organic compounds

3,3-Diphenyl-6-(*p*-toluenesulfonyl)-6-aza-3-silabicyclo[3.1.0]hexane

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The title compound, $C_{23}H_{23}NO_2SSi$, at 100 K adopts a boat conformation which brings the C—H bond of an axial phenyl substituent into proximity [C$\cdots$N = 3.376 (1) Å] with the aziridine lone pair. The factors which favour this conformation for bicyclo[3.1.0]hexane systems are considered.

Comment

While developing synthetic routes to novel amino acids and other compounds of biological interest, we have prepared and characterized the bicyclic compound 3,3-diphenyl-6-(*p*-toluenesulfonyl)-6-aza-3-silabicyclo[3.1.0]hexane, (I). The most striking structural feature revealed by our X-ray analysis is the boat conformation adopted by the bridged six-membered Si1/C1/C2/N1/C3/C4 ring (Fig. 1). This conformation places the aziridine system of (I) in a sterically hindered environment and we therefore offer some comments on the factors which favour its adoption.
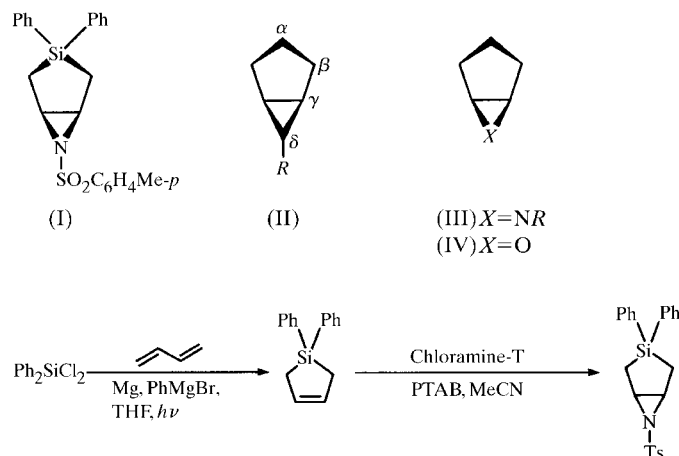
The torsion angles in (I) (Table 1) indicate that the sequence of four carbon atoms C1–C4 is essentially planar. Atoms N1 and Si1 lie on the same side of the plane defined by these four C atoms so that it makes dihedral angles of 77.9 (1) and 12.5 (1)° with the C2/C3/N1 and Si1/C1/C4 flaps, respec-

tively. The aziridine ring is thus almost normal to the rather flat envelope-shaped silacyclopentane ring. Excluding the *N*-tosyl substituent, the molecule has approximate C_s symmetry; the mirror plane passes through Si1, N1 and the midpoint of C2—C3, nearly coincides with the plane of the axial phenyl group attached to Si1 and is normal to the equatorial phenyl group. Exact C_s symmetry would lead to C26—C21—Si1—C11 and C21—Si1—C11—C12 torsion angles of 0 and 90°, respectively; the observed values in the structure are 4.90 (9) and 93.70 (9)°, respectively. The adoption of this conformation orients the C22—H22 bond of the axial phenyl group almost directly towards N1; the resulting H$\cdots$N contact (Table 2) is 2.59 (2) Å, decreasing to 2.47 Å if the C—H bond is normalized to its neutron diffraction value (Jeffrey & Lewis, 1978; Taylor & Kennard, 1983). Although this contact is substantially shorter than 2.75 Å, the sum of the Bondi (1964) contact radii for H and N, its interpretation as a weak hydrogen bond still appears controversial (Mascal, 1998; Jeffrey, 1997).

To the best of our knowledge, (I) is the first silabicyclohexane derivative to be structurally characterized. However, more than 20 years ago, Morris and co-workers (1977) showed by X-ray analysis that the bicyclo[3.1.0]hexane derivative (II) with R = C(O)NHN=CMe$_2$ adopts the boat conformation despite an unfavourable α–δ interaction. These authors argued that the boat form was energetically preferable to the chair conformer which would have eclipsed H—C—C—H arrangements across the C$_\beta$—C$_\gamma$ bonds and two unfavourable β–δ interactions. Mastryukov *et al.* (1977) showed by electron diffraction and microwave spectroscopy that the parent hydrocarbon bicyclo[3.1.0]hexane (II) with R = H also prefers the boat conformation. The current version of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) contains results for 47 bicyclic compounds of types (II), (III) or (IV) (see Scheme). The puckering parameters (Cremer & Pople, 1975; Boeyens, 1978) for the bridged six-membered rings indicate that two well defined conformations represent this population. 37 molecules (including all ten epoxides and the single aziridine) have puckering parameters centred on a point in conformational space (Q = 1.03 Å, θ = 71° and φ = 180°)

(I)   (II)   (III) *X* = N*R*
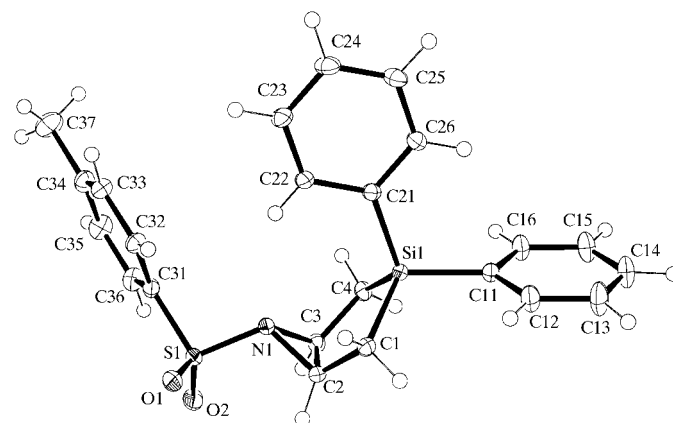   (IV) *X* = O

Figure 1
View of (I) (50% probability displacement ellipsoids). H atoms are shown as spheres of arbitrary radii.

which defines a ring intermediate between the ideal boat (θ = 90 and φ = 180°) and envelope (θ = 55° and φ = 180°) transition state between boat and chair. Compound (I), with Q = 1.061 (1) Å, θ = 69.0 (1)° and φ = 179.4 (1)°, clearly belongs to this conformational type. The remaining eight molecules have puckering parameters close to Q = 0.80 Å, θ = 33° and φ = 180°, and a conformation intermediate between envelope (θ = 55°) and chair (θ = 0°); all these molecules have at least three non-H substituents distributed over the C_α and C_δ ring atoms. This analysis indicates that the boat forms of (II)–(IV) are more stable than the corresponding chairs for the reasons given by Morris *et al.* (1977). Chair conformations are adopted only to relieve severe steric crowding of bulky substituents on the α and δ ring atoms. Compound (I) retains the boat conformation despite the resultant crowding of the aziridine group. We are planning further studies to see whether crowding lessens the reactivity of these systems.

In (I), C2—C3 [1.4979 (14) Å] is a little shorter than the adjacent C1—C2 and C3—C4 bonds [mean 1.5153 (11) Å], and the same trend is found in the 47 related molecules present in the CSD, for which the corresponding mean values are 1.495 (3) and 1.512 (3) Å. This may reflect a substituent-induced shortening of the distal bonds of the three-membered rings of the type discussed by Allen (1980). Nonetheless, Mastryukov *et al.* (1977) pointed out that the C_γ—C_γ bond shared by the three- and five-membered rings of bicyclo[3.1.0]hexane, where no substituent effects are to be expected, is also unusually short [1.454 (9) Å]. The remaining bond lengths in (I) are unexceptional, although the S—O, S—N and N—C bonds are slightly longer than the corresponding mean values from the CSD (1.430, 1.642 and 1.472 Å, respectively; Allen *et al.*, 1992).

Molecules of (I) interact mainly through C—H···O contacts; those with C—H···X > 120° and H···X < 2.60 Å are listed in Table 2 as potential hydrogen bonds. The intermolecular contacts involve only O1; the O2 atom is less available for such interactions because it is eclipsed by both C3 and C36 [C3—N1—S1—O2 = 3.43 (9)° and C36—C31—S1—O2 = −10.55 (10)°]. Distortions in bond angles involving S1 and N1 help to relieve the resulting overcrowding [*e.g. cf* N1—S1—O2 111.86 (4)° and N1—S1—O1 105.65 (5)°].

Finally, we note that the structure of (I) at 295 K, determined from two data sets measured at normal resolution [to θ(Mo $K\alpha$) > 27°] on CCD and serial diffractometers, is essentially the same as that described here, except that the mean S—O bond length at 295 K (1.432 Å) agrees better with the value suggested by Allen *et al.* (1992). The results of the analyses of (I) at 295 K are included in the data deposited with this paper.

Experimental

Reaction of diphenyldichlorosilane with magnesium and butadiene yields a silacyclopentene (see Scheme) which is thought to be formed *via* a diphenylsilylene intermediate (Mignani *et al.*, 1995). Direct aziridination of its double bond using the protocol of Jeong *et al.* (1998), which involves reaction with chloramine-T in the presence of

phenyltrimethylammonium tribromide (PTAB), produced the title compound (m.p. 370 K), which was characterized using IR, NMR and MS. ν_{max} (KBr)/cm^{-1}: 3434, 3067, 3046, 3014, 2949, 2911, 1597, 1486, 1428, 1395, 1358, 1317, 1209, 1181, 1159, 807. δ_H (CDCl$_3$, 400 MHz): 1.34 (2H, *d*, *J* = 16 Hz), 1.55 (2H, *d*, *J* = 16 Hz), 2.35 (3H, *s*), 3.42 (2H, *s*), 7.19–7.62 (14H, *m*, aryl H). δ_C (CDCl$_3$, 100 MHz): 14.6 (2C), 22.0, 46.9 (2C), 127.9, 128.1, 128.5, 129.8, 129.9, 130.2, 134.9, 135.0, 135.1, 135.8, 136.6, 144.4. *m/z* (EI): 406.1 (MH$^+$, 84%), 352 (100), 328 (76), 250 (63), 222 (17), 105 (7).

Crystal data

C$_{23}$H$_{23}$NO$_2$SSi	D_x = 1.277 Mg m^{-3}
M_r = 405.57	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 39587
a = 9.2955 (1) Å	reflections
b = 8.6076 (1) Å	θ = 1–35°
c = 26.5354 (3) Å	μ = 0.229 mm^{-1}
β = 96.440 (1)°	T = 100 (2) K
V = 2109.75 (4) Å^3	Block, colourless
Z = 4	0.3 × 0.2 × 0.2 mm

Data collection

KappaCCD diffractometer	θ_{max} = 34.94°
φ and ω scans with κ offsets	$h = -14 \rightarrow 14$
26 689 measured reflections	$k = -13 \rightarrow 11$
8784 independent reflections	$l = -40 \rightarrow 40$
7613 reflections with $I > 2\sigma(I)$	Intensity decay: negligible
R_{int} = 0.039	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2$
$R(F)$ = 0.041	$+ 0.7900P]$
$wR(F^2)$ = 0.116	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max}$ = 0.001
8784 reflections	$\Delta\rho_{max}$ = 0.47 e Å^{-3}
334 parameters	$\Delta\rho_{min}$ = −0.45 e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.4399 (8)	Si1—C4	1.8991 (10)
S1—O2	1.4413 (8)	N1—C2	1.4958 (12)
S1—N1	1.6597 (8)	N1—C3	1.4918 (12)
Si1—C11	1.8756 (9)	C1—C2	1.5153 (13)
Si1—C21	1.8682 (10)	C2—C3	1.4979 (14)
Si1—C1	1.9004 (10)	C3—C4	1.5153 (13)
O1—S1—N1	105.65 (5)	C2—C1—Si1	104.51 (6)
O2—S1—N1	111.86 (4)	C1—C2—C3	116.44 (8)
C1—Si1—C4	96.65 (4)	C2—C3—C4	116.04 (8)
C2—N1—S1	115.30 (6)	C3—C4—Si1	104.67 (6)
C3—N1—S1	119.20 (6)		
C4—Si1—C1—C2	−11.25 (7)	C2—C3—C4—Si1	−9.49 (10)
Si1—C1—C2—C3	7.62 (9)	C1—Si1—C4—C3	11.92 (7)
C1—C2—C3—C4	1.30 (12)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C22—H22···N1	0.92 (2)	2.59 (2)	3.376 (1)	143 (1)
C2—H2···O1^i	0.96 (2)	2.59 (2)	3.457 (1)	151 (1)
C32—H32···O1^{ii}	0.97 (2)	2.57 (2)	3.348 (1)	138 (1)

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $-x, 2 - y, 1 - z$.

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H atoms were refined freely [C—H = 0.924 (17)–1.000 (18) Å], except for those of the C37 methyl group, which was defined as a riding rigid group and only its orientation was refined.

Data collection: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *SCALEPACK* and *DENZO*; data reduction: *SCALEPACK* and *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1028). Services for accessing these data are described at the back of the journal.

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