organic compounds

4-Nitro-1-[(trimethylsilyl)ethynyl]-benzene: low-temperature polymorph at 100 K[1]

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The title compound, $C_{11}H_{13}NO_2Si$, is a low-temperature form of the previously reported room-temperature structure [Garcia *et al.* (1998). *Acta Cryst.* C**54**, 489–491]. At 298 K, the material crystallizes in the space group *Pnma* and occupies a crystallographic mirror plane, but at 100 K the space group changes to $P2_12_12_1$, the volume decreases by 5% and the molecule distorts. The greatest molecular distortions from C_s symmetry are rotations of the trimethylsilyl and nitro groups by 10.56 (8) and 11.47 (9)°, respectively, to the benzene mean plane. At low temperature, the crystal also becomes an inversion twin, the refined ratio of the twin components being 0.35 (15):0.65 (15).

Related literature

For the synthesis of the title compound, see: Takahashi *et al.* (1980). For the crystal structure of the room temperature form of the title compound, see: Garcia *et al.* (1998). For a description of the Cambridge Structural Database, see: Allen (2002). For Hooft analysis of Bijvoet pairs, see: Hooft *et al.* (2008).
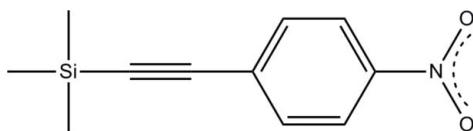
Experimental

Crystal data

$C_{11}H_{13}NO_2Si$	$V = 1204.9\,(5)$ Å^3
$M_r = 219.31$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 10.222\,(2)$ Å	$\mu = 0.18$ mm^{-1}
$b = 7.128\,(2)$ Å	$T = 100$ K
$c = 16.537\,(4)$ Å	$0.20 \times 0.15 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer	17805 measured reflections
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997) $T_{min} = 0.966$, $T_{max} = 0.979$	4690 independent reflections
	3538 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
$wR(F^2) = 0.123$	$\Delta\rho_{min} = -0.32$ e Å^{-3}
$S = 1.02$	Absolute structure: Flack (1983), 1953 Bijvoet pairs
4690 reflections	Flack parameter: 0.35 (15)
139 parameters	
H-atom parameters constrained	

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2491).

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[1] CAS 75867-38-8.

supporting information

4-Nitro-1-[(trimethylsilyl)ethynyl]benzene: low-temperature polymorph at 100 K

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S1. Comment

At 298 K title molecule has C_s symmetry (Garcia *et al.*, 1998; CSD refcode NILWIO; Allen, 2002), with all but two methyl groups lying in the mirror plane. When the temperature is reduced to 100 K, the inversion center vanishes and the space group changes from *Pnma* to $P2_12_12_1$, the unit cell volume is reduced from 1261.8 (3) to 1204.9 (5) Å^3, and the molecular symmetry is reduced to C_1. The mean plane of the six benzene C atoms, (mean deviation $\delta_{r.m.s.} = 0.004$ Å), is normal to the *b* axis at 298 K but inclines +4.51 (8)° from normal at 100 K, while the C1—Si1—C9 plane is rotated off-normal by -6.05 (8)° and the NO$_2$ group is rotated off-normal by +15.78 (9)°.

  Other geometrical parameters in the two polymorphs are similar, for example [those at 298 K are in parentheses] : C1≡C2 = 1.209 (2) [1.199 (4)] Å, Si1—C1 = 1.845 (2) [1.839 (3)] Å, Si1—C9 = 1.856 (2) [1.831 (4)] Å, Si1—C10 = 1.853 (2) [1.838 (3)] Å, Si1—C10B = 1.856 (2)[1.838 (3)] Å, N1—O1 = 1.219 (2) [1.201 (4)] Å, N1—O2 = 1.221 (2) [1.175 (4)] Å, Si1—C1≡C2 = 176.1 (2) [177.9 (3)]°, C1≡C2—C3 = 175.9 (2) [178.0 (3)]°, O1—N1—O2 = 123.5 (2) [122.9 (3)]°.

S2. Experimental

The compound was prepared by palladium(II) coupling of trimethylsilylacetylene with 4-nitroiodobenzene as described by (Takahashi *et al.*, 1980).

S3. Refinement

Analysis of 1953 Bijvoet pairs yields a Hooft (Hooft *et al.*, 2008) parameter *y* = 0.42 (6) and P3(rac-twin) = 1.000. The model was therefore refined as an inversion twin (*SHELXL* commands TWIN and BASF) giving the refined ratio 0.35 (15):0.65 (15) for the twin components. The C-bound H atoms were placed in calculated positions, guided by difference maps, and treated as riding atoms: C—H = 0.95 and 0.98 Å for CH(aromatic) and CH$_3$ H atoms, respectively, with $U_{iso} = k \times U_{eq}(C)$, where k = 1.5 for CH$_3$ H atoms and = 1.2 for other H atoms. A torsional parameter was refined for each methyl group.
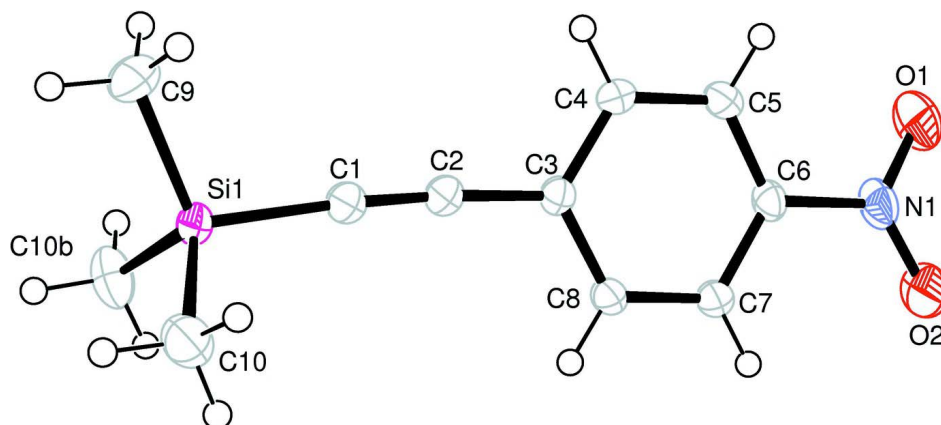
Figure 1

View of the molecular structure of the title compound, with atom numbering. The displacement ellipsoids are drawn at the 50% probability level.

4-Nitro-1-[(trimethylsilyl)ethynyl]benzene

Crystal data

$C_{11}H_{13}NO_2Si$	$F(000) = 464$
$M_r = 219.31$	$D_x = 1.209$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 2709 reflections
$a = 10.222$ (2) Å	$\theta = 2.5$–34.3°
$b = 7.128$ (2) Å	$\mu = 0.18$ mm^{-1}
$c = 16.537$ (4) Å	$T = 100$ K
$V = 1204.9$ (5) Å^3	Needle fragment, yellow
$Z = 4$	$0.20 \times 0.15 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer	$T_{min} = 0.966$, $T_{max} = 0.979$
Radiation source: sealed tube	17805 measured reflections
Horizonally mounted graphite crystal monochromator	4690 independent reflections
	3538 reflections with $I > 2\sigma(I)$
Detector resolution: 9 pixels mm^{-1}	$R_{int} = 0.032$
ω and φ scans	$\theta_{max} = 33.8°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)	$h = -15 \rightarrow 15$
	$k = -11 \rightarrow 11$
	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.123$	
$S = 1.02$	H-atom parameters constrained
4690 reflections	$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.4973P]$ where $P = (F_o^2 + 2F_c^2)/3$
139 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
0 constraints	$\Delta\rho_{max} = 0.36$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Absolute structure: Flack (1983), 1953 Bijvoet pairs	Absolute structure parameter: 0.35 (15)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.67962 (16)	0.2773 (3)	0.66604 (9)	0.0270 (3)
C2	0.77829 (16)	0.2789 (3)	0.70632 (9)	0.0252 (3)
C3	0.89002 (14)	0.2769 (3)	0.75911 (9)	0.0218 (3)
C4	1.01780 (16)	0.2851 (3)	0.72849 (9)	0.0262 (3)
H4	1.0316	0.2956	0.6719	0.031*
C5	1.12430 (15)	0.2779 (3)	0.78050 (10)	0.0265 (3)
H5	1.2111	0.2842	0.7602	0.032*
C6	1.10107 (14)	0.2614 (3)	0.86239 (9)	0.0234 (3)
C7	0.97590 (14)	0.2541 (3)	0.89480 (9)	0.0242 (3)
H7	0.9629	0.2433	0.9515	0.029*
C8	0.87080 (14)	0.2629 (3)	0.84253 (9)	0.0225 (3)
H8	0.7843	0.2594	0.8635	0.027*
C9	0.5612 (2)	0.2384 (5)	0.50094 (10)	0.0415 (5)
H9A	0.6112	0.1226	0.4926	0.062*
H9B	0.6129	0.3459	0.4825	0.062*
H9C	0.4794	0.2322	0.4702	0.062*
C10	0.4263 (2)	0.0658 (3)	0.64911 (14)	0.0376 (5)
H10A	0.4097	0.0836	0.707	0.056*
H10B	0.475	−0.0512	0.6409	0.056*
H10C	0.3429	0.0593	0.6201	0.056*
C10B	0.4280 (2)	0.4829 (3)	0.62787 (15)	0.0394 (5)
H10D	0.477	0.5912	0.6075	0.059*
H10E	0.4124	0.4982	0.686	0.059*
H10F	0.3439	0.4742	0.5996	0.059*
N1	1.21298 (13)	0.2499 (3)	0.91772 (9)	0.0345 (3)
O1	1.32160 (13)	0.2830 (3)	0.89090 (11)	0.0531 (4)
O2	1.19270 (16)	0.2043 (4)	0.98780 (9)	0.0670 (7)
Si1	0.52365 (4)	0.26554 (7)	0.61012 (3)	0.02349 (11)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0248 (7)	0.0341 (10)	0.0221 (7)	0.0007 (8)	−0.0007 (6)	−0.0014 (7)
C2	0.0248 (7)	0.0291 (9)	0.0219 (6)	0.0008 (7)	−0.0009 (5)	−0.0006 (7)
C3	0.0208 (6)	0.0240 (8)	0.0207 (6)	0.0008 (7)	−0.0020 (5)	0.0005 (6)
C4	0.0247 (7)	0.0345 (9)	0.0194 (6)	0.0007 (8)	0.0022 (6)	0.0026 (6)
C5	0.0189 (6)	0.0334 (10)	0.0270 (7)	−0.0001 (7)	0.0027 (5)	0.0008 (8)

C6	0.0183 (6)	0.0274 (9)	0.0245 (6)	0.0001 (8)	−0.0048 (5)	−0.0022 (8)
C7	0.0223 (6)	0.0311 (8)	0.0192 (5)	0.0013 (8)	−0.0001 (5)	−0.0013 (7)
C8	0.0177 (6)	0.0285 (9)	0.0212 (6)	−0.0005 (7)	0.0001 (5)	−0.0016 (7)
C9	0.0392 (9)	0.0626 (15)	0.0228 (7)	−0.0031 (12)	−0.0018 (7)	−0.0023 (10)
C10	0.0296 (10)	0.0364 (12)	0.0467 (12)	0.0002 (8)	0.0011 (9)	0.0090 (9)
C10B	0.0310 (10)	0.0343 (11)	0.0530 (13)	0.0074 (8)	−0.0112 (10)	−0.0091 (9)
N1	0.0235 (6)	0.0442 (10)	0.0357 (7)	0.0034 (8)	−0.0094 (6)	−0.0075 (9)
O1	0.0217 (6)	0.0733 (12)	0.0641 (10)	−0.0078 (7)	−0.0111 (7)	0.0065 (11)
O2	0.0388 (8)	0.136 (2)	0.0264 (7)	0.0166 (12)	−0.0122 (6)	−0.0023 (10)
Si1	0.02129 (18)	0.0293 (2)	0.01984 (18)	0.00030 (19)	−0.00383 (15)	−0.00043 (19)

Geometric parameters (Å, º)

C1—C2	1.209 (2)	C9—Si1	1.8560 (18)
C1—Si1	1.8450 (17)	C9—H9A	0.98
C2—C3	1.438 (2)	C9—H9B	0.98
C3—C8	1.397 (2)	C9—H9C	0.98
C3—C4	1.402 (2)	C10—Si1	1.853 (2)
C4—C5	1.388 (2)	C10—H10A	0.98
C4—H4	0.95	C10—H10B	0.98
C5—C6	1.380 (2)	C10—H10C	0.98
C5—H5	0.95	C10B—Si1	1.856 (2)
C6—C7	1.388 (2)	C10B—H10D	0.98
C6—N1	1.4671 (19)	C10B—H10E	0.98
C7—C8	1.380 (2)	C10B—H10F	0.98
C7—H7	0.95	N1—O1	1.219 (2)
C8—H8	0.95	N1—O2	1.221 (2)
C2—C1—Si1	176.09 (16)	H9A—C9—H9C	109.5
C1—C2—C3	175.90 (18)	H9B—C9—H9C	109.5
C8—C3—C4	119.38 (13)	Si1—C10—H10A	109.5
C8—C3—C2	119.25 (14)	Si1—C10—H10B	109.5
C4—C3—C2	121.36 (14)	H10A—C10—H10B	109.5
C5—C4—C3	120.35 (14)	Si1—C10—H10C	109.5
C5—C4—H4	119.8	H10A—C10—H10C	109.5
C3—C4—H4	119.8	H10B—C10—H10C	109.5
C6—C5—C4	118.44 (14)	Si1—C10B—H10D	109.5
C6—C5—H5	120.8	Si1—C10B—H10E	109.5
C4—C5—H5	120.8	H10D—C10B—H10E	109.5
C5—C6—C7	122.73 (14)	Si1—C10B—H10F	109.5
C5—C6—N1	118.86 (13)	H10D—C10B—H10F	109.5
C7—C6—N1	118.42 (14)	H10E—C10B—H10F	109.5
C8—C7—C6	118.29 (13)	O1—N1—O2	123.47 (16)
C8—C7—H7	120.9	O1—N1—C6	118.21 (16)
C6—C7—H7	120.9	O2—N1—C6	118.31 (15)
C7—C8—C3	120.81 (13)	C1—Si1—C10	108.92 (10)
C7—C8—H8	119.6	C1—Si1—C10B	109.77 (10)
C3—C8—H8	119.6	C10—Si1—C10B	107.68 (10)

Si1—C9—H9A	109.5	C1—Si1—C9	108.27 (8)
Si1—C9—H9B	109.5	C10—Si1—C9	111.68 (12)
H9A—C9—H9B	109.5	C10B—Si1—C9	110.51 (12)
Si1—C9—H9C	109.5		
C8—C3—C4—C5	0.5 (3)	C6—C7—C8—C3	0.6 (3)
C2—C3—C4—C5	−178.28 (19)	C4—C3—C8—C7	−1.0 (3)
C3—C4—C5—C6	0.4 (3)	C2—C3—C8—C7	177.76 (18)
C4—C5—C6—C7	−0.9 (3)	C5—C6—N1—O1	10.6 (3)
C4—C5—C6—N1	178.80 (18)	C7—C6—N1—O1	−169.7 (2)
C5—C6—C7—C8	0.3 (3)	C5—C6—N1—O2	−168.0 (2)
N1—C6—C7—C8	−179.33 (18)	C7—C6—N1—O2	11.7 (3)