molecular contact of type C(1)—H$\cdots$O(1) occurs in this compound with an H$\cdots$O(1) distance of 2·35 Å (the sum of the van der Waals radii being 2·5 Å) and an angle C(1)—H$\cdots$O(1) of 170°. Several examples of short C$\cdots$O distances have been summarized by Sutor (1963) and later discussed by Rich & Davidson (1968) with a view to rejecting them as true hydrogen bonds. However, according to severe geometrical considerations (Table 5) and regarding some recent examples (Martínez-Ripoll & Lorenz, 1974, 1976), this C—H$\cdots$O contact could be accepted as a hydrogen bond.

Thanks are given to the staff of the CPD del Ministerio de Educación, Madrid, for computing facilities.

References

CABEZUELO, M. D., CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). Acta Cryst. B33, 3598–3601.

CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). Tetrahedron, 33, 797–802.

ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1979). Acta Cryst. B35, 2795–2797.

ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1982a). Acta Cryst. B38, 1124–1128.

ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1982b). Acta Cryst. B38, 1128–1133.

GILLESPIE, R. J., IRELAND, P. R. & VEKRIS, J. E. (1975). Can. J. Chem. 53, 3147–3152.

GOYA, P. & STUD, M. (1978). J. Heterocycl. Chem. 15, 253–256.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). PESOS program. Instituto Rocasolano, CSIC, Serrano 119, Madrid 6, Spain.

MARTÍNEZ-RIPOLL, M. & LORENZ, H. P. (1974). Acta Cryst. B30, 793–796.

MARTÍNEZ-RIPOLL, M. & LORENZ, H. P. (1976). Acta Cryst. B32, 2325–2328.

NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. (1965). Ric. Sci. 35, 807–810.

RICH, A. & DAVIDSON, N. (1968). Structural Chemistry and Molecular Biology, p. 459. San Francisco: Freeman.

SCHUSTER, P., ZUNDEL, G. & SANDORFY, C. (1976). The Hydrogen Bond, p. 394. Amsterdam: North-Holland.

SCHWARZENBACH, D. (1972). ORABS program, Zürich.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

SUTOR, D. J. (1963). J. Chem. Soc. 1, 1105–1110.

Structure of Octafluoro-4,4'-bis(phenylethynyl)biphenyl*

By Neil Goodhand and Thomas A. Hamor

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

Abstract. $C_{28}H_{10}F_8$, $M_r = 498\cdot4$, monoclinic, $C2/c$, $a = 23\cdot86$ (2), $b = 6\cdot22$ (1), $c = 14\cdot98$ (1) Å, $\beta = 100\cdot01$ (5)°, $U = 2189$ Å^3, $Z = 4$, $D_c = 1\cdot51$ Mg m^{-3}; molecular symmetry C_2. The structure was refined to $R = 0\cdot042$ for 1387 observed counter amplitudes. The acetylenic triple-bond length is $1\cdot187$ (3) Å. The inter-ring bond of the octafluorobiphenyl system is $1\cdot477$ (4) Å and the inter-ring dihedral angle $56\cdot7$ (3)°.

Introduction. In earlier papers of this series, the structures of a number of fluorinated biphenyls (Hamor & Hamor, 1978; Goodhand & Hamor, 1978; Brock, Naae, Goodhand & Hamor, 1978) and of perfluorodiphenylethyne (Goodhand & Hamor, 1979) have been described and compared with hydrocarbon analogues. Of particular interest in the biphenyls has been the absence of any relationship between dihedral angle and the length of the inter-ring bond (Goodhand, Hamor & Hamor, 1978). We now report the crystal structure of octafluoro-4,4'-bis(phenylethynyl)biphenyl (Coe, Tatlow & Terrell, 1967) as part of a continuing study of fluorinated biphenyls and of the effect of fluorinated phenyl groups on an adjacent acetylenic triple bond.

---

* Structures of Polyfluoroaromatic Compounds. X. Part IX: Goodhand & Hamor (1981).

Table 1. *Fractional atomic coordinates and thermal parameters* ($\times 10^4$)

	x	y	z	U_{eq}/U (Å²)*
C(1)	5167 (1)	−163 (3)	2964 (1)	439 (11)
C(2)	5129 (1)	1494 (3)	3567 (1)	451 (12)
C(3)	5437 (1)	1494 (3)	4430 (1)	472 (12)
C(4)	5799 (1)	−190 (4)	4743 (1)	487 (12)
C(5)	5838 (1)	−1848 (3)	4145 (1)	505 (12)
C(6)	5534 (1)	−1830 (3)	3281 (1)	485 (12)
C(7)	6116 (1)	−188 (4)	5646 (2)	569 (14)
C(8)	6368 (1)	−190 (4)	6402 (2)	566 (13)
C(9)	6661 (1)	−232 (4)	7326 (1)	508 (13)
C(10)	7003 (1)	1472 (5)	7677 (2)	640 (16)
C(11)	7282 (1)	1396 (6)	8566 (2)	753 (20)
C(12)	7215 (1)	−345 (6)	9097 (2)	751 (19)
C(13)	6877 (1)	−2014 (5)	8755 (2)	705 (18)
C(14)	6602 (1)	−1990 (4)	7871 (2)	602 (15)
F(2)	4775 (1)	3140 (2)	3318 (1)	584 (8)
F(3)	5376 (1)	3132 (2)	4984 (1)	668 (8)
F(5)	6186 (1)	−3513 (2)	4409 (1)	708 (9)
F(6)	5608 (1)	−3454 (2)	2724 (1)	670 (9)
H(10)	7028 (10)	2677 (46)	7314 (17)	841 (84)
H(11)	7484 (11)	2507 (48)	8755 (18)	872 (96)
H(12)	7420 (10)	−349 (48)	9705 (17)	959 (93)
H(13)	6839 (11)	−3220 (47)	9096 (17)	907 (89)
H(14)	6365 (9)	−3152 (39)	7602 (15)	697 (71)

* For C and F, $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$. For H, U is the refined isotropic thermal parameter.

Suitable crystals were obtained from toluene. A crystal $0.5 \times 0.4 \times 0.4$ mm was aligned about **b**. After preliminary photographic examination, unit-cell parameters and intensities were measured on a Stoe STADI-2 diffractometer operating in the ω scan mode with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Of 3011 reflections scanned in the range $0.1 < \sin\theta/\lambda < 0.7$ Å⁻¹, 1387 $[I > 2.5\sigma(I)]$ were used in the analysis. Absorption corrections were ignored $[\mu(\text{Mo }K\alpha) = 0.091 \text{ mm}^{-1}]$.

The systematic absences were consistent with space groups Cc and $C2/c$. However, the E statistics indicated the centrosymmetric $C2/c$ which was confirmed by the subsequent successful refinement in this space group.

The structure was solved by direct methods with *SHELX* (Sheldrick, 1978) and refined by least squares. H atoms were located from a Fourier difference synthesis. In the final cycles of least-squares calculations, the positional parameters of all the atoms, anisotropic thermal parameters for C and F, and isotropic thermal parameters for H were varied. Refinement was terminated when all shifts were $<0.01\sigma$ and $R = 0.042$ ($R_w = 0.041$). The weighting scheme used was $w = 1/\sigma^2(F)$ where $\sigma(F)$ is the e.s.d. in the observed amplitudes based on counting statistics. Atomic scattering factors were taken from *Inter-*

national Tables for X-ray Crystallography (1974). Final atomic parameters are in Table 1.*

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

Discussion. The molecule possesses exact C_2 symmetry with the crystallographic twofold axis perpendicular to and bisecting the central bond [C(1)–C(1′)]. Fig. 1 shows a view of the molecule along the symmetry axis and also indicates the atom numbering. Bond lengths corrected for the effects of rigid-body thermal libration (Schomaker & Trueblood, 1968) are listed in Table 2 beside the uncorrected values. In these calculations the two ring systems were treated as independent units. Details of the calculations have been deposited.

Table 2. *Molecular dimensions*

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

C(1)–C(1′)	1.477 (4)				
C(7)–C(8)	1.187 (3)				
C(4)–C(7)	1.430 (3)		C(8)–C(9)	1.439 (3)	
C(1)–C(2)	1.383 (3)	1.390	C(9)–C(10)	1.384 (3)	1.395
C(2)–C(3)	1.371 (3)	1.376	C(10)–C(11)	1.383 (4)	1.389
C(3)–C(4)	1.387 (3)	1.394	C(11)–C(12)	1.369 (4)	1.380
C(4)–C(5)	1.379 (3)	1.387	C(12)–C(13)	1.360 (4)	1.370
C(5)–C(6)	1.370 (3)	1.374	C(13)–C(14)	1.371 (3)	1.377
C(6)–C(1)	1.387 (3)	1.394	C(14)–C(9)	1.385 (3)	1.396
C(2)–F(2)	1.339 (2)	1.346	C(10)–H(10)	0.933 (27)	
C(3)–F(3)	1.338 (2)	1.346	C(11)–H(11)	0.862 (28)	
			C(12)–H(12)	0.954 (24)	
C(5)–F(5)	1.343 (2)	1.350	C(13)–H(13)	0.921 (27)	
C(6)–F(6)	1.341 (2)	1.348	C(14)–H(14)	0.962 (23)	

(b) Selected non-bonded distances (Å)

F(2)···F(2′)	2.844 (3)		F(6)···F(6′)	2.860 (3)
F(2)···C(2′)	3.049 (3)		F(6)···C(6′)	3.046 (3)

(c) Bond angles (°)

|				
C(4)–C(7)–C(8)	178.5 (2)			
C(7)–C(8)–C(9)	178.4 (3)			
C(6)–C(1)–C(2)	116.3 (2)		C(14)–C(9)–C(10)	119.6 (2)
C(1′)–C(1)–C(2)	121.9 (2)		C(8)–C(9)–C(10)	120.4 (2)
C(1′)–C(1)–C(6)	121.8 (2)		C(8)–C(9)–C(14)	120.0 (2)
C(1)–C(2)–C(3)	122.1 (2)		C(9)–C(10)–C(11)	119.5 (3)
C(1)–C(2)–F(2)	119.9 (2)		C(9)–C(10)–H(10)	119.2 (16)
C(3)–C(2)–F(2)	118.1 (2)		C(11)–C(10)–H(10)	121.2 (16)
C(2)–C(3)–C(4)	121.3 (2)		C(10)–C(11)–C(12)	120.1 (3)
C(2)–C(3)–F(3)	119.2 (2)		C(10)–C(11)–H(11)	115.9 (19)
C(4)–C(3)–F(3)	119.5 (2)		C(12)–C(11)–H(11)	123.9 (19)
C(3)–C(4)–C(5)	116.9 (2)		C(11)–C(12)–C(13)	120.3 (3)
C(3)–C(4)–C(7)	121.1 (2)		C(11)–C(12)–H(12)	117.6 (18)
C(5)–C(4)–C(7)	122.1 (2)		C(13)–C(12)–H(12)	122.0 (18)
C(4)–C(5)–C(6)	121.6 (2)		C(12)–C(13)–C(14)	120.6 (3)
C(4)–C(5)–F(5)	119.5 (2)		C(12)–C(13)–H(13)	121.4 (17)
C(6)–C(5)–F(5)	118.9 (2)		C(14)–C(13)–H(13)	117.9 (17)
C(5)–C(6)–C(1)	121.9 (2)		C(13)–C(14)–C(9)	119.8 (3)
C(5)–C(6)–F(6)	118.5 (2)		C(13)–C(14)–H(14)	123.0 (14)
C(1)–C(6)–F(6)	119.6 (2)		C(9)–C(14)–H(14)	117.2 (14)
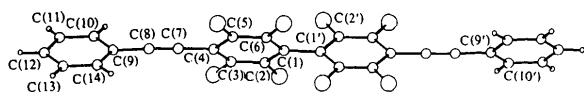
Fig. 1. View of the molecule parallel to **b** (along the crystallographic twofold axis).

The aromatic rings C(1)–(6) and C(9)–(14) are each planar to within the limits of experimental error. F substituents are displaced from the plane of their ring by up to 0·05 Å, the largest displacements occurring at the 2 and 6 positions and are in such a direction as to increase the separation between these substituents and the *ortho* C atoms and F substituents of the neighbouring ring C(1′)–(6′). The interplanar angle in the central biphenyl system [56·7 (3)°] is comparable with the corresponding angles in perfluorobiphenyl (59·6°) (Gleason & Britton, 1976), 2,3,4,5,6-pentafluorobiphenyl (52·9°) (Brock *et al.*, 1978), 2,3,5,6-tetrafluorobiphenyl (57·9°) (Goodhand & Hamor, 1978) and 2*H*-nonafluorobiphenyl (59·5°) (Hamor & Hamor, 1978). The shortest non-bonded distances between the rings (Table 2) are all greater than or equal to the sum of the Pauling (1960) van der Waals radii (F = 1·35, C = 1·7 Å) of the atoms concerned. If, however, the radii of F and C are taken as 1·5 and 1·77 Å (Bondi, 1964) then these distances are 0·15 (F···F) and 0·2 Å (F···C) shorter than the sum of the van der Waals radii. On either set of radii, however, it is the interaction of the *ortho* F substituents of one ring with the *ortho* C atoms of the other, which, in opposition to the packing forces, appears to determine the inter-ring angle.

The angle between the rings across the acetylenic triple bond is 54·5 (3)°, in sharp contrast to the situation in diphenylethyne (Mavridis & Moustakali-Mavridis, 1977) and in the perfluoro derivative (Goodhand & Hamor, 1979) where the rings are essentially coplanar. This is consistent with the results of CNDO and INDO molecular-orbital calculations (Liberles & Matlosz, 1971; Mavridis & Moustakali-Mavridis, 1977) which show that there is no strongly preferred orientation of the two phenyl groups in diphenylethynes.

The orientations of rings C(1)–(6) and C(9)–(14) are such that the symmetrically related ring C(1′)–(6′) is nearly parallel to ring C(9)–(14), interplanar angle 3·2°. The two rings, however, deviate considerably from coplanarity because of a significant bending of the long axis of the molecule, atoms C(12), C(9), C(8), C(7), C(4), C(1) and the symmetry-related C(1′)···C(12′).

The C(7)–C(8) triple-bond length of 1·187 (3) Å is slightly shorter than the length of 1·198 Å in both diphenylethyne and perfluorodiphenylethyne. However, these differences are barely significant. The lengths of the C(sp^2)–C(sp) bonds are 1·430 (3) Å
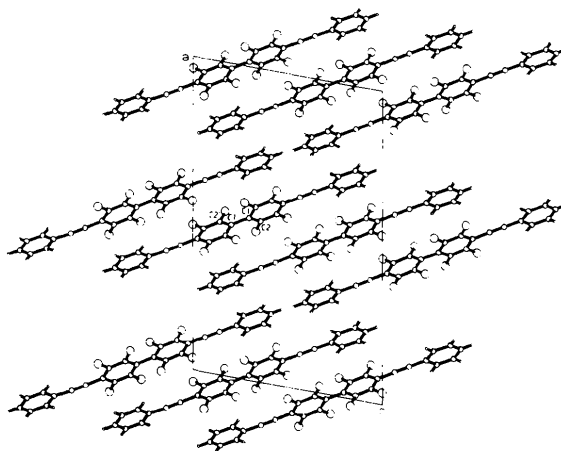

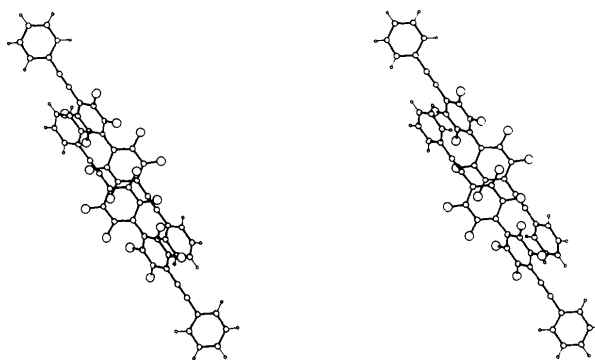Fig. 2. The crystal structure projected along **b**.

Fig. 3. Stereoscopic view of a pair of molecules related by a centre of symmetry.

adjacent to the fluorinated ring and 1·439 Å adjacent to the hydrocarbon ring. These compare with mean lengths of 1·438 and 1·419 Å for the corresponding bonds in diphenylethyne and the perfluoro derivative, respectively. There may, therefore, be a slight, but real shortening of C(sp^2)–C(sp) bonds adjacent to a fluorinated aromatic ring. The C(1)–C(1′) inter-ring bond, 1·477 (4) Å, is slightly shorter than the lengths commonly found for this bond in biphenyls (*ca* 1·49 Å) but falls within the accepted range for a single bond between trigonally hybridized C atoms. C–F bonds are 1·346–1·350 Å (corrected), in good agreement with previous results.

Bond angles in the hydrocarbon ring are all close to 120°. In the fluorinated ring, however, the angles at C(1) and C(4) are significantly smaller, 116·3 (2) and 116·9 (2)°, presumably due to the hybridization changes brought about by the lower electronegativity of the substituents at these atoms compared with F (Bent, 1961; Domenicano, Vaciago & Coulson, 1975).

The packing arrangement in the unit cell is shown in Fig. 2. The molecules pack in stacks with three pairs

of near-parallel rings of centrosymmetrically related molecules overlying one another (Fig. 3). Two of these pairs of overlying rings involve a fluorinated and an unfluorinated ring, the third, two fluorinated rings. No abnormally short contact distances occur between these rings. Overlying fluorinated and unfluorinated rings are a feature of the crystal structures of 2,3,4,5,6-pentafluorobiphenyl and 2,3,5,6-tetrafluoro-biphenyl; the nature of the forces between such rings has been discussed by Brock *et al.* (1978).

References

BENT, H. A. (1961). *Chem. Rev.* **61**, 275–311.
BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
BROCK, C. P., NAAE, D. G., GOODHAND, N. & HAMOR, T. A. (1978). *Acta Cryst.* B**34**, 3691–3696.
COE, P. L., TATLOW, J. C. & TERRELL, R. C. (1967). *J. Chem. Soc. C*, pp. 2626–2628.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B**31**, 221–234.
GLEASON, W. B. & BRITTON, D. (1976). *Cryst. Struct. Commun.* **5**, 483–488.
GOODHAND, N., HAMOR, M. J. & HAMOR, T. A. (1978). *Acta Cryst.* A**34**, S93.
GOODHAND, N. & HAMOR, T. A. (1978). *Acta Cryst.* B**34**, 1644–1647.
GOODHAND, N. & HAMOR, T. A. (1979). *Acta Cryst.* B**35**, 704–707.
GOODHAND, N. & HAMOR, T. A. (1981). *J. Fluorine Chem.* **17**, 289–298.
HAMOR, M. J. & HAMOR, T. A. (1978). *Acta Cryst.* B**34**, 863–866.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
LIBERLES, A. & MATLOSZ, B. (1971). *J. Org. Chem.* **36**, 2710–2713.
MAVRIDIS, A. & MOUSTAKALI-MAVRIDIS, I. (1977). *Acta Cryst.* B**33**, 3612–3615.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
SHELDRICK, G. M. (1978). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

Désoxy-1 *O*-Isopropylidène-2,3 [(Méthoxycarbonyl-2 phényl)-3 uréïdo]-1 *O*-(*p*-Nitrobenzoyl)-5 α-D-Ribofurannose

PAR R. ROQUES*

Laboratoire de Cristallographie de l'Université Nationale de Côte d'Ivoire, 04 BP 322 Abidjan, Côte d'Ivoire

J. L. MONTÉRO

Laboratoire de Chimie Organique, Université Nationale de Côte d'Ivoire, 04 BP 322 Abidjan 04, Côte d'Ivoire

M. RODRIGUEZ ET J. L. IMBACH

Laboratoire de Chimie Bioorganique USTL, 34060 Montpellier CEDEX, France

ET J. P. DECLERCQ ET G. GERMAIN

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1348 Louvain-la-Neuve, Belgique

Abstract. $C_{24}H_{25}N_3O_{10}$, orthorhombic, $P2_12_12_1$, $a = 7.578$ (3), $b = 10.294$ (7), $c = 31.328$ (17) Å, $V = 2444$ (2) Å^3 and $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares calculations to $R = 4.5\%$ for 1639 observed reflexions using Mo $K\alpha$ radiation. The configuration of this adduct is α and the conformation of the ribofuranose ring is E_O.

Introduction. La synthèse totale de nucléosides à partir de glycosyl isocyanates présente le double avantage

* Adresse actuelle: Laboratoire Structure et Vie, Université Paul Sabatier, 118 route de Narbonne, 31077 Toulouse CEDEX, France.