Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{\min} = 0.973$, $T_{\max} = 0.975$
2542 measured reflections
2352 independent reflections
1974 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.008$
$\theta_{\max} = 26.3°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 0$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 0.7%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.043$
$S = 1.11$
1974 reflections
172 parameters
H atoms: see below
$w = \sigma^2(F) + 0.0004F^2 + 0.50$
$(\Delta/\sigma)_{\max} = 0.0002$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Cl—C4	1.745 (2)	O2—C7	1.224 (3)
S—C8	1.792 (2)	N—C6	1.412 (2)
S—C9	1.766 (2)	N—C7	1.335 (2)
O1—C1	1.361 (3)	C7—C8	1.521 (3)
C8—S—C9	103.2 (1)	N—C6—C5	124.4 (2)
C6—N—C7	128.8 (2)	O2—C7—N	124.1 (2)
O1—C1—C2	123.9 (2)	O2—C7—C8	119.5 (2)
O1—C1—C6	116.4 (1)	N—C7—C8	116.4 (2)
Cl—C4—C3	119.5 (2)	S—C8—C7	118.8 (1)
Cl—C4—C5	118.6 (2)	S—C9—C10	123.5 (2)
N—C6—C1	115.6 (2)	S—C9—C14	117.5 (2)
C9—S—C8—C7	80.3 (2)	O2—C7—C8—S	−160.3 (2)
C6—N—C7—C8	178.1 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H01···O2$^{\rm i}$	0.94	1.74	2.683 (4)	176
C2—H2···O2$^{\rm i}$	0.95	2.63	3.304 (5)	128

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

All non-H atoms were refined with anisotropic displacement parameters. The H atoms, except H01, H1, H81 and H82, were placed geometrically 0.95 Å from their corresponding C atoms, with $U_{\rm iso}({\rm H}) = 1.3U_{\rm eq}({\rm C})$. The H01, H1, H81 and H82 atoms were taken from a difference Fourier map. A riding model was used for all H atoms.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *MolEN* version of *ORTEP*. Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1319). Services for accessing these data are described at the back of the journal.

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4-Nitro-1-(trimethylsilylethynyl)benzene

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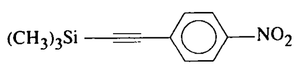
Abstract

The title molecule, $C_{11}H_{13}NO_2Si$, lies on a mirror plane, with only one methyl group lying out of plane. The C≡C triple bond has a length of 1.199 (4) Å. Bond angles Si—C≡C and C≡C—C(Ar) are 177.9 (3) and 178.0 (3)°, respectively. The Si—C_{sp^3} bond lengths are 1.831 (4) and 1.838 (3) Å, while the Si—C_{sp} distance is 1.839 (3) Å.

Comment

The title compound, (I), was prepared as part of a structural study involving substituted silylethynylbenzene derivatives. The molecule lies on a mirror plane, with



(I)

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only the C10 atom lying out of plane. The acetylenic bond distance [C1—C2 1.199 (4) Å] is in agreement with the average value for $C_{sp}{\equiv}C_{sp}{-}C_{sp^2}(Ar)$ reported by Allen *et al.* (1987), and is also in agreement with those of related compounds, *i.e.* 2,3,5,6-tetrakis[1-ethynyl-2-(trimethylsilyl)]pyridine [1.190 (4) and 1.191 (4) Å; Garcia *et al.*, 1997], 2,3,5,6-tetrakis[1-ethynyl-2-(trimethylsilyl)]pyrazine [1.198 (5) and 1.199 (6) Å; Garcia *et al.*, 1997], 2,3,4,5-tetrakis-[1-ethynyl-2-(trimethylsilyl)]thiophene [1.190 (4) and 1.190 (4) Å; Garcia *et al.*, 1997], 3,4-dibromo-2,5-bis-[1-ethynyl-2-(trimethylsilyl)]-*N*-methylpyrrole [1.189 (5) and 1.194 (4) Å; Garcia *et al.*, 1997], 2-[(2,6-dihydroxyphenyl)ethynyl]benzoic acid [1.195 (2) Å; Huang *et al.*, 1992], methyl 2-[(2,6-dimethoxyphenyl)ethynyl]-benzoate [1.195 (2) Å; Huang *et al.*, 1991], methyl 2-[(2,6-dimethoxyphenyl)ethynyl]-3-methoxybenzoate [1.195 (2) Å; Evans *et al.*, 1990], 3,3-diphenyl-1-propyn-3-ol [1.169 (2) Å; Garcia *et al.*, 1995], phenyl 2-(trimethylsilylethynyl)phenyl methanone and 2-(trimethylsilylethynyl)benzaldehyde [1.199 (3) and 1.192 (3) Å, respectively; Garcia *et al.*, 1996], 3-[4-(3-cyanophenylethynyl)phenyl]-5-methoxymethyl-2-oxazolidinone [1.190 (20) Å; Durant *et al.*, 1982] and bis(*p*-nitrophenyl)butadiyne [1.195 (4) Å; Mayerle *et al.*, 1979].

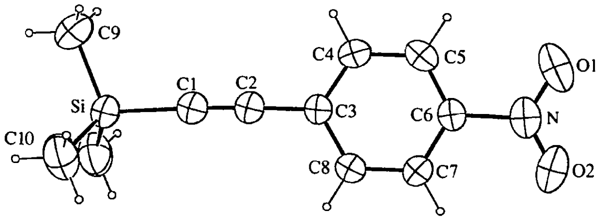

Fig. 1. The title molecule with ellipsoids at the 40% probability level and H atoms represented with arbitrary radii.

The packing is illustrated in Fig. 2, in which the herring-bone pattern is evident. The molecules lie on a mirror plane allowing them to stack in the **b** direction with parallel aromatic rings and a spacing of **b**/2 = 3.6553 (3) Å. The rings are offset from exact overlap, however, with their centroids separated by 4.179 Å. These centroids form zigzag chains in the **b** direction, forming angles of 122.0°.

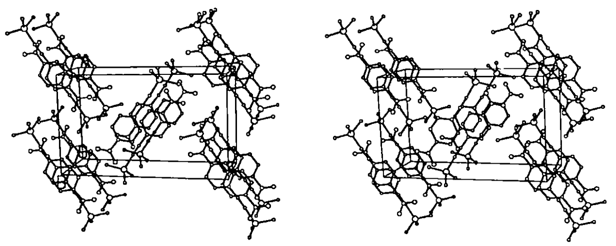

Fig. 2. Stereoview of the unit cell, viewed slightly oblique to the **b** direction, with **c** horizontal. H atoms are not shown.

Experimental

The title compound was prepared by a palladium(II)-catalyzed coupling (Austin *et al.*, 1980) of trimethylsilylacetylene with 4-nitroiodobenzene.

Crystal data

$C_{11}H_{13}NO_2Si$
$M_r = 219.32$
Orthorhombic
Pnma
$a = 10.3139\ (9)$ Å
$b = 7.3105\ (5)$ Å
$c = 16.735\ (1)$ Å
$V = 1261.8\ (3)$ Å^3
$Z = 4$
$D_x = 1.154$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 9$–28°
$\mu = 1.50$ mm^{-1}
$T = 298$ K
Needle
0.48 × 0.22 × 0.13 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.773$, $T_{max} = 0.823$
2606 measured reflections
1405 independent reflections

1027 reflections with $I > \sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 75°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 9$
$l = -9 \rightarrow 20$
3 standard reflections frequency: 120 min intensity decay: 1.6%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.051$
$S = 2.17$
1027 reflections
89 parameters
H atoms calculated, with $U = 1.3U$ of the bonded atom
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$

$(\Delta/\sigma)_{max} = 0.07$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $4.6\ (3) \times 10^{-6}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Si	0.47230 (8)	1/4	−0.14033 (5)	0.0794 (3)
O1	−0.3165 (2)	1/4	0.1330 (2)	0.155 (1)
O2	−0.1936 (3)	1/4	0.2321 (2)	0.198 (2)
N	−0.2104 (2)	1/4	0.1627 (2)	0.106 (1)
C1	0.3218 (3)	1/4	−0.0814 (2)	0.082 (1)
C2	0.2260 (3)	1/4	−0.0407 (2)	0.079 (1)
C3	0.1143 (2)	1/4	0.0103 (1)	0.0656 (8)
C4	−0.0108 (3)	1/4	−0.0206 (2)	0.084 (1)
C5	−0.1167 (3)	1/4	0.0286 (2)	0.086 (1)
C6	−0.0966 (3)	1/4	0.1094 (2)	0.0718 (9)
C7	0.0235 (3)	1/4	0.1419 (2)	0.079 (1)
C8	0.1292 (3)	1/4	0.0926 (2)	0.075 (1)
C9	0.4288 (4)	1/4	−0.2464 (2)	0.133 (2)
C10	0.5687 (2)	0.0470 (4)	−0.1145 (2)	0.122 (1)

Table 2. *Selected geometric parameters (Å, °)*

O1—N	1.201 (4)	C1—C2	1.199 (4)
O2—N	1.175 (4)		
O1—N—O2	122.9 (3)	Si—C1—C2	177.9 (3)

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual.* Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN.* Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN.*

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1347). Services for accessing these data are described at the back of the journal.

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Structure and Photochemistry of Four Adamantylacetophenones

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Abstract

The photochemistry and crystal structures of four α-adamantylacetophenones have been studied, namely, 1-(4-fluorophenyl)-2-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)-ethanone [(1*a*), $C_{18}H_{21}FO$], 1-(4-cyanophenyl)-2-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)ethanone [(1*b*), $C_{19}H_{21}NO$], 1-(4-cyanophenyl)-2-(3-methyltricyclo[3.3.1.1^{3,7}]dec-1-yl)ethanone [(1*c*), $C_{20}H_{23}NO$] and 1-(4-carboxyphenyl)-2-(3-methyltricyclo[3.3.1.1^{3,7}]dec-1-yl)ethanone [(1*d*), $C_{20}H_{24}O_3$]. All four molecules adopt fairly similar conformations, with short γH···O contacts permitting hydrogen abstraction in the photochemical reactions. However, three of the compounds, (1*a*), (1*b*) and (1*d*), are photostable in the solid state and possible reasons for this unreactivity are considered.

Comment

Study of the photochemical Norrish type II γ-hydrogen-abstraction reaction of α-adamantylacetophenones is simplified by the fact that products formed by cleavage of the intermediate 1,4-biradicals are not possible, since they would include the highly strained adamantene (Evans & Trotter, 1989*a*,*b*; Jones *et al.*, 1994). For reactants of type (1) (*R* = H), the favoured products are two cyclobutanols, with *cis*-OH, (2), or *trans*-OH substituents (relative to the ring junction H atom). The major photoproduct is usually the *trans*-OH isomer, which is presumably more stable than the *cis*-OH isomer, since the latter exhibits greater steric repulsions between a pseudo-axial aryl substituent on the folded four-membered ring and the adamantyl group. Production of the *trans*-OH isomer involves rotation of the adamantyl group by about 90° from the observed solid-state molecular conformation of the adamantyl-acetophenones; since even the solid-state photoreactions yield the *trans*-OH isomer as the major product, rotation of the approximately spherical adamantyl group appears to be a preferred (energetically favourable) reaction pathway.

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