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2,2-Dimethyl-2,3-dihydro-1*H*-2-silacyclopenta[*l*]phenanthrene†

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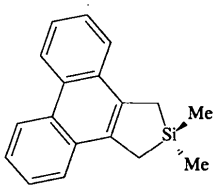
Abstract

Starting from 9,10-dimethylphenanthrene, the title compound, $C_{18}H_{18}Si$, was synthesized in two steps. Bond lengths and angles within the planar carbon skeleton show no deviation from normal values. The five-membered ring adopts an envelope conformation. Molecules pack in a herring-bone-type layer structure. There are no intermolecular C—H distances below 2.90 Å.

Comment

2,2-Dimethyl-2,3-dihydro-1*H*-2-silacyclopenta[*l*]phenanthrene, (I), crystallizes in the orthorhombic space group *Pbca*, with $Z = 8$. The molecules form *ABAB* layers along the crystallographic *b* axis, *A* and *B* being related by a center of symmetry. We note that the molecular axes, defined by the vector from the midpoint of the C4—C5 bond to the Si atom, point in the same direction within each layer. The interplanar angle between adjacent molecules in one layer (related by the screw axis parallel to **a**) is 58°, and in this way the crystal structure resembles those found for phenanthrene (Trotter, 1963) and 9,10-dimethylphenanthrene (Johnson & Jones, 1989). A stereoview of the packing has been deposited.



(I)

The carbon skeleton of the title compound is essentially planar [maximum deviation from the best plane through C1–C16 is 0.018 (2) Å for C1]. The Si atom is displaced by 0.204 (1) Å from this plane, giving rise to an interplanar angle of 8.8 (3)° between the Si, C15, C16 plane and that of the phenanthrene nucleus. As expected, the allylic Si—C bonds are significantly longer [0.020 (2) Å] than the aliphatic bonds (*cf.* Table 1).

Corresponding bond lengths and angles are equivalent within the limits of their estimated standard deviations. The idealized local symmetry is therefore *m*. On the NMR time scale, the molecular symmetry is *mm*2. Both an average structure due to rapid interconversion between different conformers and a planar *mm*2 structure in solution are in agreement with these experimental results. *AM*1 (Dewar & Jie, 1987) calculations show no significant energy difference (less than 0.1 kcal mol^{-1}) between the latter (high symmetry) and the conformation found in the solid state.

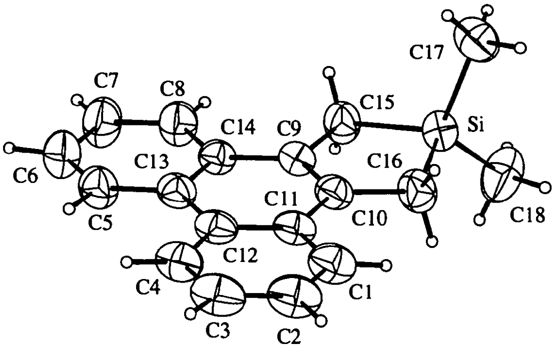


Fig. 1. Displacement-ellipsoid drawing (50% probability) (Erlebacher & Carrell, 1992), with H atoms drawn as small circles of arbitrary radii. The labeling scheme refers to that of phenanthrene (Trotter, 1963).

Experimental

The title compound was prepared by metallation of 9,10-dimethylphenanthrene with 2.1 equivalents of Lochmann–Schlosser base (Lochmann, Pospisil & Lim, 1966; Schlosser, 1967) and quenching with Me_2SiCl_2. After evaporation, the crude product was purified chromatographically (Al_2O_3/hexane). Suitable crystals were obtained from hexane. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.68 (*m*, 2H), 8.08 (*m*, 2H), 7.61 (*m*, 4H), 2.41 (*s*, 4H), 0.35 (*s*, 6H) p.p.m. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 136.2, 132.5, 129.7, 126.3, 125.7, 125.3, 122.5, 19.3, −1.8 p.p.m. ^{29}Si NMR (99.3 MHz, $CDCl_3$): δ 16.3 p.p.m. MS: 262 (M^+, 53%), 248 (M^+-CH_2, 100%), 247 (M^+−Me, 100%); m.p. 433–434 K.

Crystal data

$C_{18}H_{18}Si$
$M_r = 262.43$
Orthorhombic
Pbca
$a = 10.005\ (3)$ Å
$b = 17.535\ (3)$ Å
$c = 16.509\ (2)$ Å
$V = 2896\ (2)$ Å^3
$Z = 8$
$D_x = 1.20$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 23$–$23°$
$\mu = 1.263$ mm^{-1}
$T = 293$ K
Irregular parallelepiped
$0.65 \times 0.60 \times 0.40$ mm
Colorless

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† The authors would like to dedicate this publication to Professor Dr G. E. Herberich on the occasion of his 60th birthday.

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.528$, $T_{max} = 0.603$
2624 measured reflections
2624 independent reflections
2240 reflections with $I > \sigma(I)$
$\theta_{max} = 64.94°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.040$
$wR = 0.059$
$S = 2.203$
2240 reflections
245 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.14×10^{-5}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Si—C15	1.879 (1)	C6—C7	1.390 (2)
Si - C16	1.874 (1)	C7—C8	1.374 (2)
Si—C17	1.853 (2)	C8—C14	1.401 (2)
Si—C18	1.854 (2)	C9—C10	1.358 (2)
C1—C2	1.372 (2)	C9—C14	1.446 (2)
C1—C11	1.407 (2)	C9—C15	1.516 (2)
C2—C3	1.388 (2)	C10—C11	1.449 (2)
C3—C4	1.365 (2)	C10—C16	1.512 (2)
C4—C12	1.413 (2)	C11—C12	1.420 (2)
C5—C6	1.360 (2)	C12—C13	1.450 (2)
C5—C13	1.410 (2)	C13—C14	1.418 (2)
C15—Si—C16	95.20 (6)	C16—Si—C18	114.3 (1)
C15—Si—C17	111.28 (8)	C17—Si—C18	111.16 (9)
C15—Si—C18	113.06 (7)	Si—C15—C9	104.17 (8)
C16—Si—C17	110.95 (8)	Si—C16—C10	104.23 (8)

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *BEGIN* in *SDP-Plus* (Frenz, 1990). Program(s) used to solve structure: *FOUR* in *SDP-Plus*. Program(s) used to refine structure: *LSFM* in *SDP-Plus*. Molecular graphics: *ICRVIEW* (Erlebacher & Carrell, 1992). Software used to prepare material for publication: *CIFVAX* in *MolEN* (Fair, 1990).

The authors thank Dr Ulli Englert for helpful discussions.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: MU1274). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,3-Bis(*p*-fluorophenyl)triazene

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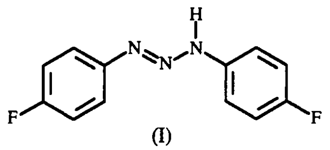
Abstract

Molecules of the title compound, $C_{12}H_9F_2N_3$, contain a triazene group (–N═N—NH), having an extended conformation, and are linked by N—H···N hydrogen bonds to form chains.

Comment

p-Substituted derivatives of formamidine having the amidine group (N═CH—NH) form cyclic dimers in crystals as a result of two N—H···N hydrogen bonds (Anulewicz, Krygowski & Pniewska, 1987, 1990; Anulewicz, Krygowski, Jaroszewska-Manaj & Pniewska, 1991; Anulewicz, Wawer, Krygowski, Männle & Limbach, 1997). The structure of 1,3-bis(*p*-fluorophenyl)triazene, (I) (Fig. 1), has been determined in order to check whether the title molecule, containing a triazene group (–N═N—NH), forms similar dimers. The triazene group adopts an extended conformation with the 1,3-positioned phenyl rings arranged *cis* with respect to one another. The same arrangement is observed in other 1,3-diaryltriazene derivatives (Walton, Jenkins & Neidle, 1991). The molecule is nearly planar and the angles between the triazene group and the phenyl rings are 1.1 (3) and 10.1 (3)°.



(I)

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