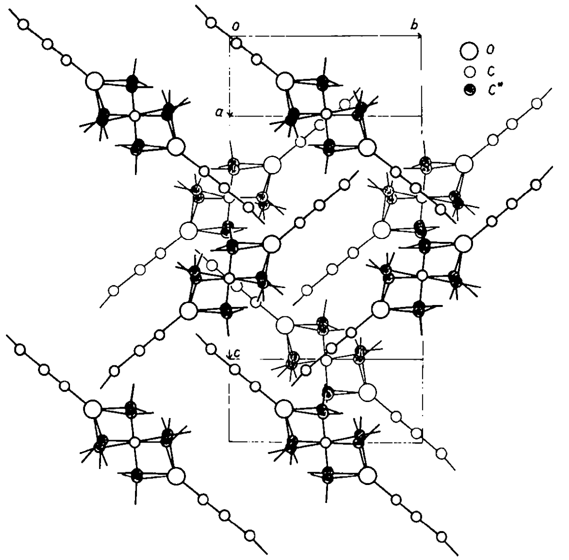

Fig. 3. Packing in the structure viewed approximately along [40$\bar{1}$]. Partially occupied positions of C atoms are hatched.

The conformation of the seven-membered ring has C_2 symmetry within the limits of error, in agreement with the suggestion of Archer, Claret & Hayman (1971) based on UV spectra; the whole molecule has near D_2 symmetry. Values of the torsion angles for the seven-membered rings are similar to those in SND.

The packing in the structure is shown in Fig. 3. As in the case of SND, the disordered atoms are not in close contact, and interact primarily with the planar parts of neighbouring molecules so that the environments of the partially occupied positions are very similar. It seems worth noting that this type of disorder is the second observation of enantiomeric molecules being randomly located at a crystal site (De Camp, 1978). The shortest intermolecular approach distance is 2·41 Å for H(72) to H(2) in position $(2-x, \frac{1}{2}+y, \frac{1}{2}-z)$. All other H···H distances are greater than 2·5 Å.

We thank Professor Smoliński who kindly provided us with the crystals. We also thank the X-ray Laboratory of ŚLAFiBS, Kraków, for making the diffractometer available.

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Biphenyl–Perfluorobiphenyl; 1:1 Molecular Complex

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(*Received* 1 *May* 1979; *accepted* 6 *July* 1979)

Abstract. $C_{12}H_{10}.C_{12}F_{10}$, monoclinic, $C2/c$, a = 21·995 (32), b = 7·570 (8), c = 12·828 (6) Å, β = 112·33 (7)°, $Z = 4$, $D_c = 1·64$, $D_m = 1·60$ (1) Mg m^{-3}. The perfluorobiphenyl and biphenyl molecules are packed alternately in infinite columns. The C_6F_5 and C_6H_5 rings of each molecule are inclined 25·4 and 18·3° respectively to the stack axis. The mean distance from each C_6H_5 ring to the plane of the C_6F_5 ring is 3·41 Å. The packing is very similar to that found in 2,3,4,5,6-pentafluorobiphenyl.

Introduction. Previously, we had reported that the crystalline, 1:1 molecular complex between biphenyl ($C_{12}H_{10}$) and perfluorobiphenyl ($C_{12}F_{10}$) exhibits very low reactivity with gaseous methylamine (Lin & Naae, 1978). This low reactivity was also observed for 2,3,4,5,6-pentafluorobiphenyl ($C_{12}H_5F_5$) and was attributed to the packing in the crystal. Due to their similar lack of solid-state reactivity and also to their similar elevated melting points (388–390 K for the 1:1 complex and 383–385 K for $C_{12}H_5F_5$ – relative to $C_{12}H_{10}$, 343–344 K, and $C_{12}F_{10}$, 340–341 K), we felt that a comparison of the two crystal structures would be informative regarding the similarity of the intermolecular interactions. In addition, the interactions present in the complex were expected to resemble those

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found in the 1:1 complexes of hexafluorobenzene with *p*-xylene, mesitylene, durene, hexamethylbenzene, and *N*,*N*-dimethylaniline (Dahl, 1971, 1973, 1975*a*,*b*, 1977) and in the naphthalene–octafluoronaphthalene 1:1 complex (Potenza & Mastropaolo, 1975).

Colorless, elongated plates of the title complex were obtained by the slow evaporation of an ethanol solution containing equimolar amounts of biphenyl and perfluorobiphenyl. One of the crystals was cut to give a data crystal, 0·35 × 0·35 × 0·6 mm, which was mounted in a glass capillary to prevent sublimation. Weissenberg photographs showed systematic absences *hkl* for *h* + *k* odd and *h*0*l* for *l* odd. This indicated either space group *Cc* or *C*2/*c*. The crystal was then mounted on a Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer, using graphite-monochromated Mo *Kα* radiation.* Cell constants were obtained by computer-centering 25 reflections, followed by least-squares refinement of the setting angles. Intensity measurements were made at 296 ± 1 K for 1439 unique reflections with $2\theta \leq 45°$ using the θ–2θ scan technique with a variable scan rate. Moving-crystal moving-counter background counts were taken at each end of the scan range with a ratio of scan time to background time of 2·0. Three reflections were measured periodically as a check on crystal and electronic stability. No significant change in intensity of these standard reflections was observed during data collection.

A total of 874 reflections had $I > 3\sigma(I)$ where $\sigma(I) = \{S^2[\mathrm{CT} + 4(B_1 + B_2)] + (pI)^2\}^{1/2}$; S is the scan speed, CT is the scan count, B_1 and B_2 are the background counts, and the factor p was set at 0·05 to downweight intense reflections. Lorentz and polarization corrections were applied to the data and normalized structure factors generated (E's). A correction for absorption was not performed (μ = 0·177 mm^{-1}).

The solution of the structure was accomplished by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). In using this program the space group was assumed to be *Cc*. An *E* map was generated which revealed the positions of all non-hydrogen atoms. Full-matrix least-squares refinement followed using a modified version of Busing, Martin & Levy's (1962) *ORFLS* program. Scattering factors for F, C, and H atoms were taken from Cromer & Waber (1974). In the refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$.

At the end of isotropic refinement ($R = \sum ||F_o| - |F_c||/\sum |F_o| = 0{\cdot}108$) it was observed that the $C_{12}F_{10}$ and $C_{12}H_{10}$ molecules lie on twofold axes parallel to *b*, thus indicating space group *C*2/*c*. It was decided to proceed with two parallel refinements, one in *Cc* and the other in *C*2/*c* in the hope of determining the correct space group.

Anisotropic refinement in *C*2/*c* (after transformation of atomic coordinates and with isotropic refinement of H atoms which were located in a difference map) proceeded smoothly and converged at $R = 0{\cdot}036$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0{\cdot}043$ for 874 data and 174 variables. The maximum parameter shift in the final cycle was 0·2σ; no evidence of extinction was observed. The ring C—C bond lengths [calculated using Busing, Martin & Levy's (1964) *ORFFE* error function program] varied from 1·374 to 1·395 Å (average, 1·385 Å) in $C_{12}H_{10}$ and varied from 1·366 to 1·391 Å (average, 1·375 Å) in $C_{12}F_{10}$.

Anisotropic refinement in *Cc* (the original atomic coordinates were used where the molecules are not near a pseudo twofold axis) proceeded smoothly and converged at R = 0·032 and R_w = 0·038 for 347 variables. The C—C bond lengths varied from 1·312 to 1·437 Å (average, 1·385 Å) in $C_{12}H_{10}$ and from 1·325 to 1·420 Å (average, 1·375 Å) in $C_{12}F_{10}$. As these bond lengths varied much more than would be expected chemically, it was concluded that *C*2/*c* was the correct space group. In addition, Hamilton's (1965) *R* ratio test was not significant even at the 0·50 level for the increase in the number of variables from *C*2/*c* to *Cc*.

At the completion of refinement in *C*2/*c* the error in an observation of unit weight was calculated to be 1·39. A final difference electron density map showed no important features and had no peaks as large as a H atom from a previous difference map. Atomic coordi-

Table 1. *Fractional coordinates for the* $C_{12}H_{10}$. $C_{12}F_{10}$ *complex with estimated standard deviations in parentheses*

	x	*y*	*z*
C(1)	−0·03619 (12)	0·3413 (3)	0·23522 (22)
C(2)	−0·07919 (15)	0·3899 (4)	0·12476 (25)
C(3)	−0·14657 (15)	0·3884 (4)	0·10026 (31)
C(4)	−0·17225 (17)	0·3385 (6)	0·17816 (31)
C(5)	−0·13008 (15)	0·2896 (4)	0·28498 (30)
C(6)	−0·06312 (13)	0·2910 (4)	0·31273 (25)
C(7)	−0·03630 (12)	0·1567 (3)	0·73119 (20)
C(8)	−0·07672 (13)	0·0895 (4)	0·62691 (21)
C(9)	−0·14362 (14)	0·0879 (4)	0·59228 (23)
C(10)	−0·17280 (14)	0·1526 (4)	0·66135 (29)
C(11)	−0·13484 (14)	0·2206 (4)	0·76494 (25)
C(12)	−0·06806 (13)	0·2228 (3)	0·78764 (21)
F(8)	−0·05007 (7)	0·02048 (20)	0·55774 (11)
F(9)	−0·18088 (8)	0·02172 (25)	0·49117 (13)
F(10)	−0·23826 (7)	0·14928 (26)	0·62869 (16)
F(11)	−0·16338 (8)	0·28472 (24)	0·83266 (15)
F(12)	−0·03238 (8)	0·29604 (21)	0·89805 (12)
H(2)	−0·0639 (13)	0·421 (4)	0·0713 (22)
H(3)	−0·1759 (15)	0·418 (4)	0·0309 (26)
H(4)	−0·2174 (17)	0·330 (4)	0·1609 (26)
H(5)	−0·1478 (17)	0·257 (4)	0·3430 (29)
H(6)	−0·0333 (14)	0·256 (4)	0·3860 (23)

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* Data were collected at Molecular Structure Corporation, College Station, Texas.

nates and their standard deviations are given in Table 1.*

Discussion. A view of the two molecules in the complex is shown in Fig. 1; bond lengths and bond angles in the aromatic rings are shown. The dimensions of $C_{12}F_{10}$ are very similar to the values reported for crystalline perfluorobiphenyl (Gleason & Britton, 1976), except that the average C–F distance of 1·342 Å in the complex is slightly larger than the value of 1·339 Å in crystalline perfluorobiphenyl. A least-squares plane through the six C atoms of the C_6F_5 group gives a r.m.s. deviation of 0·004 Å. Inclusion of the F atoms in the plane raises this value to 0·008 Å. The dihedral angle between the aromatic rings is 50·8°; for comparison, the dihedral angle in crystalline perfluorobiphenyl is 59·6°. This compression of the dihedral angle may be due to the packing in the complex.

The bond lengths and angles for $C_{12}H_{10}$ are very close to the values reported for crystalline biphenyl (Charbonneau & Delugeard, 1976). A least-squares plane through the six C atoms of the C_6H_5 group has a r.m.s. deviation of 0·001 Å. The dihedral angle between the planes of the phenyl rings is 36·6°. The dihedral angle for crystalline biphenyl is not known as the structure is most probably disordered; however, the values of four 4,4′-disubstituted biphenyls are known and these should be a suitable model for $C_{12}H_{10}$. The following dihedral angles have been reported for 4,4′-X–C_6H_4–C_6H_4–Y: $X = Y =$ Cl, 39, 42° (Brock, Kuo & Levy, 1978); $X = Y =$ Br, 38, 42° (Kronebusch, Gleason & Britton, 1976*b*); $X =$ Br, $Y =$ CN, 42, 42° (Kronebusch, Gleason & Britton, 1976*a*); and $X = Y = CH_3$, 36, 40° (Casalone, Mariani, Mugnoli & Simonetta, 1969); two angles are given for each compound because each structure contains two independent molecules. Thus, the dihedral angle in $C_{12}H_{10}$ is slightly less than the values listed above.

The stereoscopic view of the unit cell in Fig. 2 shows that the molecules are stacked alternately along *b*; the twofold symmetry axis passes through the central C–C bond of each molecule. The angle between the normal of each plane and the stack axis is 25·4° for the C_6F_5 and 18·3° for the C_6H_5 groups. These values are similar to the stack angles of 29·2 and 23·7° present in 2,3,4,5,6-pentafluorobiphenyl ($C_{12}H_5F_5$) (Brock, Naae, Goodhand & Hamor, 1978) and are 5–14° larger than the stack angles reported by Dahl (1971, 1973, 1975*a*,*b*, 1977) in the 1:1 addition compounds of hexafluorobenzene with substituted benzenes.

Within each stack the perpendicular distances from the center of a C_6H_5 ring to the planes of the C_6F_5 rings above and below it are 3·43 and 3·38 Å (mean, 3·41 Å). Thus, the C_6F_5 ring is slightly closer to one of the phenyl rings in the stack than to the other. This was

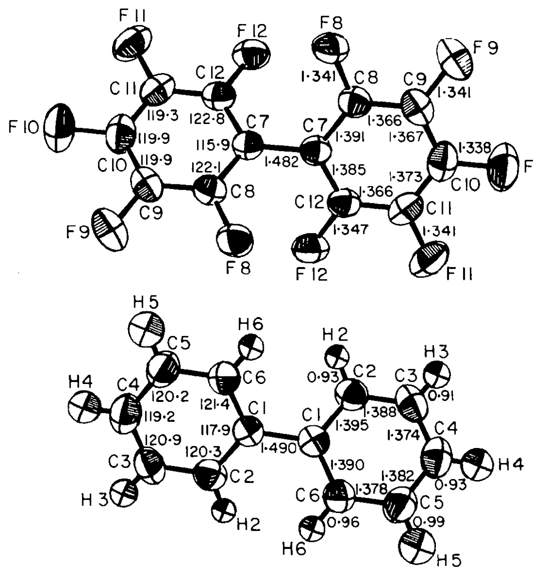

Fig. 1. A drawing of the $C_{12}F_{10}$ and $C_{12}H_{10}$ molecules showing the atom-numbering scheme, bond lengths (Å), and ring bond angles (°). The e.s.d.'s of the C–C bonds are ±0·004–0·005 Å, the C–F bonds ±0·003 Å, and the C–H bonds ±0·03–0·04 Å; the e.s.d.'s of angles are ±0·3°. In this and Fig. 2 the shapes of the atoms correspond to 50% contours of thermal motion.

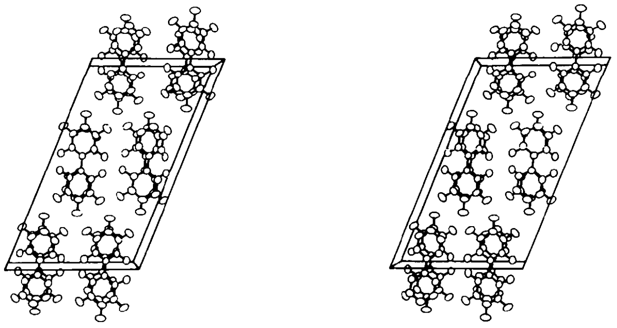

Fig. 2. A stereoscopic view of the unit cell of $C_{12}F_{10}.C_{12}H_{10}$. The *a* axis is vertical, the *b* axis points out of the paper, and the *c* axis is horizontal. The H atoms have been omitted for clarity.

Table 2. *Interatomic contacts* (Å) *less than* 3·60 Å *between rings in the stack*

C(6)–F(12)	3·297 (5)	H(5)–F(11)	3·48 (3)
H(3)–F(9)	3·36 (3)	C(1)–F(8)	3·500 (4)
C(2)–F(8)	3·361 (5)	C(4)–C(11)	3·515 (6)
H(2)–F(8)	3·37 (3)	C(1)–C(8)	3·525 (5)
C(3)–F(9)	3·371 (5)	C(1)–C(12)	3·528 (5)
H(6)–F(12)	3·40 (3)	C(4)–C(9)	3·544 (5)
C(5)–F(11)	3·411 (5)	H(4)–F(11)	3·58 (3)
C(1)–F(12)	3·431 (4)	C(3)–C(11)	3·588 (5)
C(4)–F(11)	3·436 (4)	C(4)–F(9)	3·589 (4)

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34583 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

also noticed in $C_{12}H_5F_5$ where the mean distance between the C_6H_5 group and the C_6F_5 plane was found to be 3·43 Å. Table 2 lists some interatomic contacts between molecules in the stack. No important contacts were noticed between the stacks.

The molecular packing of the $C_{12}F_{10}.C_{12}H_{10}$ complex is very similar to that present in $C_{12}H_5F_5$. The similarity of the stack angles, interplanar separations, and their melting points indicates that the intermolecular interactions are nearly identical in the two crystals. The geometries of the $C_{12}F_{10}$ and $C_{12}H_{10}$ molecules in the complex are virtually unchanged from those in single crystals, except for the dihedral angle in $C_{12}F_{10}$ which has been compressed by 8·8°.

Acknowledgement is made to the Donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this work. We also thank Mr Stephen O. Teremi for the characterization and initial X-ray work on the structure of the complex.

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Acta Cryst. (1979). B**35**, 2768–2771

Structure of Tris(hydroxymethyl)acetic Acid*

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(*Received* 27 *February* 1979; *accepted* 6 *July* 1979)

Abstract. $C_5H_{10}O_5$, monoclinic, *I2/a* (non-standard setting of *C2/c*), a = 10·417 (1), b = 5·727 (1), c = 22·774 (2) Å, β = 98·05 (1)°, V = 1345 Å^3, Z = 8, D_c = 1·464, D_m = 1·468 Mg m^{-3} (in carbon tetrachloride and xylene), μ(Mo $K\alpha$) = 0·142 mm^{-1}. The structure was solved using *MULTAN* and refined to R = 0·051 for 683 unique reflections. This polyhydric plastic-crystal precursor crystallizes in a three-dimensional hydrogen-bonded network involving all of the O and hydroxy H atoms as well as the carboxyl H atom.

Introduction. The structure of the title compound, $(CH_2OH)_3CCOOH$ (designated hereafter as *R*COOH), was determined as part of our continuing investigation of hydrogen-bonded poly(hydroxymethyl) compounds known to undergo solid–solid phase transitions between ordered and orientationally disordered (plastic) phases. Doshi, Furman & Rudman (1973) reported that upon warming to 394·7 K, *R*COOH undergoes a phase transition to an orientationally disordered face-centered cubic lattice with $a \sim$ 8·9 Å. The crystal and molecular structures of the ordered phase of this compound, stable at room temperature, are reported here.

Single crystals were grown from a saturated solution of ethanol using the crystal-growing device described

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* Polymorphism of Crystalline Poly(hydroxymethyl) Compounds. II. Part I: Eilerman & Rudman (1979).

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