})	2.97 (1)	C(10)⋯F(6 ^v)	3.20 (2)
F(4)⋯F(8 ^{iv})	3.09 (1)	F(9)⋯C(7 ^v)	3.22 (2)

Symmetry code

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

Table 4. Displacements (Å) of atoms from least-squares planes

(I) Central ring C(1)—C(4)		(II) Terminal ring C(5)—C(10)	
*C(1)	-0.007 (13)	C(2)	0.031 (13)
*C(2)	0.013 (13)	*C(5)	0.000 (7)
*C(3)	-0.014 (13)	*C(6)	0.004 (7)
*C(4)	0.007 (13)	*C(7)	-0.009 (7)
C(5)	0.019 (19)	*C(8)	0.010 (7)
Br	0.050 (13)	*C(9)	-0.005 (7)
F(3)	0.002 (16)	*C(10)	0.000 (7)
F(4)	0.019 (21)	F(6)	0.015 (11)
		F(7)	0.016 (11)
		F(8)	-0.008 (11)
		F(9)	0.003 (11)
		F(10)	-0.019 (11)

Equations of the planes (x, y and z are fractional coordinates)

$$(I) \quad 8.233x + 0.047y + 5.188z = 4.167$$

$$(II) \quad 15.424x + 6.562y - 2.986z = 8.234$$

Angle between planes (I) and (II) = $78.3 (7)^\circ$

* Atoms defining the plane.

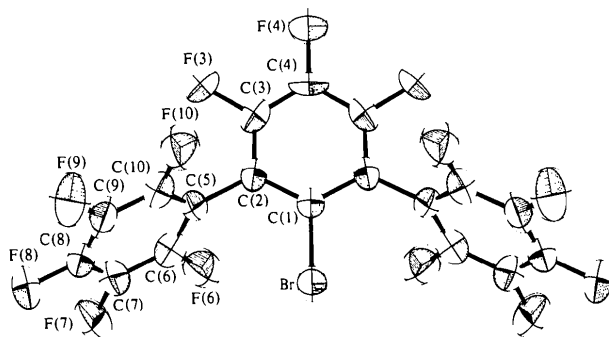


Fig. 1. ORTEP plot (Johnson, 1965) of the $C_{18}BrF_{13}$ molecule, with 50% probability thermal ellipsoids and atom labelling.

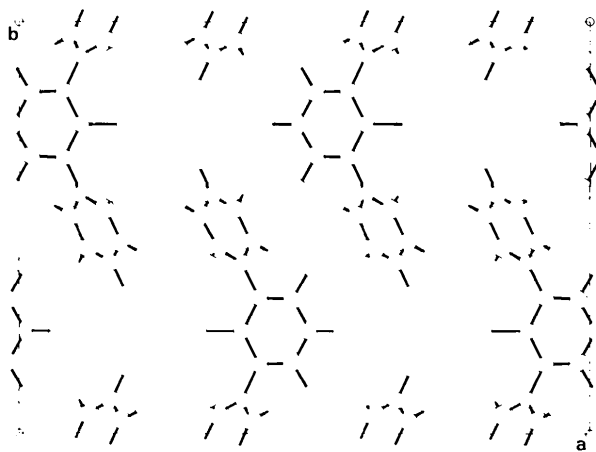


Fig. 2. Projection of the cell contents down c .

proposed aryne mechanism for its formation from 2-lithiononafluorobiphenyl.

The phenyl rings are planar to within ± 0.01 Å, although packing effects are possibly indicated by the small displacement (up to 0.05 Å) of substituents from their respective ring planes. The dihedral angle between the central and terminal rings is $78.3(7)^\circ$ which minimizes non-bonding interactions. Evidence for repulsion between Br and the terminal rings is afforded by the fact that C(1)–C(2)–C(5) is 5° greater than C(3)–C(2)–C(5), and the displacement of Br from the plane of the central ring is about 0.03 Å greater than that of C(5).

C–F lengths lie within the range 1.333 to 1.360 Å with a mean of 1.347 Å. Intra-ring C–C lengths range from 1.353 to 1.385 Å with a mean of 1.370 Å and the inter-ring C–C length is 1.473 (14) Å. All bond lengths are uncorrected for thermal libration.

Molecular dimensions of *m*-perfluoroterphenyl and its other 2-substituted derivatives are not available for comparison. The inter-ring bond length and dihedral

angle are both less (by 0.02 Å and 7° respectively) than in 2-nitrononafluorobiphenyl (Hamor & Hamor, 1978).

There are no significantly short intermolecular contacts (Table 3).

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References

- COHEN, S. C., TOMLINSON, A. J., WILES, M. R. & MASSEY, A. G. (1968). *J. Organomet. Chem.* **11**, 385–392.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 HAMOR, M. J. & HAMOR, T. A. (1978). *Acta Cryst.* **B34**, 2994–2997.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 XRAY system (1972). Version of June 1972. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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3-Chloro-1-ethyl-2-methyl-1-phenylindene

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Abstract. C₁₈H₁₇Cl, tetragonal, *P4*₁ or *P4*₃, $a = b = 11.493(2)$, $c = 11.013(2)$ Å, $Z = 4$, $D_m = 1.22$, $D_x = 1.23$ Mg m⁻³; m.p. 348 K. The structure was solved by *MULTAN*. A full-matrix least-squares refinement using 1530 symmetrically independent reflections with $\sin \theta / \lambda \leq 0.619$ Å⁻¹ gave an *R* value of 0.029 ($R_w = 0.026$, $w = 1$). Bond distances and angles are normal. The planes through the phenyl and indene rings make an angle of $80.3(8)^\circ$.

Introduction. The title compound was obtained by the reaction of 1-phenylpropyne with hydrogen chloride (Vittinghoff, 1980). This reaction was of interest in the investigation of the electrophilic addition of hydrogen halides to phenyl-substituted acetylenes, involving the initial formation of vinyl cation intermediates. The structure determination was undertaken to find out the correct substitution pattern of the indene ring.

Colourless prismatic crystals were obtained by recrystallization from an acetone–pentane solution. The space group and preliminary cell constants were determined by precession photographs which showed the tetragonal symmetry *4/m* and systematic absences *00l* with $l \neq 4n$. Characteristic space groups are *P4*₁ or *P4*₃. The cell parameters given above were obtained from the least-squares refinement of the angular positions for 17 reflections carefully centred on a Picker four-circle diffractometer, which was also used to collect the diffraction data.

A prismatic crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was chosen for data collection with the θ – 2θ scan technique (Mo *K* α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The background was measured for 20 s at each limit of the scan range, which was varied to account for the α_1 – α_2 separation. Three reference reflections were measured at intervals of 100 reflections and no significant