

6-Methyl-4-[[4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl]methyl]-2*H*-chromen-2-one

Sowmiya Carmel Y.,^a N. L. Prasad,^a Noor Shahina Begum^{a*} and Hari Prasad Suresh^b

^aDepartment of Studies in Chemistry, Bangalore University, Inana Bharathi Campus, Bangalore-560 056, Karnataka, India, and ^bDepartment of Studies in Chemistry, Bengaluru Central University, Central College Campus, Bengaluru-560 001, Karnataka, India. *Correspondence e-mail: noorsb05@gmail.com

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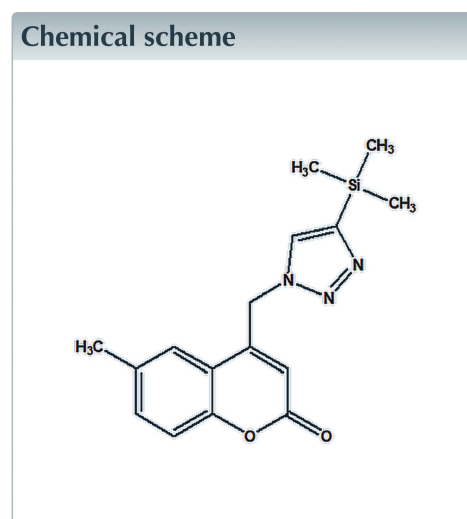
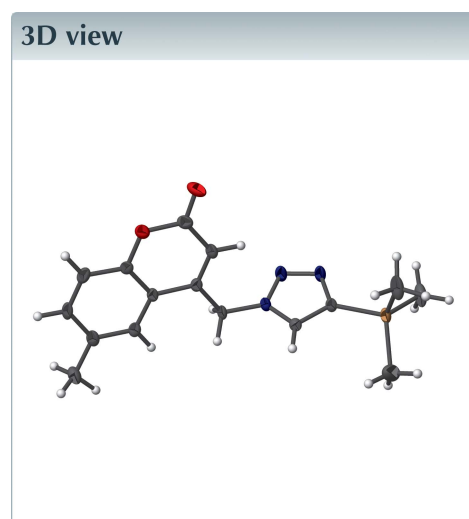
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Keywords: crystal structure; coumarin; weak C—H···O interactions.

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In the title compound, C₁₆H₁₉N₃O₂Si, the dihedral angle between the coumarin ring system (r.m.s. deviation = 0.031 Å) and the triazole ring is 73.81 (8)°. In the crystal, molecules are linked into [010] chains by weak C—H···O interactions.



Structure description

Coumarins are a family of benzopyrones and are widely distributed in nature (Venugopala *et al.*, 2013). They have been extensively studied as a result of their broad array of biological activities, low toxicity and low drug resistance properties (Lipeeva *et al.*, 2019). As part of our work in this area, we now describe the synthesis and crystal structure of the title compound in which the coumarin ring system bears a trimethylsilyl triazole substituent.

The title compound crystallizes in the monoclinic crystal system in space group *C*2/*c* with one molecule in the asymmetric unit (Fig. 1). The dihedral angle between the C1—C9/O1 chromen-2-one fused ring system (r.m.s. deviation = 0.031 Å) and the N1—N3/C11/C12 1,2,3-triazole ring is 73.81 (8)°. In the crystal, weak C—H···O hydrogen bonds (Table 1) link the molecules into [010] chains, with atom O2 accepting two such bonds from the adjacent molecule (Fig. 2) related by simple translation.

Synthesis and crystallization

Trimethylsilyl acetylene (2.00 mmol) was added dropwise over a period of 30 min to an ice-cold suspension of bromomethylcoumarin (2.00 mmol), sodium azide (1.50 mmol) and copper iodide (1 μmol) in 10 ml (1:1 *v/v*) water/acetone. The resulting mixture was allowed to warm to room temperature and stirred for 8 h: progress of the reaction was

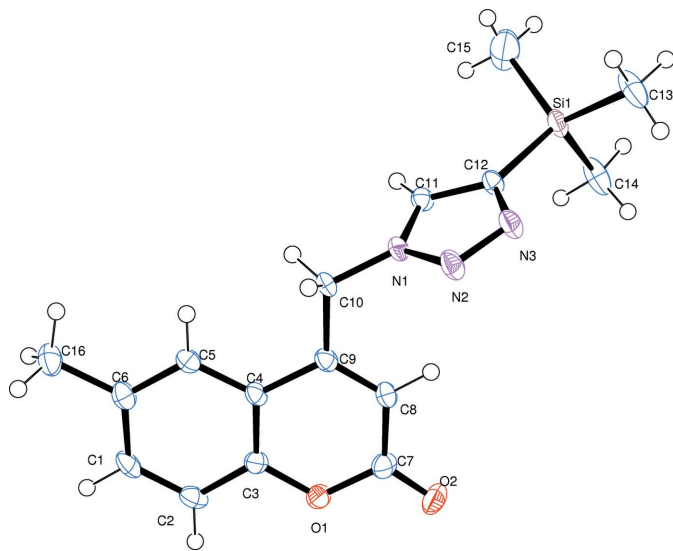


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Labels on the small side and displaced a long way from their respective atoms

monitored by TLC and GC through micro-workup of aliquots. After the completion of the reaction as indicated by the chromatograms, the excess acetone was removed under rotary evaporation and the crude product was purified by column chromatography, using silica gel (100–200 mesh) and 2:5 ethyl acetate–petroleum benzene (60–74°C fraction) eluent to obtain the title compound as a buff-coloured solid (91%); melting point: 110–112°C; (KBr disk, cm^{-1}): 3126, 2920, 2850, 1705, 1573, 1492, 1382, 1247, 1193, 1116, 1056, 950, 825, 756, 630, 557, 509; ^1H NMR (400 MHz, CDCl_3): δ 0.34 (s, 9 H), 2.42 (s, 3 H), 5.74 (s, 2 H), 5.92 (s, 1H), 7.26–7.57 (m, 4 H, 3 H of coumarinyl aromatic protons and 1 H of triazolyl aromatic proton); ^{13}C NMR (100 MHz, CDCl_3): δ -1.0, 21.2, 49.5, 114.9, 116.9, 117.4, 123.4, 129.6, 133.8, 134.8, 148.2, 148.5, 151.9, 160.3; MS: calculated 313.12, found m/z (relative abundance) 313.22 (9.75%), 314.26 ($M + 1 = 3.45\%$), 73.13 (100%); CHNS: Calculated C: 61.31%, H: 6.11%, N:13.41% Found C: 60.92%,

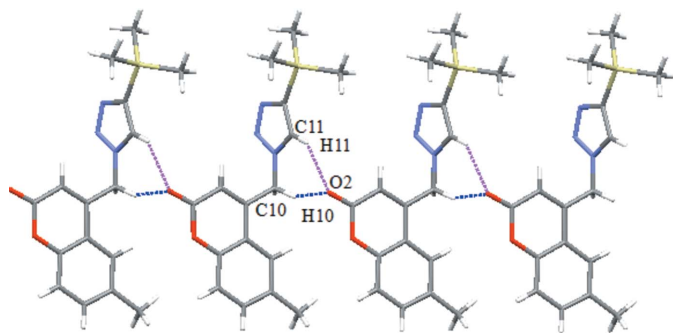


Figure 2
Part of a [010] chain in the crystal of the title compound showing C–H...O interactions as dotted lines. H-atoms not involved in hydrogen bonding have been excluded.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C10-H10A\cdots O2^i$	0.99	2.61	3.427 (1)	140
$C11-H11\cdots O2^i$	0.95	2.45	3.242 (1)	141

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

Table 2
Experimental details.

Crystal data	$C_{16}H_{19}N_3O_2Si$
Chemical formula	313.43
M_r	Monoclinic, $C2/c$
Crystal system, space group	100
Temperature (K)	a, b, c (\AA)
a, b, c (\AA)	20.869 (2), 6.5971 (6), 24.561 (2)
β ($^\circ$)	103.419 (4)
V (\AA^3)	3289.1 (5)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.15
Crystal size (mm)	$0.14 \times 0.14 \times 0.12$
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 1998)
T_{\min} , T_{\max}	0.979, 0.982
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21620, 3589, 2644
R_{int}	0.071
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.125, 0.99
No. of reflections	3589
No. of parameters	203
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.42, -0.31

Computer programs: *SMART* (Bruker, 1998), *SAINT-Plus* (Bruker, 1998), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *CAMERON* (Watkin *et al.*, 1996).

H: 6.04%, N: 13.33%. Colourless blocks of the title compound were recrystallized from ethanol solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2020). 5, x200427 [https://doi.org/10.1107/S2414314620004277]

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6-Methyl-4-[[4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl]methyl]-2*H*-chromen-2-one*Crystal data*

$C_{16}H_{19}N_3O_2Si$

$M_r = 313.43$

Monoclinic, $C2/c$

$a = 20.869$ (2) Å

$b = 6.5971$ (6) Å

$c = 24.561$ (2) Å

$\beta = 103.419$ (4)°

$V = 3289.1$ (5) Å³

$Z = 8$

$F(000) = 1328$

$D_x = 1.266$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3589 reflections

$\theta = 2.9$ – 27.0 °

$\mu = 0.15$ mm⁻¹

$T = 100$ K

Block, colorless

$0.14 \times 0.14 \times 0.12$ mm

Data collection

Bruker SMART APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 1998)

$T_{\min} = 0.979$, $T_{\max} = 0.982$

21620 measured reflections

3589 independent reflections

2644 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.071$

$\theta_{\max} = 27.0$ °, $\theta_{\min} = 2.9$ °

$h = -26 \rightarrow 26$

$k = -8 \rightarrow 8$

$l = -31 \rightarrow 31$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.125$

$S = 0.99$

3589 reflections

203 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 6.1123P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.42$ e Å⁻³

$\Delta\rho_{\min} = -0.31$ e Å⁻³

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. The H atoms were placed at calculated positions in the riding-model approximation with C—H = 0.95 Å, 1.00 Å and 0.96 Å for aromatic, methyne and methyl H-atoms respectively, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for other hydrogen atoms.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Si1	0.03716 (3)	0.5449 (10)	0.15123 (2)	0.02394 (18)
O1	0.23596 (8)	−0.0948 (2)	0.43023 (6)	0.0249 (4)
O2	0.15849 (8)	−0.2426 (2)	0.36664 (6)	0.0326 (4)
N1	0.20048 (8)	0.3969 (3)	0.26552 (7)	0.0191 (4)
N2	0.20697 (9)	0.2741 (3)	0.22317 (7)	0.0254 (4)
N3	0.15636 (9)	0.3094 (3)	0.18156 (7)	0.0250 (4)
C1	0.35583 (11)	0.2153 (4)	0.52305 (8)	0.0252 (5)
H1	0.3807	0.2112	0.5607	0.030*
C2	0.31413 (11)	0.0572 (3)	0.50291 (9)	0.0247 (5)
H2	0.3101	−0.0547	0.5262	0.030*
C3	0.27813 (10)	0.0645 (3)	0.44800 (8)	0.0202 (5)
C4	0.28295 (10)	0.2265 (3)	0.41304 (8)	0.0187 (4)
C5	0.32612 (10)	0.3849 (3)	0.43475 (8)	0.0210 (5)
H5	0.3304	0.4963	0.4114	0.025*
C6	0.36260 (10)	0.3823 (3)	0.48958 (9)	0.0234 (5)
C7	0.19476 (11)	−0.0985 (3)	0.37792 (9)	0.0247 (5)
C8	0.19909 (11)	0.0696 (3)	0.34119 (8)	0.0223 (5)
H8	0.1708	0.0714	0.3048	0.027*
C9	0.24152 (10)	0.2231 (3)	0.35664 (8)	0.0195 (4)
C10	0.24919 (10)	0.3949 (3)	0.31845 (8)	0.0207 (5)
H10A	0.2464	0.5245	0.3381	0.025*
H10B	0.2936	0.3870	0.3107	0.025*
C11	0.14617 (10)	0.5105 (3)	0.25053 (8)	0.0190 (4)
H11	0.1309	0.6089	0.2728	0.023*
C12	0.11697 (10)	0.4563 (3)	0.19648 (8)	0.0191 (4)
C13	0.03782 (12)	0.5050 (5)	0.07685 (9)	0.0384 (7)
H13A	0.0740	0.5828	0.0678	0.058*
H13B	−0.0042	0.5505	0.0531	0.058*
H13C	0.0440	0.3606	0.0703	0.058*
C14	−0.03101 (12)	0.3935 (4)	0.16733 (9)	0.0368 (6)
H14A	−0.0733	0.4511	0.1476	0.055*
H14B	−0.0280	0.3963	0.2077	0.055*
H14C	−0.0278	0.2531	0.1552	0.055*
C15	0.02778 (15)	0.8163 (4)	0.16805 (14)	0.0603 (10)
H15A	0.0610	0.8968	0.1554	0.091*
H15B	0.0337	0.8320	0.2086	0.091*
H15C	−0.0163	0.8320	0.1490	0.091*

C16	0.40799 (11)	0.5535 (4)	0.51336 (9)	0.0297 (5)
H16A	0.4063	0.6577	0.4846	0.045*
H16B	0.4531	0.5021	0.5255	0.045*
H16C	0.3942	0.6124	0.5454	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.0243 (3)	0.0291 (4)	0.0149 (3)	0.0056 (3)	-0.0026 (2)	-0.0034 (3)
O1	0.0367 (9)	0.0208 (8)	0.0168 (7)	-0.0033 (7)	0.0049 (7)	0.0003 (6)
O2	0.0487 (11)	0.0256 (9)	0.0241 (8)	-0.0140 (8)	0.0100 (7)	-0.0068 (7)
N1	0.0222 (9)	0.0219 (9)	0.0119 (8)	0.0000 (8)	0.0012 (7)	-0.0007 (7)
N2	0.0279 (10)	0.0316 (11)	0.0148 (9)	0.0071 (9)	0.0012 (7)	-0.0039 (8)
N3	0.0261 (10)	0.0320 (11)	0.0147 (9)	0.0060 (8)	-0.0001 (7)	-0.0019 (8)
C1	0.0281 (12)	0.0331 (13)	0.0122 (10)	0.0068 (10)	0.0006 (9)	0.0015 (9)
C2	0.0313 (12)	0.0252 (12)	0.0178 (10)	0.0067 (10)	0.0059 (9)	0.0058 (9)
C3	0.0250 (11)	0.0187 (11)	0.0169 (10)	0.0023 (9)	0.0051 (8)	-0.0010 (8)
C4	0.0217 (11)	0.0215 (11)	0.0125 (9)	0.0030 (9)	0.0030 (8)	-0.0011 (8)
C5	0.0225 (11)	0.0233 (11)	0.0169 (10)	0.0010 (9)	0.0041 (8)	0.0024 (8)
C6	0.0215 (11)	0.0299 (12)	0.0184 (11)	0.0022 (10)	0.0038 (9)	-0.0022 (9)
C7	0.0346 (13)	0.0217 (12)	0.0191 (11)	-0.0010 (10)	0.0087 (9)	-0.0034 (9)
C8	0.0264 (11)	0.0246 (12)	0.0142 (10)	-0.0007 (10)	0.0013 (8)	-0.0017 (9)
C9	0.0225 (11)	0.0211 (11)	0.0146 (10)	0.0035 (9)	0.0035 (8)	-0.0004 (8)
C10	0.0224 (11)	0.0235 (11)	0.0129 (10)	-0.0006 (9)	-0.0024 (8)	0.0011 (8)
C11	0.0218 (11)	0.0206 (11)	0.0148 (10)	0.0009 (9)	0.0047 (8)	-0.0004 (8)
C12	0.0206 (10)	0.0228 (11)	0.0134 (9)	0.0013 (9)	0.0029 (8)	-0.0003 (8)
C13	0.0306 (13)	0.0660 (19)	0.0164 (11)	-0.0041 (13)	0.0008 (10)	0.0070 (11)
C14	0.0266 (12)	0.0652 (19)	0.0174 (11)	0.0048 (13)	0.0028 (9)	-0.0006 (11)
C15	0.0529 (19)	0.0388 (17)	0.070 (2)	0.0193 (15)	-0.0244 (16)	-0.0181 (15)
C16	0.0290 (12)	0.0383 (14)	0.0198 (11)	-0.0060 (11)	0.0014 (9)	-0.0023 (10)

Geometric parameters (Å, °)

Si1—C13	1.849 (2)	C6—C16	1.502 (3)
Si1—C14	1.854 (3)	C7—C8	1.446 (3)
Si1—C15	1.858 (3)	C8—C9	1.341 (3)
Si1—C12	1.869 (2)	C8—H8	0.9500
O1—C7	1.370 (3)	C9—C10	1.503 (3)
O1—C3	1.375 (3)	C10—H10A	0.9900
O2—C7	1.207 (3)	C10—H10B	0.9900
N1—C11	1.337 (3)	C11—C12	1.373 (3)
N1—N2	1.350 (2)	C11—H11	0.9500
N1—C10	1.453 (2)	C13—H13A	0.9800
N2—N3	1.309 (2)	C13—H13B	0.9800
N3—C12	1.375 (3)	C13—H13C	0.9800
C1—C2	1.375 (3)	C14—H14A	0.9800
C1—C6	1.401 (3)	C14—H14B	0.9800
C1—H1	0.9500	C14—H14C	0.9800

C2—C3	1.384 (3)	C15—H15A	0.9800
C2—H2	0.9500	C15—H15B	0.9800
C3—C4	1.389 (3)	C15—H15C	0.9800
C4—C5	1.402 (3)	C16—H16A	0.9800
C4—C9	1.453 (3)	C16—H16B	0.9800
C5—C6	1.385 (3)	C16—H16C	0.9800
C5—H5	0.9500		
C13—Si1—C14	108.43 (11)	C4—C9—C10	117.21 (18)
C13—Si1—C15	112.47 (15)	N1—C10—C9	114.30 (17)
C14—Si1—C15	110.24 (15)	N1—C10—H10A	108.7
C13—Si1—C12	109.47 (10)	C9—C10—H10A	108.7
C14—Si1—C12	109.08 (10)	N1—C10—H10B	108.7
C15—Si1—C12	107.11 (11)	C9—C10—H10B	108.7
C7—O1—C3	121.84 (16)	H10A—C10—H10B	107.6
C11—N1—N2	110.77 (16)	N1—C11—C12	106.13 (18)
C11—N1—C10	128.60 (17)	N1—C11—H11	126.9
N2—N1—C10	120.63 (17)	C12—C11—H11	126.9
N3—N2—N1	106.71 (16)	C11—C12—N3	106.42 (17)
N2—N3—C12	109.96 (16)	C11—C12—Si1	128.90 (16)
C2—C1—C6	121.8 (2)	N3—C12—Si1	124.57 (14)
C2—C1—H1	119.1	Si1—C13—H13A	109.5
C6—C1—H1	119.1	Si1—C13—H13B	109.5
C1—C2—C3	118.6 (2)	H13A—C13—H13B	109.5
C1—C2—H2	120.7	Si1—C13—H13C	109.5
C3—C2—H2	120.7	H13A—C13—H13C	109.5
O1—C3—C2	116.45 (19)	H13B—C13—H13C	109.5
O1—C3—C4	121.63 (18)	Si1—C14—H14A	109.5
C2—C3—C4	121.9 (2)	Si1—C14—H14B	109.5
C3—C4—C5	118.08 (18)	H14A—C14—H14B	109.5
C3—C4—C9	117.72 (19)	Si1—C14—H14C	109.5
C5—C4—C9	124.18 (19)	H14A—C14—H14C	109.5
C6—C5—C4	121.4 (2)	H14B—C14—H14C	109.5
C6—C5—H5	119.3	Si1—C15—H15A	109.5
C4—C5—H5	119.3	Si1—C15—H15B	109.5
C5—C6—C1	118.2 (2)	H15A—C15—H15B	109.5
C5—C6—C16	121.6 (2)	Si1—C15—H15C	109.5
C1—C6—C16	120.21 (19)	H15A—C15—H15C	109.5
O2—C7—O1	116.9 (2)	H15B—C15—H15C	109.5
O2—C7—C8	126.0 (2)	C6—C16—H16A	109.5
O1—C7—C8	117.04 (19)	C6—C16—H16B	109.5
C9—C8—C7	122.4 (2)	H16A—C16—H16B	109.5
C9—C8—H8	118.8	C6—C16—H16C	109.5
C7—C8—H8	118.8	H16A—C16—H16C	109.5
C8—C9—C4	119.28 (19)	H16B—C16—H16C	109.5
C8—C9—C10	123.50 (19)		
C11—N1—N2—N3	-0.5 (2)	C7—C8—C9—C4	-2.7 (3)

C10—N1—N2—N3	-179.99 (18)	C7—C8—C9—C10	177.1 (2)
N1—N2—N3—C12	0.4 (2)	C3—C4—C9—C8	2.3 (3)
C6—C1—C2—C3	0.1 (3)	C5—C4—C9—C8	-176.1 (2)
C7—O1—C3—C2	175.88 (19)	C3—C4—C9—C10	-177.55 (18)
C7—O1—C3—C4	-2.5 (3)	C5—C4—C9—C10	4.1 (3)
C1—C2—C3—O1	-178.51 (19)	C11—N1—C10—C9	100.6 (2)
C1—C2—C3—C4	-0.1 (3)	N2—N1—C10—C9	-79.9 (2)
O1—C3—C4—C5	178.70 (18)	C8—C9—C10—N1	8.1 (3)
C2—C3—C4—C5	0.4 (3)	C4—C9—C10—N1	-172.13 (18)
O1—C3—C4—C9	0.3 (3)	N2—N1—C11—C12	0.3 (2)
C2—C3—C4—C9	-178.0 (2)	C10—N1—C11—C12	179.78 (19)
C3—C4—C5—C6	-0.7 (3)	N1—C11—C12—N3	0.0 (2)
C9—C4—C5—C6	177.7 (2)	N1—C11—C12—Si1	176.29 (16)
C4—C5—C6—C1	0.6 (3)	N2—N3—C12—C11	-0.3 (2)
C4—C5—C6—C16	-178.9 (2)	N2—N3—C12—Si1	-176.77 (16)
C2—C1—C6—C5	-0.3 (3)	C13—Si1—C12—C11	157.8 (2)
C2—C1—C6—C16	179.2 (2)	C14—Si1—C12—C11	-83.7 (2)
C3—O1—C7—O2	-178.32 (19)	C15—Si1—C12—C11	35.6 (3)
C3—O1—C7—C8	2.1 (3)	C13—Si1—C12—N3	-26.5 (2)
O2—C7—C8—C9	-179.0 (2)	C14—Si1—C12—N3	92.0 (2)
O1—C7—C8—C9	0.5 (3)	C15—Si1—C12—N3	-148.7 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C10—H10 <i>A</i> \cdots O2 ⁱ	0.99	2.61	3.427 (1)	140
C11—H11 \cdots O2 ⁱ	0.95	2.45	3.242 (1)	141

Symmetry code: (i) *x*, *y*+1, *z*.