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Structures of Substituted Perfluoropolyphenyls. III. Structure of 1-Bromo-4,5,6-trifluoro-2,3-bis(pentafluorophenyl)benzene, C₁₈BrF₁₃

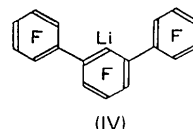
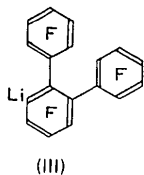
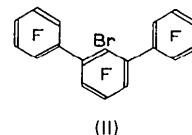
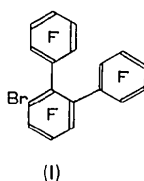
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Abstract. $M_r = 543.081$, triclinic, $P\bar{1}$, $a = 14.671$ (5), $b = 10.547$ (6), $c = 7.29$ (4) Å, $\alpha = 78.0$ (5), $\beta = 95.2$ (5), $\gamma = 127.4$ (5)°, $U = 875.85$ Å³, $Z = 2$, D_m (pycnometric) = 2.041, $D_x = 2.060$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 4.930$ mm⁻¹, $F(000) = 520$, measurement temperature, $T = 293$ K. $R = 0.083$ for 1576 observed reflexions with $I > 3\sigma(I)$. The dihedral angles between the central phenyl ring and those *ortho* and *meta* to bromine are 65.6 (15) and 63.3 (11)°, respectively. The corresponding inter-ring bond lengths are 1.49 (2) and 1.50 (2) Å (uncorrected for thermal libration).

Introduction. The title compound (I) and its isomer (II) have been synthesized by Cohen, Tomlinson, Wiles & Massey (1968) from 2-lithiononafluorobiphenyl and (pentafluorophenyl)lithium. They proposed an aryne mechanism for the reaction, elimination of LiF from 2-lithiononafluorobiphenyl giving 1-pentafluorophenyl-2,3,4-trifluorobenzene. Addition of (pentafluorophenyl)lithium to this aryne yields 1-lithio-4,5,6-trifluoro-2,3-bis(pentafluorophenyl)benzene (III) and 1-lithio-3,4,5-trifluoro-2,6-bis(pentafluorophenyl)benzene (IV). Li–Br exchange with (III) and (IV) in the presence of 2-bromononafluorobiphenyl produces isomers (I) and (II).



The evidence for this mechanism has been strengthened by the confirmation of the structure of (II) (Bowen Jones & Brown, 1980). The structure of its isomer (I) is now reported.

This analysis is also part of a series of studies on the correlation between inter-ring bond lengths and dihedral angles in substituted perfluoropolyphenyls. No such correlation has been found in substituted perfluorobiphenyls (Goodhand, Hamor & Hamor, 1978; Bowen Jones & Brown, 1982).

Experimental. Preparation by the method of Cohen, Tomlinson, Wiles & Massey (1968); colourless crystals obtained by vapour diffusion with methanol and a solution of $C_{18}BrF_{13}$ in toluene; crystal, $1.0 \times 0.3 \times 0.1$ mm, mounted in a sealed Lindemann-glass capillary; preliminary cell dimensions determined from rotation and Weissenberg photographs taken from crystals mounted about **a** and **c**; refined cell dimensions from a Stoe Stadi-2 two-circle diffractometer; intensity data collected for six layers in l , ω scan, graphite-monochromated $Cu K\alpha$ radiation; 2845 reflexions measured, 1576 of which had $I > 3\sigma(I)$ and were classed as observed; $2\theta_{max} = 135^\circ$, no correction for absorption and extinction; standard check reflexion measured for each layer, no significant anomalies noted; Br-atom position from Patterson function and all other atoms from successive difference syntheses; full-matrix least squares refinement, minimizing $\sum w(\Delta F)^2$ and allowing anisotropic motion for all atoms; calculated shifts in the final cycle $< 0.1\sigma$, $R_w = 0.102$, $S = 8.07$; $w = 1$ for $F_o \leq 20$ and $w = (20/F_o)^2$ for $F_o > 20$; no features in the final difference map $> 0.8 e \text{ \AA}^{-3}$; scattering factors from Cromer & Mann (1968); all calculations carried out with the XRAY system (1972) implemented at the University of Manchester Regional Computer Centre.

Discussion. Final atomic coordinates are listed in Table 1,* and bond lengths and angles in Table 2. The molecular structure and atom-numbering are given in Fig. 1, and the projection of the cell contents down **c** is shown in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters, least-squares-planes' data, intermolecular contacts, bond-length comparison and geometric data for some substituted perfluorobiphenyls have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38378 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

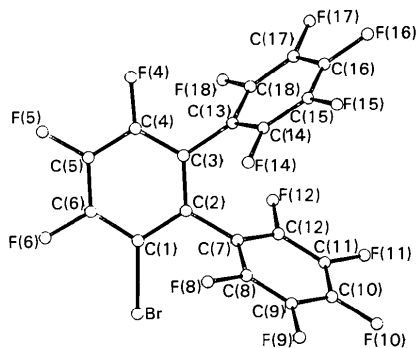


Fig. 1. ORTEP plot (Johnson, 1965) of the title compound, with atom labelling.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters

	$B_{eq} = \frac{1}{3} \sum_i B_{ii}$			$B_{eq} (\text{\AA}^2)$
	x	y	z	
Br	4897 (1)	11543 (2)	1800 (2)	7.1 (10)
C(1)	3674 (10)	9620 (16)	1143 (19)	5.4 (14)
C(2)	2931 (9)	9529 (14)	-311 (17)	4.7 (13)
C(3)	2074 (9)	8034 (14)	-798 (17)	4.8 (12)
C(4)	1930 (10)	6646 (15)	105 (18)	5.2 (13)
C(5)	2632 (12)	6692 (15)	1576 (20)	5.8 (15)
C(6)	3487 (11)	8176 (19)	2018 (19)	6.5 (17)
C(7)	3083 (9)	11044 (15)	-1264 (20)	5.2 (14)
C(8)	2857 (11)	11854 (16)	-269 (19)	5.6 (15)
C(9)	3044 (14)	13233 (20)	-1106 (27)	7.3 (20)
C(10)	3372 (13)	13875 (15)	-2973 (31)	7.1 (21)
C(11)	3574 (11)	13124 (18)	-3961 (19)	5.2 (15)
C(12)	3402 (10)	11693 (17)	-3106 (20)	5.2 (15)
C(13)	1287 (10)	7909 (14)	-2333 (18)	5.2 (13)
C(14)	529 (10)	8265 (14)	-2262 (18)	5.0 (13)
C(15)	-166 (10)	8131 (16)	-3675 (21)	5.9 (15)
C(16)	-148 (12)	7654 (19)	-5210 (22)	6.4 (15)
C(17)	578 (11)	7233 (18)	-5350 (20)	6.5 (17)
C(18)	1275 (10)	7402 (15)	-3945 (18)	5.1 (13)
F(4)	1149 (6)	5208 (7)	-327 (10)	5.7 (8)
F(5)	2475 (7)	5358 (10)	2476 (12)	7.9 (10)
F(6)	4163 (7)	8185 (12)	3404 (12)	8.7 (11)
F(8)	2512 (7)	11231 (10)	1537 (11)	8.0 (9)
F(9)	2829 (10)	14024 (12)	-152 (16)	11.5 (15)
F(10)	3512 (9)	15240 (10)	-3780 (15)	9.6 (13)
F(11)	3867 (8)	13707 (10)	-5773 (12)	7.6 (11)
F(12)	3591 (6)	10953 (10)	-4160 (11)	7.0 (9)
F(14)	476 (6)	8723 (9)	-705 (11)	7.0 (9)
F(15)	-911 (7)	8480 (11)	-3545 (13)	8.8 (11)
F(16)	-840 (7)	7524 (12)	-6641 (13)	9.3 (12)
F(17)	599 (7)	6761 (12)	-6907 (12)	8.9 (12)
F(18)	1993 (6)	7033 (10)	-4142 (11)	7.9 (10)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

C(1)-Br	1.84 (1)	C(12)-C(7)	1.35 (2)
C(1)-C(2)	1.42 (2)	C(8)-F(8)	1.33 (2)
C(2)-C(3)	1.39 (2)	C(9)-F(9)	1.37 (3)
C(2)-C(7)	1.49 (2)	C(10)-F(10)	1.33 (2)
C(3)-C(4)	1.37 (2)	C(11)-F(11)	1.32 (2)
C(3)-C(13)	1.50 (2)	C(12)-F(12)	1.35 (2)
C(4)-C(5)	1.41 (2)	C(13)-C(14)	1.38 (3)
C(5)-C(6)	1.37 (2)	C(14)-C(15)	1.35 (2)
C(6)-C(1)	1.39 (3)	C(15)-C(16)	1.33 (3)
C(4)-F(4)	1.32 (1)	C(16)-C(17)	1.40 (3)
C(5)-F(5)	1.31 (2)	C(17)-C(18)	1.34 (2)
C(6)-F(6)	1.35 (2)	C(18)-C(13)	1.38 (2)
C(7)-C(8)	1.42 (3)	C(14)-F(14)	1.35 (2)
C(8)-C(9)	1.32 (3)	C(15)-F(15)	1.37 (2)
C(9)-C(10)	1.37 (3)	C(16)-F(16)	1.36 (2)
C(10)-C(11)	1.34 (3)	C(17)-F(17)	1.34 (2)
C(11)-C(12)	1.38 (3)	C(18)-F(18)	1.35 (2)
C(2)-C(1)-Br	124 (1)	C(9)-C(10)-C(11)	119 (2)
C(2)-C(1)-C(6)	117 (1)	C(9)-C(10)-F(10)	121 (2)
C(6)-C(1)-Br	119 (1)	C(11)-C(10)-F(10)	121 (2)
C(1)-C(2)-C(3)	120 (1)	C(10)-C(11)-C(12)	120 (1)
C(1)-C(2)-C(7)	119 (1)	C(10)-C(11)-F(11)	120 (2)
C(3)-C(2)-C(7)	121 (1)	C(12)-C(11)-F(11)	121 (2)
C(2)-C(3)-C(4)	121 (1)	C(11)-C(12)-C(7)	122 (2)
C(2)-C(3)-C(13)	121 (1)	C(11)-C(12)-F(12)	118 (1)
C(4)-C(3)-C(13)	118 (1)	C(7)-C(12)-F(12)	120 (2)
C(3)-C(4)-C(5)	121 (1)	C(3)-C(13)-C(14)	124 (1)
C(3)-C(4)-F(4)	123 (1)	C(3)-C(13)-C(18)	121 (2)
C(5)-C(4)-F(4)	116 (1)	C(14)-C(13)-C(18)	115 (1)
C(4)-C(5)-C(6)	118 (1)	C(13)-C(14)-C(15)	122 (2)
C(4)-C(5)-F(5)	121 (1)	C(13)-C(14)-F(14)	118 (1)
C(6)-C(5)-F(5)	121 (1)	C(15)-C(14)-F(14)	120 (2)
C(5)-C(6)-C(1)	124 (1)	C(14)-C(15)-C(16)	121 (2)
C(5)-C(6)-F(6)	116 (2)	C(14)-C(15)-F(15)	120 (2)
C(1)-C(6)-F(6)	120 (1)	C(16)-C(15)-F(15)	119 (1)
C(2)-C(7)-C(8)	121 (1)	C(15)-C(16)-C(17)	120 (2)
C(2)-C(7)-C(12)	123 (2)	C(15)-C(16)-F(16)	122 (2)
C(8)-C(7)-C(12)	116 (2)	C(17)-C(16)-F(16)	119 (2)
C(7)-C(8)-C(9)	120 (1)	C(16)-C(17)-C(18)	118 (2)
C(7)-C(8)-F(8)	118 (1)	C(16)-C(17)-F(17)	120 (1)
C(9)-C(8)-F(8)	122 (2)	C(18)-C(17)-F(17)	122 (2)
C(8)-C(9)-C(10)	122 (2)	C(17)-C(18)-C(13)	124 (2)
C(8)-C(9)-F(9)	120 (2)	C(17)-C(18)-F(18)	117 (2)
C(10)-C(9)-F(9)	117 (2)	C(13)-C(18)-F(18)	119 (1)

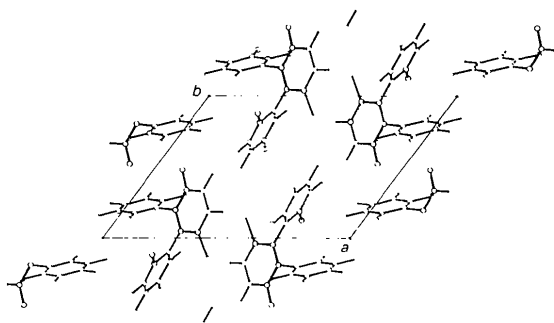


Fig. 2. *c*-axial projection of the cell contents.

Table 3. Inter-ring bond lengths (Å) and corresponding dihedral angles (°) in substituted perfluoroterphenyls

	Inter-ring bond length	Dihedral angle
Isomer (I)	1.50 (2)	63.3 (11)
Isomer (I)	1.49 (2)	65.6 (15)
Isomer (II)	1.47 (1)	78.3 (7)

The evidence for the proposed aryne mechanism for the formation of isomers (I) and (II) from 2-lithiononafluorobiphenyl has been further strengthened by the confirmation of the molecular structure of the title compound (I).

Isomer (II) is the only other substituted perfluoroterphenyl for which data are available for comparison (Bowen Jones & Brown, 1980). The dihedral angles between the central and terminal phenyl rings in (I) and (II), together with the corresponding inter-ring bond lengths, are listed in Table 3. The limited data may indicate a correlation between these two parameters in substituted perfluoroterphenyls, a smaller dihedral angle requiring a greater inter-ring bond length to minimize non-bonding interactions.

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Structure of *N,N'*-Di-*n*-hexyl-4-oxoheptanediamide, $C_{19}H_{36}N_2O_3$

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(Received 3 November 1982; accepted 3 February 1983)

Abstract. $M_r = 340.53$, monoclinic, $C2/c$, $a = 44.435$ (7), $b = 5.1929$ (5), $c = 8.918$ (1) Å, $\beta = 99.88$ (2)°, $V = 2027.2$ (8) Å³, $Z = 4$, $D_m = 1.10$, $D_x = 1.116$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $F(000) = 752$, $T = 294$ K. Final $R = 0.045$ for 1635 observed

Mean C–F and intra-ring C–C lengths are similar in the two isomers, but the C–Br bond in (I) is 0.06 (3) Å shorter than in (II). There are no significantly short intermolecular contacts in either compound.

The phenyl rings in the title compound are planar to within ± 0.02 Å and the displacement of the Br atom from the plane of the central ring is 0.110 (9) Å compared with 0.050 (13) Å in its isomer.

Each isomer may be regarded as a disubstituted perfluorobiphenyl. The inter-ring bond length and dihedral angle in their biphenyl systems have been compared* with those of other substituted perfluorobiphenyls. Goodhand, Hamor & Hamor (1978) found no correlation between these two parameters in polyfluorobiphenyls, and the data for isomers (I) and (II) and for 2*H*,2'*H*-octafluorobiphenyl (Bowen Jones & Brown, 1980, 1982) confirm this.

We thank our colleague, Dr A. G. Massey, for suggesting this programme of structure analyses and for providing a sample of the title compound.

* See deposition footnote.

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reflections. The molecule presents a W shape with a twofold axis along the ketonic bond. Molecules consecutively related by inversion centres stack along *c*. The two hydrogen bonds per molecule run in the direction of the *c* axis.

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