Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(1*E*,3*E*,5*E*)-1,2,3,4,5,6-Hexafluoro-1,6-diphenylhexatriene

Dale C. Swenson,* Xiaobang Gao and Donald J. Burton

Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA
Correspondence e-mail: dale-swenson@uiowa.edu

Received 22 February 2000
Accepted 22 May 2000

The title triene, $C_{18}H_{10}F_6$, was prepared *via* the Pd^0 coupling reaction of (*E*)-(1,2-difluoro-1,2-ethenediyl)bis(tributylstannane) with (*Z*)-β-iodo-α,β-difluorostyrene in *N*,*N*′-dimethylformamide/tetrahydrofuran. The crystal structure shows the product to be the 1*E*,3*E*,5*E* isomer. Due to steric interactions between F atoms, the double bonds are not coplanar. The planes defined by the two terminal double bonds are almost perpendicular.

Comment

The chemistry of polyfluorinated polyene systems (beyond dienes) is virtually unknown. The few compounds reported were generally mixtures of all possible *E*/*Z* isomers (Yagupol'skii *et al.*, 1976, 1977, 1985). This work was initiated to develop methodology for the stereospecific preparation of fluorinated polyenes in order to compare the effects of the fluorine substituents on conjugation, reactivity and stability of the polyene. The title triene, (I), was stereospecifically prepared *via* the route shown below.

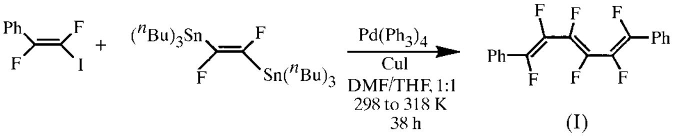

Fig. 1 shows that the triene is the 1*E*,3*E*,5*E* isomer and that the conjugated system has a conformation that is significantly distorted from overall planarity by intramolecular steric interactions. Although the overall molecule is not planar, phenyl rings 1 (C7–C12) and 2 (C13–C18), and individual double-bond moieties (Db1: C7, F1, C1, C2, F2, C3; Db2: C2, F3, C3, C4, F4, C5; Db3: C4, F5, C5, C6, F7, C13) are planar. The largest r.m.s. deviation from the least-squares plane is 0.03 Å for Db3. Ring 1 and Db1 are nearly coplanar [dihedral angle = 5.6 (2)°], as are ring 2 and Db3 [dihedral angle = 2.1 (2)°]. However, the double-bond moieties are not coplanar. Rotations of about 42° about the C2—C3 and C4—C5 bonds reduce intramolecular steric repulsion between adjacent fluoro substituents. [Note: The barrier to full rotation (perpendicular double bonds) about these bonds should be similar to that of the central bond in 1,3-butadiene, calculated value = 5.9 kcal mol^{-1} (Head-Gordon & Pople, 1993).] The longest F···F intramolecular distance is 0.375 Å shorter than the shortest F···F intermolecular distance (see Table 2). An additional result of these two rotations is that the phenyl rings are nearly perpendicular [dihedral angle = 88.3 (1)°]. Even though the double-bond moieties are not coplanar, the shortening of the C2—C3 and C4—C5 bonds show that they are part of a delocalized π system.

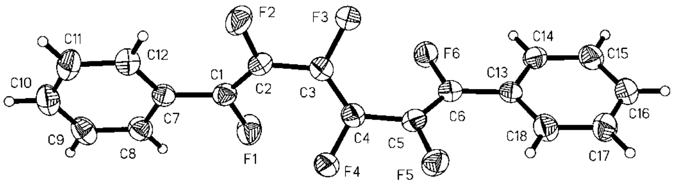

Figure 1
View of the title compound with displacement ellipsoids shown at the 35% probability level.

Fig. 2 shows that the packing of the molecules is organized by $\pi\cdots\pi$ and CH$\cdots\pi$ interactions. The molecules form a network *via* $\pi\cdots\pi$ interactions between adjacent (phenyl ring–double bond) π systems across inversion centers. The ring 1–π system (ring 1 and Db1) overlap occurs across the $(\frac{1}{2},0,\frac{1}{2})$ set of inversion centers such that C7 is approximately centered over the adjacent phenyl ring [$\pi\cdots\pi$ spacing = 3.537, C7$\cdots$*Cg*1^{i} = 3.570 Å; *Cg*1^{i} is the centroid of symmetry-related ring 1, (i) $1-x, 2-y, 1-z$]. The ring 2–π system (ring 2 and Db3) has a greater degree of overlap and a closer $\pi\cdots\pi$ spacing. This interaction occurs across the $(0,\frac{1}{2},0)$ set of inversion centers such that C6 is approximately centered over the adjacent phenyl ring [$\pi\cdots\pi$ spacing = 3.427 Å and C6$\cdots$*Cg*2^{ii} = 3.455 Å; *Cg*2^{ii} is the centroid of symmetry-related ring 2; symmetry code: (ii) $-x, 1-y, -z$]. The network also includes C15—H15$\cdots$ring 1 interactions that form dimers

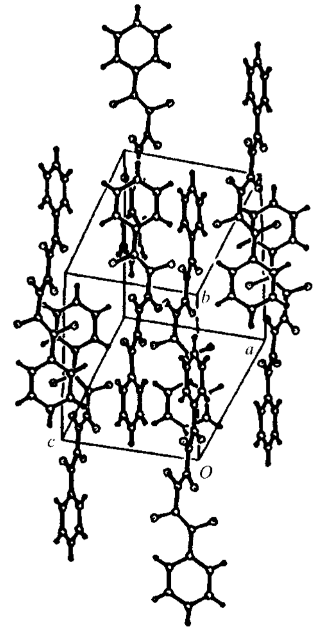

Figure 2
Packing diagram of the title compound.

across the $(\frac{1}{2},\frac{1}{2},0)$ set of inversion centers [$H15\cdots Cg1^{iii} = 2.89$ Å and $C15—H15\cdots Cg1^{iii} = 143°$; symmetry code: (iii) $1 - x$, $1 - y$, $-z$]. The crystal morphology appears to correlate with these interactions. The direction of the longest molecular dimension is approximately parallel to the $(a + b)$-face diagonal direction. The bounding faces for the largest crystal dimension are the (110) and $(\bar{1}\bar{1}0)$ faces. The direction of the C15—H15···ring 1 interaction is approximately parallel to the $(a - c)$-face diagonal. The bounding faces for the smallest crystal dimension are the $(10\bar{1})$ and $(\bar{1}01)$ faces.

Experimental

A three-neck 250 ml round-bottomed flask equipped with a teflon-coated stir bar, a cold water condenser attached to a nitrogen source, a thermometer, and a rubber septum was charged with CuI (1.48 g, 7.7 mmol), *N*,*N*′-dimethylformamide (35 ml), tetrahydrofuran (THF) (35 ml), $Pd(PPh_3)_4$ (0.44 g, 0.4 mmol), (*E*)-$^n Bu_3SnCF{=}CF^n Bu_3$ (4.95 g), and (*Z*)-PhCF=CFI (4.12 g, 15.5 mmol). The reaction mixture was stirred at room temperature for 14 h, at 310 K for 14 h, and at 318 K for 10 h. The majority of the THF was removed by rotary evaporation. The residue was diluted with 80 ml of H_2O, extracted with Et_2O (4 × 80 ml), and the combined ether layers dried over anhydrous $MgSO_4$. The majority of the solvent was removed by rotary evaporation; the residue was poured onto a silica-gel chromatography column and eluted with pentane, $R_f = 0.88$. Removal of most of the pentane yielded a mixture of the title compound, $^n Bu_3SnI$ and (*Z*)-PhCF=CFI. This mixture was recrystallized twice from hexane to give 1.0 g (40% yield) of (I) as white crystals (m.p. 344 K). ^{19}F NMR ($CDCl_3$): δ −140.8 (*dt*, 2F, *J* = 126, 24 Hz), −149.4 (*m*, 2F), −162.8 (*ddd*, 2F, *J* = 127, 15, 6 Hz); ^1H NMR ($CDCl_3$): δ 7.8 (*m*, 2H), 7.5 (*m*, 3H); ^{13}C NMR ($CDCl_3$): δ 151.2 (*dd*, *J* = 248, 42 Hz), 140.2 (*m*), 130.7 (*s*), 128.7 (*s*), 126.4 (*t*, *J* = 8 Hz), 117.4 (*d*, *J* = 337 Hz). HRMS calculated for $C_{18}H_{10}F_6$ = 340.0687, observed = 340.0679.

Crystal data

$C_{18}H_{10}F_6$
$M_r = 340.26$
Triclinic, $P\bar{1}$
$a = 9.138$ (1) Å
$b = 10.793$ (2) Å
$c = 8.249$ (1) Å
$\alpha = 90.76$ (1)°
$\beta = 94.26$ (1)°
$\gamma = 65.75$ (1)°
$V = 739.6$ (2) Å^3

$Z = 2$
$D_x = 1.528$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 45 reflections
$\theta = 11.7$–17.4°
$\mu = 0.141$ mm^{-1}
$T = 210$ (2) K
Plate, colorless
0.53 × 0.23 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
4307 measured reflections
2587 independent reflections
1706 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$

$\theta_{\rm max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -9 \rightarrow 5$
4 standard reflections
frequency: 120 min
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.122$
$S = 1.04$
2587 reflections
218 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.1953P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1995)
Extinction coefficient: 0.007 (4)

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.322 (3)	C4—F4	1.342 (3)
C1—F1	1.350 (3)	C4—C5	1.448 (3)
C1—C7	1.467 (3)	C5—C6	1.332 (3)
C2—F2	1.350 (3)	C5—F5	1.347 (2)
C2—C3	1.447 (3)	C6—F6	1.360 (2)
C3—C4	1.330 (3)	C6—C13	1.459 (3)
C3—F3	1.349 (3)		
C2—C1—F1	114.5 (2)	C3—C4—F4	117.8 (2)
C2—C1—C7	131.4 (2)	C3—C4—C5	128.4 (2)
F1—C1—C7	114.1 (2)	F4—C4—C5	113.6 (2)
C1—C2—F2	118.4 (2)	C6—C5—F5	118.7 (2)
C1—C2—C3	128.9 (2)	C6—C5—C4	129.3 (2)
F2—C2—C3	112.8 (2)	F5—C5—C4	112.1 (2)
C4—C3—F3	117.8 (2)	C5—C6—F6	114.6 (2)
C4—C3—C2	128.5 (2)	C5—C6—C13	131.3 (2)
F3—C3—C2	113.6 (2)	F6—C6—C13	114.2 (2)
F1—C1—C2—F2	174.4 (2)	C3—C4—C5—C6	−42.0 (4)
C7—C1—C2—C3	173.4 (2)	F4—C4—C5—F5	−37.3 (3)
C1—C2—C3—C4	−40.2 (4)	F5—C5—C6—F6	176.4 (2)
F2—C2—C3—F3	−36.0 (3)	C4—C5—C6—C13	176.0 (2)
F3—C3—C4—F4	170.9 (2)	C2—C1—C7—C12	−2.8 (4)
C2—C3—C4—C5	−179.2 (3)	C5—C6—C13—C14	179.6 (2)

Table 2
Selected non-bonding distances (Å).

F1···F4	2.636 (2)	F4···F5	2.614 (2)
F2···F3	2.624 (2)	F2···F5$^{\rm i}$	3.025 (2)
F3···F6	2.659 (2)		

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.

Data collection: *CAD*-4 *Operation Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operation Manual*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

DJB thanks the National Science Foundation, grant CHE-9820769, for support of this research.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1534). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1977). *CAD*-4 *Operation Manual*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
Head-Gordon, M. & Pople, J. A. (1993). *J. Phys. Chem.* **92**, 1147–1151.
Sheldrick, G. M. (1995). *SHELXTL*. Version 5.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Yagupol'skii, L. M., Kremlev, M. M., Fialkov, Yu. A., Khranovskii, V. A. & Yurchenco, V. M. (1976). *Zh. Org. Khim.* **12**, 1565.
Yagupol'skii, L. M., Kremlev, M. M., Fialkov, Yu. A., Khranovskii, V. A. & Yurchenco, V. M. (1977). *Zh. Org. Khim.* **13**, 1438–1439.
Yagupol'skii, L. M., Kremlev, M. M., Moklyachuk, L. I. & Fialkov, Yu. A. (1985). *Zh. Org. Khim.* **21**, 593.