

Data collection

Siemens SMART diffractometer	$R_{\text{int}} = 0.046$
Absorption correction: none	$\theta_{\text{max}} = 23^\circ$
10 397 measured reflections	$h = -8 \rightarrow 8$
3111 independent reflections	$k = -8 \rightarrow 10$
2730 reflections with $I > 2\sigma(I)$	$l = -44 \rightarrow 47$
	Intensity decay: $< 2\%$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 1.3262P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.133$	$(\Delta/\sigma)_{\text{max}} = -0.066$
$S = 1.132$	$\Delta\rho_{\text{max}} = 0.272 \text{ e } \text{\AA}^{-3}$
3110 reflections	$\Delta\rho_{\text{min}} = -0.259 \text{ e } \text{\AA}^{-3}$
337 parameters	Extinction correction: none
Only coordinates of H atoms refined	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: SAINT (Siemens, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XPMA (Zsolnai, 1994a) and ZORTEP (Zsolnai, 1994b). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1138). Services for accessing these data are described at the back of the journal.

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endo-3-Trimethylsilyl-2-norbornyl 2-Nitrobenzenesulfinate

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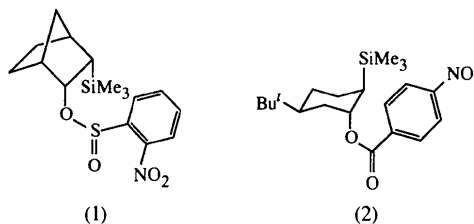
(Received 17 October 1996; accepted 3 March 1997)

Abstract

The structure of the title compound, C₁₆H₂₃NO₄SSi, was solved in order to determine the C(alkyl)—O(ester) bond distance for comparison purposes. There exists a close contact [O3···S 2.766(2) Å] between one of the nitro O atoms and the sulfinate S atom. The C—O bond distance is 1.464(3) Å.

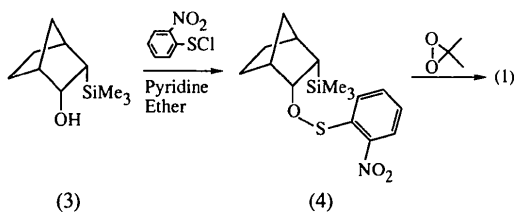
Comment

As part of our studies of the effects of silicon substituents on C—O bond lengths at the β position (White & Robertson, 1992; Kuan, Green & White, 1995; Chan *et al.*, 1996), we carried out a structural study on the title compound, (1). The norbornyl framework of (1) which was expected to enforce a synperiplanar relationship between the trimethylsilyl substituent and the 2-nitrobenzenesulfinate substituent would allow us to investigate the effects of the $\sigma(\text{C—Si})-\sigma^*(\text{C—O})$ interaction in this geometry. The $\sigma(\text{C—Si})-\sigma^*(\text{C—O})$ interaction in the antiperiplanar geometry, as in (2), has been shown to lead to significant lengthening of the C—O bond length (White & Robertson, 1992; Kuan, Green & White, 1995).



Compound (1) was prepared from endo-3-trimethylsilyl-endo-2-norborneol, (3) (Lambert & Chelius, 1990),

according to the reaction shown below. Treatment of the alcohol with 2-nitrobenzenesulfonyl chloride in ether in the presence of pyridine gave the sulfonate ester, (4). The sulfonate (4) was oxidized with dimethyldioxirane to give the sulfinate (1).



The structure of (1) (Fig. 1) clearly shows the synperiplanar relationship between the trimethylsilyl and 2-nitrobenzenesulfinate substituents [O1—C1—C2—Si—0.0(3)°]. This results in significant steric interactions between these two substituents as reflected by the bond angles Si—C2—C1, 119.2(2), and Si—C2—C3, 116.8(2)°. The nitro group deviates slightly from the plane of the phenyl ring [O3—N—C12—C11 18.0(3)°]; in this geometry, one of the nitro O atoms (O3) comes into close contact with the sulfinate S atom [O3...S 2.766(2) Å, sum of the van der Waals radii 3.32 Å (Bondi, 1964)] and makes an O3...S—O2 angle of 171.5(2)° with the S=O double bond. This structure can be compared with methyl 2-nitrobenzenesulfinate (Kuczman, Kapovits, Czugler, Parkanyi & Kalman, 1989) which has a similar non-bonded contact between one of the nitro O atoms and the sulfinate S atom of 2.743(4) Å, and an O...S=O angle of 177(1.5)°. The interaction is believed to involve donation of electron density from the nitro O atom lone-pair electrons into a low-lying vacant orbital on the S atom [either *d* orbital or $\sigma^*(\text{S—O})$ (Kuczman *et al.*, 1989)]. The C—O bond distance is 1.464(3) Å which suggests that the synperiplanar trimethylsilyl substituent has very little effect on the C—O bond length (Kuan, Green & White, 1995).

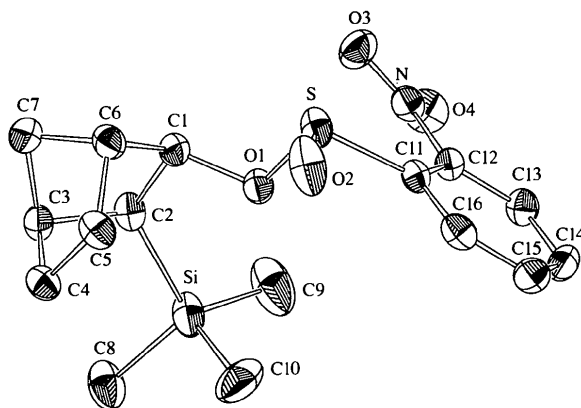


Fig. 1. ZORTEP (Zsolnai, 1995) diagram of (1). Displacement ellipsoids are drawn at the 30% probability level.

Experimental

Compound (1) was prepared according to the reaction scheme shown above. Crystals were grown from petrol (m.p. 365–369 K).

Crystal data

C₁₆H₂₃NO₄SSi
M_r = 353.51
 Monoclinic
*P*2₁/*c*
a = 14.4679(10) Å
b = 11.5916(10) Å
c = 11.456(3) Å
 β = 107.050(10)°
V = 1836.7(4) Å³
Z = 4
D_x = 1.278 Mg m⁻³
D_m not measured

Cu *K*α radiation
 λ = 1.54180 Å
 Cell parameters from 25 reflections
 θ = 25–30°
 μ = 2.348 mm⁻¹
T = 293(2) K
 Plate
 0.20 × 0.20 × 0.05 mm
 Colourless

Data collection

Enraf–Nonius CAD-4S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: Gaussian (SHELX76; Sheldrick, 1976)
T_{min} = 0.58, *T_{max}* = 0.88
 6633 measured reflections
 3772 independent reflections

2866 reflections with *I* > 2σ(*I*)
R_{int} = 0.035
 θ_{max} = 74.86°
h = -17 → 0
k = 0 → 14
l = -13 → 14
 3 standard reflections frequency: 160 min intensity decay: 2%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.050
wR(*F*²) = 0.146
S = 1.049
 3772 reflections
 301 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0759P)^2 + 0.6946P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = -0.042

$\Delta\rho_{\text{max}}$ = 0.73 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.56 e Å⁻³
 Extinction correction: SHELXL93 (Sheldrick, 1993)
 Extinction coefficient: 0.0003(2)
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S—O2	1.470(2)	Si—C2	1.901(3)
S—O1	1.626(2)	C1—O1	1.464(3)
S—C11	1.817(2)	N—O3	1.216(3)
Si—C9	1.850(5)	N—O4	1.227(3)
Si—C8	1.862(4)	O3...S	2.766(2)
Si—C10	1.885(6)		
O2—S—O1	107.66(12)	O1—C1—C6	115.3(2)
O2—S—C11	103.40(14)	C1—C2—Si	119.2(2)
O1—S—C11	91.40(10)	C3—C2—Si	116.8(2)
C10—Si—C2	116.1(2)	O3—S—O2	171.5(2)
O1—C1—C2—Si	0.0(3)	C11—C12—N—O3	18.0(3)
O2—S—C11—C16	-0.8(2)	C6—C1—O1—S	-65.8(2)
O1—S—C11—C16	-109.4(2)	C2—C1—O1—S	177.5(2)
O2—S—C11—C12	176.3(2)	O2—S—O1—C1	101.4(2)
O1—S—C11—C12	67.7(2)		

Data were collected at room temperature. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990). The refinement was performed using *SHELXL93* (Sheldrick, 1993) using anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for the H atoms. The figures were drawn using *ZORTEP* (Zsolnai, 1995) and the tables were prepared using *SHELXL93*. All calculations were carried out on a VAXstation 4000VLC computer system.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KH1145). Services for accessing these data are described at the back of the journal.

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3,3-Dimethyl-*N*-nitroso-2-phenyldecahydroquinolin-4-one

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Abstract

The molecule of the title compound, C₁₇H₂₂N₂O₂, consists of a piperidin-4-one ring *trans* fused to a cyclohexane moiety. The piperidine ring has a twist conformation.

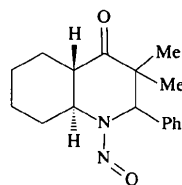
The ring N atom has a trigonal planar geometry. The cyclohexane ring adopts a chair conformation. The nitroso group is almost coplanar to the best plane of the piperidine ring. The phenyl ring is in the axial position.

Comment

Decahydroquinolines are important fused bicyclic systems containing an N atom. Their stereochemistry is of interest as they occur in many alkaloids such as lupinine, reserpine and yohimbine (Eliel, 1975; Norman, 1978; Nasipuri, 1992). Many nitrosamines are known to exhibit carcinogenic properties (Magee, Montesano & Preussmann, 1976; Ferguson, 1975; Loepky, Tomasik & Kerrick, 1987). Certain *N*-nitrosoarenes are used as antitumor agents or antibiotics (Lomax & Narayanan, 1988; Sapse, Allen & Lown, 1988).

The preferred conformation of the piperidine ring in decahydroquinoline precursors has been shown to be a chair with a slight twist or distortion of the ring dependent upon the position and size of the substituents (Booth & Bostock, 1972; Coz, Martin, Wartski, Penne, Bois & Levisalles, 1990). The substitution of a methyl or a nitroso group at the N-atom position has been shown to exert a large influence on the conformation of the ring and the orientation of the ring substituents (Vierhapper, 1980; Baliah & Natarajan, 1989).

The decahydroquinolines can have either *cis* or *trans* fusion of the two rings. The *trans* form is rigid. The title compound, (I), was found to exist in a *trans* configuration from analysis of the coupling constant of the H9 and H10 protons. From the X-ray crystal structure analysis, the torsion angle H9—C9—C10—H10 is found to be -177° , confirming *trans* fusion.



(I)

In piperidine derivatives, the substituents at nitrogen may be planar or perpendicular with respect to the ring (Lunazzi & Macciantelli, 1981; Lunazzi, Cerioni, Foresti & Macciantelli, 1978; Lunazzi, Cerioni & Ingold, 1976). The former is the case in the present compound. The ring N atom is planar and the N1—N11 bond length falls within the normal range for a partial double bond (Allen *et al.*, 1987).

The phenyl ring is substituted on the C2 atom in an axial position [C9—N1—C2—C21 107.9(2)°]. The angles between the best planes of the phenyl, piperidine and cyclohexane rings are: phenyl/piperidine 82.6(1), phenyl/cyclohexane 89.4(1) and piperidine/cyclohexane 17.3(2)°.