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# Structures of Substituted Perfluoropolyphenyls. IV. Structure of 2-Bromononafluorobiphenyl

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**Abstract.** $C_{12}BrF_9$, $M_r = 395.041$, orthorhombic, *Pbca*, $a = 12.610$ (5), $b = 23.565$ (5), $c = 8.029$ (4) Å, $U = 2385.85$ Å$^3$, $Z = 8$, $D_m = 2.183$, $D_x = 2.200$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 34.40$ cm$^{-1}$, $F(000) = 1504$, $T = 293$ K. Final $R = 0.055$ for 988 observed reflections with $I > 3\sigma(I)$. The dihedral angle between the rings is $79.6$ (10)° and the inter-ring bond length is $1.502$ (15) Å (uncorrected for thermal libration).

**Introduction.** 2,2'-Disubstitution of perfluorobiphenyl with bromine has no significant effect on the inter-ring bond length of 1·486 (5) Å, but increases the dihedral angle from 59·5 to 75·9 (5)° (Gleason & Britton, 1976; Hamor & Hamor, 1980). This analysis investigates the effect on these two parameters of 2-substitution with bromine, and is the fourth in a series of investigations into the correlation between inter-ring bond length and dihedral angle in substituted perfluoropolyphenyls.

On the assumption of an aryne mechanism it was proposed that 2-bromononafluorobiphenyl would be formed from pentafluorophenyllithium (Fenton, Park, Shaw & Massey, 1964; Fenton & Massey, 1965), according to the following scheme:
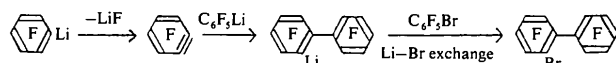


Our confirmation of the structure of the product affords further evidence for this mechanism.

**Experimental.** Preparation by the method of Fenton, Park, Shaw & Massey (1964); $D_m$ measured pycnometrically; colourless, rectangular block-shaped crystals obtained from ethanol; crystal, $0.38 \times 0.27 \times 0.12$ mm, sealed in a Lindemann-glass capillary, mounted about *c*; preliminary lattice constants determined from oscillation and Weissenberg photographs;

refined lattice constants from a Stoe Stadi-2 two-circle diffractometer, using axial-row reflections ($\theta$ range $11 \rightarrow 32°$); no correction for absorption and extinction; $2\theta_{max} = 60°$; index range: $0 \le h \le 14$; $0 \le k \le 30$; $0 \le l \le 8$; one standard reflection every 50 reflections, no significant change; 3072 reflections measured, 2699 being unique and 988 having $I > 3\sigma(I)$; Br located by Patterson synthesis, other atoms by successive $\Delta F$ syntheses; anisotropic refinement by full-matrix least squares on $F$ with unit weights gave final $R = 0.055$; $\Delta/\sigma \nRightarrow 0.001$; $\Delta\rho$ excursions = $+0.67$ to $-0.75$ e Å$^{-3}$, maximum and minimum density occurring near the Br positions; scattering factors from Cromer & Mann (1968); calculations carried out with *SHELX*76 (Sheldrick, 1976) implemented at Loughborough University of Technology Computer Centre, and with *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) implemented at the University of Manchester Regional Computer Centre.*

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

The confirmation that the structure of the reaction product is indeed 2-bromononafluorobiphenyl strengthens the evidence for the proposed aryne mechanism (Fenton, Park, Shaw & Massey, 1964; Fenton & Massey, 1965).

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Both phenyl rings in the title compound are planar to within ±0·013 (10) Å and inclined at 79·6 (10)° to one another. The bromine atom is displaced by 0·018 (10) Å, and the fluorine atoms by no more than 0·032 (13) Å, from the least-squares ring-planes. The C(1)—C(1') length of 1·502 (15) Å indicates that the two $sp^2$ hybridized carbons are united by a single bond (Coulson, 1948) which, together with the large dihedral

angle, precludes delocalization of $\pi$ electrons over both rings. Not surprisingly, the inter-ring bond length and dihedral angle are similar to those in 2-bromo-3-(pentafluorophenyl)octafluorobiphenyl (Bowen Jones & Brown, 1980).

Intra-ring C—C lengths lie within the range 1·324 (16) to 1·412 (15) Å with a mean of 1·381 (5) Å. C—F lengths range from 1·311 (13) to 1·405 (13) Å with a mean of 1·348 (4) Å. These ranges are wider than those for C—F and intra-ring C—C lengths in perfluorobiphenyl and a number of its derivatives, but the means are similar (Gleason & Britton, 1976; Hamor & Hamor, 1978a,b, 1980). The unusually large C(6')—F(6') length of 1·405 (13) Å was also found when the structure was solved using Cu Kα data (Bowen Jones & Brown, unpublished work). The C—Br bond [1·911 (10) Å] is slightly longer than either of the C—Br bonds [1·857 (5) and 1·869 (5) Å] in 2,2'-dibromooctafluorobiphenyl (Hamor & Hamor, 1980). There are no abnormal intermolecular contact distances.

The van der Waals interpenetration energy is minimized by the deformation of the two phenyl rings, notably the shortening of the C(2)—C(3) bond to 1·324 (16) Å, and by the distortion of the angles C(2)—C(1)—C(1') and C(1)—C(1')—C(2') to 123·5 (9) and 122·9 (10)°, respectively. The molecular axis C(4)—C(1)—C(1')—C(4') is also distorted, the ring axes

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

$B_{eq} = \frac{1}{3}\sum_i B_{ii}$.

| | x | y | z | $B_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| Br | 7287 (1) | 6661 (1) | 339 (2) | 4·74 (6) |
| C(1) | 5143 (8) | 6304 (4) | 878 (13) | 2·3 (5) |
| C(2) | 5795 (8) | 6666 (5) | −78 (15) | 3·3 (5) |
| C(3) | 5412 (9) | 7024 (5) | −1195 (17) | 3·6 (6) |
| C(4) | 4325 (10) | 7056 (5) | −1535 (17) | 3·7 (6) |
| C(5) | 3679 (9) | 6686 (6) | −630 (16) | 3·7 (6) |
| C(6) | 4076 (9) | 6332 (5) | 539 (16) | 3·3 (6) |
| C(1') | 5564 (8) | 5900 (5) | 2167 (13) | 2·6 (5) |
| C(2') | 6008 (9) | 5384 (5) | 1772 (16) | 3·5 (6) |
| C(3') | 6354 (9) | 5011 (5) | 2966 (18) | 3·6 (6) |
| C(4') | 6270 (8) | 5158 (6) | 4663 (17) | 3·7 (6) |
| C(5') | 5837 (9) | 5679 (6) | 5072 (14) | 3·5 (6) |
| C(6') | 5477 (8) | 6035 (5) | 3874 (17) | 3·2 (6) |
| F(3) | 6032 (6) | 7375 (3) | −2093 (10) | 5·3 (4) |
| F(4) | 3933 (6) | 7408 (3) | −2650 (10) | 5·4 (4) |
| F(5) | 2606 (5) | 6712 (4) | −886 (10) | 5·7 (4) |
| F(6) | 3412 (5) | 5981 (3) | 1371 (9) | 4·4 (4) |
| F(2') | 6088 (6) | 5237 (3) | 156 (9) | 4·3 (4) |
| F(3') | 6756 (6) | 4512 (3) | 2534 (11) | 5·2 (4) |
| F(4') | 6593 (6) | 4801 (3) | 5811 (10) | 5·0 (4) |
| F(5') | 5752 (6) | 5812 (3) | 6705 (9) | 5·2 (4) |
| F(6') | 5031 (5) | 6553 (3) | 4388 (8) | 3·8 (3) |

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

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1·412 (15) | C(1')—C(2') | 1·377 (15) |
| C(1)—C(1') | 1·502 (15) | C(2')—C(3') | 1·372 (17) |
| C(2)—C(3) | 1·324 (16) | C(2')—F(2') | 1·346 (13) |
| C(2)—Br | 1·911 (10) | C(3')—C(4') | 1·410 (18) |
| C(3)—C(4) | 1·400 (16) | C(3')—F(3') | 1·325 (13) |
| C(3)—F(3) | 1·346 (13) | C(4')—C(5') | 1·385 (17) |
| C(4)—C(5) | 1·396 (17) | C(4')—F(4') | 1·311 (13) |
| C(4)—F(4) | 1·318 (13) | C(5')—C(6') | 1·355 (16) |
| C(5)—C(6) | 1·352 (16) | C(5')—F(5') | 1·352 (13) |
| C(5)—F(5) | 1·371 (12) | C(6')—C(1') | 1·411 (16) |
| C(6)—C(1) | 1·375 (14) | C(6')—F(6') | 1·405 (13) |
| C(6)—F(6) | 1·354 (12) | | |
| | | | |
| C(2)—C(1)—C(6) | 115·7 (10) | C(1)—C(1')—C(2') | 122·9 (10) |
| C(2)—C(1)—C(1') | 123·5 (9) | C(1)—C(1')—C(6') | 120·0 (10) |
| C(6)—C(1)—C(1') | 120·8 (9) | C(2')—C(1')—C(6') | 117·1 (10) |
| C(1)—C(2)—C(3) | 122·8 (10) | C(1')—C(2')—C(3') | 122·3 (12) |
| C(1)—C(2)—Br | 118·3 (8) | C(1')—C(2')—F(2') | 118·6 (11) |
| C(3)—C(2)—Br | 118·8 (9) | C(3')—C(2')—F(2') | 119·0 (11) |
| C(2)—C(3)—C(4) | 121·5 (11) | C(2')—C(3')—C(4') | 119·6 (12) |
| C(2)—C(3)—F(3) | 122·9 (11) | C(2')—C(3')—F(3') | 120·4 (13) |
| C(4)—C(3)—F(3) | 115·6 (11) | C(4')—C(3')—F(3') | 119·9 (11) |
| C(3)—C(4)—C(5) | 115·9 (11) | C(3')—C(4')—C(5') | 118·5 (11) |
| C(3)—C(4)—F(4) | 122·2 (11) | C(3')—C(4')—F(4') | 119·9 (13) |
| C(5)—C(4)—F(4) | 121·9 (11) | C(5')—C(4')—F(4') | 121·6 (13) |
| C(4)—C(5)—C(6) | 122·1 (11) | C(4')—C(5')—C(6') | 120·9 (12) |
| C(4)—C(5)—F(5) | 118·1 (11) | C(4')—C(5')—F(5') | 117·8 (11) |
| C(6)—C(5)—F(5) | 119·8 (12) | C(6')—C(5')—F(5') | 121·2 (12) |
| C(1)—C(6)—C(5) | 122·0 (11) | C(1')—C(6')—C(5') | 121·6 (12) |
| C(1)—C(6)—F(6) | 118·6 (10) | C(1')—C(6')—F(6') | 120·8 (10) |
| C(5)—C(6)—F(6) | 119·4 (10) | C(5')—C(6')—F(6') | 117·6 (11) |
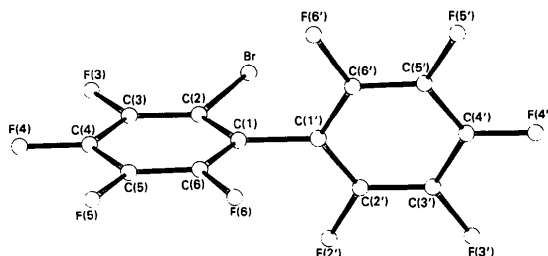


Fig. 1. ORTEP plot (Johnson, 1965) of the title compound, with atom labelling.
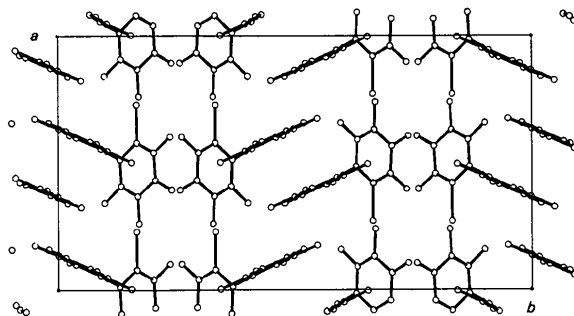


Fig. 2. c-axial projection of the cell contents.

C(1)–C(4) and C(1')–C(4') being inclined to the inter-ring axis C(1)–C(1') at 0·8 (9) and 2·6 (9)° respectively, with C(4) and C(4') cis. A similar distortion was found in 2H,2'H-octafluorobiphenyl (Bowen Jones & Brown, 1982), and in both molecules the atoms C(4), C(1), C(1') and C(4') are coplanar, none being displaced by more than 0·005 (4) Å from their least-squares plane.

This analysis has shown that 2-substitution of perfluorobiphenyl with bromine increases the dihedral angle from 59·6° (Gleason & Britton, 1976) to 79·6 (10)°. This is a slightly larger increase than that produced by 2,2'-disubstitution with bromine (Hamor & Hamor, 1980). In contrast, neither of these substitutions has a significant effect on the interannular distance, which has been found to be virtually invariant and independent of dihedral angle in a number of biphenyl systems (Goodhand, Hamor & Hamor, 1978; Bowen Jones & Brown, 1982). The structural analysis of 2-bromononafluorobiphenyl corroborates these findings.

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

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# Structure of the 1:1 Adduct Formed by Diphenylmethanol with Triphenylphospine Oxide

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**Abstract.** $C_{13}H_{12}O.(C_6H_5)_3PO$, $M_r = 462·53$, monoclinic, $P2_1/n$, $a = 11·074$ (4), $b = 18·081$ (2), $c = 12·887$ (4) Å, $\beta = 95·13$ (3)°, $V = 2570$ (2) Å³, $Z = 4$, $D_m = 1·202$ (2) (flotation), $D_x = 1·195$ (2) g cm⁻³, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 0·95$ cm⁻¹, $F(000) = 976$, room temperature. Direct methods, final $R = 0·070$ for 2060 observed reflections. Phenyl rings of diphenylmethanol are disordered. The adduct is formed by hydrogen bonding between the O atoms of the phosphine oxide and alcohol, with an O···O distance of 2·672 (5) Å. The P=O distance [1·482 (4) Å] in triphenylphosphine oxide is significantly longer than in the free molecule [1·46 (1) Å].

**Introduction.** It was shown by Lechat (1984) that the hydrogen-bond distance in adducts formed by strong and medium hydrogen bonds, where the hydrogen-bond donor and acceptor atoms are O atoms, may be correlated with the values of the difference of $pK_a$ of the acids and bases involved in the adducts. This crystal-structure determination has been undertaken in order to gather structural information for an adduct presenting a unique hydrogen bond of medium strength.

**Experimental.** Transparent colourless crystals were obtained by slowly evaporating a solution of the title compound in benzene. Technique as well as reagents