ORGANIC COMPOUNDS

Acta Cryst. (1998). C54, 1856–1858

trans-7,7-Diphenyl-7-silabicyclo[3.3.0]octan-3-one *p*-Tosylhydrazone Tetrahydrofuran Solvate†

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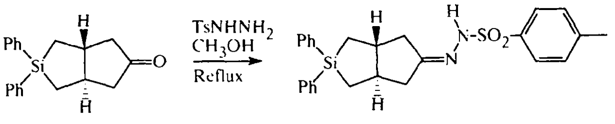
(*Received 21 November 1997; accepted 6 April 1998*)

Abstract

The structure of the title compound has been determined as a tetrahydrofuran solvate, $C_{26}H_{28}N_2O_2SSi.C_4H_8O$, at 193 K. This compound, which crystallizes in the monoclinic space group $C2/c$, is disordered. The distances between the bridgehead atoms were restrained to be 1.510 ± 0.015 Å and refined to 1.515 (11) (C1*A*—C5*A*) and 1.505 (12) Å (C1*B*—C5*B*). The *trans*-fusion of the system results in a rather flat geometry, with the two cyclopentane rings adopting envelope conformations.

Comment

It is well known that some silicon-containing compounds show extremely high biological activity, *e.g.* silatranes, which are much more toxic than strychnine (Tacke & Wannagat, 1975, 1979; Voronkov, 1979). The introduction of silicon into the scaffold of bi- and polyquinanes (Aebi *et al.*, 1994) is of general interest with regard to the biological activity of these compounds and it is important to get relevant structural information about *trans*-fused bicyclo[3.3.0]octanes like (1) (see scheme). Common methods for the synthesis of bicyclo[3.3.0]octanes lead to the thermodynamically favoured *cis* isomer. Only a few methods are known for the preparation of *trans*-bicyclo[3.3.0]octanes (Negishi *et al.*, 1987; Taber *et al.*, 1994; Bourgin *et al.*, 1994). We have found that the Cp_2Zr-induced cyclization–carbonylation of diallyldiphenylsilane leads to the exclusive formation of *trans*-7-silabicyclo[3.3.0]octane-3-one, (1) (Teng *et al.*, 1997). In order to determine structural features, the title tosylhydrazone, (2), was prepared from *trans*-7,7-diphenyl-7-silabicyclo[3.3.0]octan-3-one, (1), and its structure determined by X-ray diffraction.



(1) (2)

Compared with the known structures of all-carbon *cis*-bicyclo[3.3.0]octane derivatives which generally show a roof-like geometry of the bicyclic subunit, not depending on the substitution pattern, compound (2) contains a flat bicyclic unit. The molecules are disordered with the bridgehead atoms C1 and C5 occupying two possible positions (*A* and *B*) with occupancies of 0.54 (2) and 0.46 (2), respectively. The distances between the bridgehead C atoms were restrained to be 1.51±0.015 Å and refined to 1.515 (11) (C1*A*—C5*A*) and 1.505 (12) Å (C1*B*—C5*B*). The known structures of all-carbon bicyclo[3.3.0]octanes exhibit bond lengths for the bond between the bridgehead C atoms in the usual range for a C—C single bond. The bond angles within the bicyclic ring range from 102–110°, and the acyclic bond angles vary from 119–125°. Both five-membered rings have an envelope conformation. The remaining bond lengths and angles in (2) are normal within experimental error. The title compound crystallizes as a tetrahydrofuran solvate. This solvent molecule undergoes considerable thermal motion and the best resulting geometry found for this molecule is rather poor.

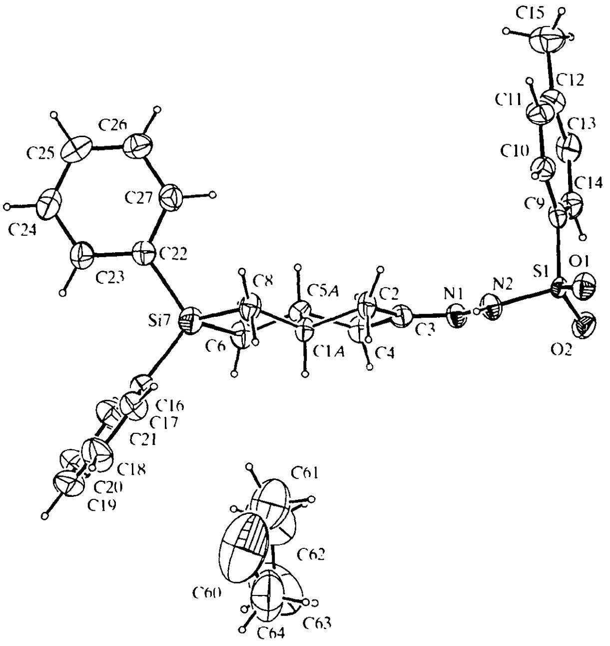


Fig. 1. Perspective view of (2).THF. Displacement ellipsoids are shown at the 50% probability level.

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† Alternative numbering: *trans*-3,3-diphenyl-3-silabicyclo[3.3.0]octan-7-one *p*-tosylhydrazone tetrahydrofuran solvate.

In the crystal, there are no short non-bonded distances (<3.2 Å) involving the tetrahydrofuran solvent molecule and (2). However, the tosylhydrazone moieties of two symmetry-related molecules of (2) are linked by hydrogen bonds involving the H atom of N2 as donor and atom O1 as acceptor [N2—H2 0.88, H2···O1^{i} 2.244, N2···O1^{i} 2.961 (5) Å and N2—H2···O1^{i} 138.5°; symmetry code: (i) $-x$, $-y$, $1-z$]. This leads to a head-to-head arrangement of two molecules, the separation of the hydrophilic and hydrophobic regions and a rather high density of 1.263 Mg m^{-3}.

Experimental

The tosylhydrazone (2) was obtained as a white powder from stereoisomerically pure (1) (Teng *et al.*, 1997) by reflux with an equal amount of tosylhydrazide in MeOH for 5 h. Recrystallization from THF gave pale-yellow crystals of (2).THF [m.p. 468–470 K (decomposition)]. R_f (ether–hexane 2:1) 0.36. ^{1}H NMR: 0.80 (*t*, 1H), 0.90 (*m*, 1H), 1.29 (*s*, 1H), 1.55 (*dm*, 2H), 1.64–1.86 (*st*, 3H), 2.08 (*t*, 1H), 2.43 (*s*, 3H), 2.54–2.72 (*m*, 2H), 7.33 (*d*, 2H), 7.34–7.44 (*st*, 6H), 7.52 (*m*, 4H), 7.86 (*d*, 2H). ^{13}C NMR: 16.12 (*t*), 16.41 (*t*), 21.58 (*q*), 35.16 (*t*), 40.48 (*d*), 46.38 (*d*), 46.40 (*d*), 127.96 (*d*), 128.02 (*d*), 129.03 (*s*), 129.56 (*d*), 129.60 (*d*), 134.51 (*d*), 135.79 (*s*), 143.69 (*s*), 167.80 (*s*). MS: 461([$M+1$]$^+$, 2), 460 (M^+, 8), 368 (27), 305 (42), 198 (13), 181 (39), 166 (45), 156 (27), 107 (21), 92 (35), 91 (100).

Crystal data

$C_{26}H_{28}N_2O_2SSi.C_4H_8O$
M_r = 532.76
Monoclinic
$C2/c$
a = 28.834 (3) Å
b = 6.2885 (5) Å
c = 30.971 (3) Å
β = 93.778 (13)°
V = 5603.5 (10) Å^3
Z = 8
D_x = 1.263 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 5000 reflections
θ = 2.0–25.0°
μ = 0.192 mm^{-1}
T = 193 (2) K
Plate
0.50 × 0.50 × 0.15 mm
Pale yellow

Data collection

Stoe IPDS diffractometer
φ rotation scans
Absorption correction: none
14 122 measured reflections
4704 independent reflections
3164 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.127
$\theta_{\rm max}$ = 25°
$h = -34 \rightarrow 34$
$k = -7 \rightarrow 7$
$l = -36 \rightarrow 36$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.225
S = 0.989
4704 reflections
351 parameters
H atoms riding (see below)
$w = 1/[\sigma^2(F_o^2) + (0.1521P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = 0.005
$\Delta\rho_{\rm max}$ = 0.761 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.675 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1*A*—C5*A*	1.515 (11)	C8—Si7	1.889 (4)
C1*A*—C8	1.529 (9)	C9—S1	1.767 (4)
C1*A*—C2	1.563 (8)	C16—Si7	1.880 (4)
C5*A*—C6	1.533 (12)	C22—Si7	1.873 (4)
C5*A*—C4	1.537 (11)	N1—N2	1.407 (5)
C2—C3	1.520 (5)	N2—S1	1.625 (3)
C3—N1	1.274 (5)	O1—S1	1.438 (3)
C3—C4	1.518 (6)	O2—S1	1.427 (3)
C6—Si7	1.904 (4)		
C5*A*—C1*A*—C8	108.6 (8)	C5*A*—C6—Si7	100.7 (5)
C5*A*—C1*A*—C2	102.5 (8)	C1*A*—C8—Si7	101.6 (4)
C8—C1*A*—C2	120.3 (7)	C3—N1—N2	115.7 (3)
C1*A*—C5*A*—C6	108.8 (8)	N1—N2—S1	116.0 (2)
C1*A*—C5*A*—C4	103.4 (7)	C22—Si7—C16	109.72 (17)
C6—C5*A*—C4	122.7 (9)	C22—Si7—C8	111.4 (2)
C3—C2—C1*A*	101.9 (4)	C16—Si7—C8	113.35 (19)
N1—C3—C4	120.7 (3)	C22—Si7—C6	112.14 (18)
N1—C3—C2	129.0 (4)	C16—Si7—C6	113.14 (19)
C4—C3—C2	110.3 (3)	C8—Si7—C6	96.64 (17)
C3—C4—C5*A*	102.4 (5)		
C8—C1*A*—C5*A*—C6	−54.9 (14)	C2—C3—C4—C5*A*	13.0 (6)
C2—C1*A*—C5*A*—C6	176.8 (6)	C1*A*—C5*A*—C4—C3	−35.7 (11)
C8—C1*A*—C5*A*—C4	173.2 (6)	C6—C5*A*—C4—C3	−158.8 (7)
C2—C1*A*—C5*A*—C4	44.9 (13)	C1*A*—C5*A*—C6—Si7	39.8 (11)
C5*A*—C1*A*—C2—C3	−35.6 (11)	C4—C5*A*—C6—Si7	160.4 (7)
C8—C1*A*—C2—C3	−156.1 (7)	C4—C3—N1—N2	−175.9 (3)
C1*A*—C2—C3—N1	−165.6 (6)	C2—C3—N1—N2	3.3 (6)
C1*A*—C2—C3—C4	13.7 (6)	C3—N1—N2—S1	−163.5 (3)
N1—C3—C4—C5*A*	−167.6 (6)		

H atoms were included in calculated positions using *SHELXL*97 (Sheldrick, 1997*a*) default parameters (*AFIX* 137 for methyl H atoms). The bridgehead C atoms C1 and C5 were found to occupy two alternative positions (*A* and *B*), and their occupancies were refined to be 0.543 (17) and 0.457 (17), respectively. The rather high $R_{\rm int}$ value may be explained by the presence of the disordered tetrahydrofuran solvent molecule which may have resulted in a small decomposition of the crystal during data collection. For the moment, such decomposition cannot be corrected for using the software provided with the Image Plate Diffraction System (IPDS). The refined extinction coefficient was less than its standard deviation. The absorption coefficient was 0.192 mm^{-1}, and the maximum and minimum transmission factors estimated by *SHELXL*97 from the size of the crystal were 0.97 and 0.91, respectively. Hence, in the final cycles of least-squares refinement, no correction for absorption or extinction was applied.

Data collection: *EXPOSE* (Stoe & Cie, 1997*a*). Cell refinement: *CELL* (Stoe & Cie, 1997*b*). Data reduction: *INTEGRATE* (Stoe & Cie, 1997*c*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *PLATON*/*PLUTON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*97.

This work has been supported by the Swiss National Science Foundation (project No. 20-43565.95) and the Stipendienfonds der Schweizerischen Chemischen Industrie.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1537). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1858–1859

Diethyl *N*,*N*′-(Naphthalene-1,8-diyl)-dioxamate

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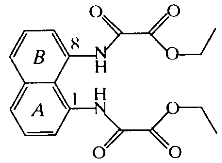
(*Received 13 May 1998; accepted 15 July 1998*)

Abstract

The reaction of ethyloxalyl chloride and naphthalene-1,8-diamine in refluxing tetrahydrofuran yielded the title compound, $C_{18}H_{18}N_2O_6$. The crystal structure analysis reveals a molecule with one oxamate substituent nearly coplanar with the aromatic naphthalene system, while the second is strongly twisted with respect to the naphthalene system. Three strong intramolecular hydrogen bonds are observed, one in each oxamic acid ethyl ester group and one linking the two substituents. Symmetry-related molecules are connected by a fourth intermolecular hydrogen bond.

Comment

In recent years, special attention has been devoted to transition metal compounds with oxamate ligands. In particular, bimetallic chain compounds with Mn^{II} and Cu^{II} have been studied in order to understand their magnetic properties (Stumpf, Pei, Kahn *et al.*, 1993; Stumpf, Pei, Ouahab *et al.*, 1993). In addition, the presence of strong electron-donor atoms, such as the amide N atom, stabilizes high oxidation states for transition metals. Some electrochemical studies have been carried out with copper(II)–oxamate complexes (see, for example, Cervera *et al.*, 1998). In the present paper, we report the crystal structure of the diethyl ester, (I), of *N*,*N*′-(naphthalene-1,8-diyl)bis(oxamic acid), an oxamate ligand which has not been described before.



(I)

The molecular structure of the title compound together with the atom-numbering scheme is shown in Fig. 1. Two oxamic acid ethyl ester groups are connected to the naphthalene system in positions 1 and 8. A planar arrangement of the two substituents with respect to the naphthalene system is hindered due to the steric interactions between them. This results in one substituent (described by the best plane through atoms N2, O4, O5 and O6) being strongly twisted [57.5 (1)°] around the C8—N2 bond with respect to the plane described by aromatic ring *B* (C5–C10), while the other substituent (atoms N1, O1, O2 and O3) is more coplanar [14.0 (1)°] with aromatic ring *A* (C1–C4, C9, C10). The naphthalene system is also affected and exhibits a small distortion [dihedral angle *A*/*B* = 5.8 (1)°] and a large exocyclic

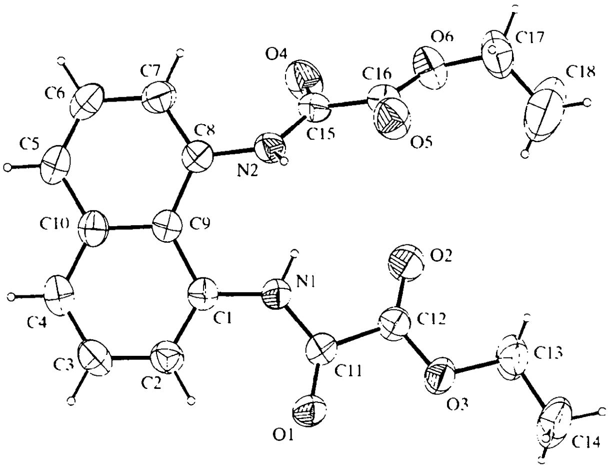


Fig. 1. *PLATON* (Spek, 1990) representation of the title compound showing 50% probability displacement ellipsoids.