

C2—O1—C10a	114.1 (3)	N5—C4a—C4	115.5 (4)
C3—O3—C31	117.8 (4)	N5—C4a—C10a	107.1 (3)
C4—O4—C41	116.9 (4)	C4—C4a—C10a	114.7 (4)
C8—O8—C81	116.9 (4)	N5—C5a—C6	120.0 (4)
C4a—N5—C5a	114.1 (3)	N5—C5a—C9a	118.6 (4)
C4a—N5—C51	117.8 (4)	C6—C5a—C9a	119.9 (4)
C5a—N5—C51	123.7 (4)	O6—C6—N7	119.9 (4)
C6—N7—C7	117.9 (4)	O6—C6—C5a	125.7 (4)
C6—N7—C8	120.6 (4)	N7—C6—C5a	114.5 (4)
C7—N7—C8	121.4 (4)	O8—C8—N7	112.6 (4)
C8—N9—C9a	116.2 (4)	O8—C8—N9	122.1 (4)
C9a—N10—C10a	121.6 (4)	N7—C8—N9	125.4 (4)
O1—C2—C3	112.9 (4)	N9—C9a—N10	116.2 (4)
O3—C3—C2	109.6 (4)	N9—C9a—C5a	122.4 (4)
O3—C3—C4	107.2 (4)	N10—C9a—C5a	121.4 (4)
C2—C3—C4	111.3 (4)	O1—C10a—N10	111.5 (4)
O4—C4—C3	106.1 (4)	O1—C10a—C4a	111.5 (3)
O4—C4—C4a	111.0 (3)	N10—C10a—C4a	110.6 (3)
C3—C4—C4a	110.7 (4)		
C9a—N9—C8—N7	−2.0 (4)	C4—C4a—C10a—O1	−47.1 (5)
N5—C4a—C10a—N10	−52.0 (5)		

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A
N10—H10...O6 ⁱ	1.99	2.816 (5)	145
C3—H3...O31	2.23	2.640 (7)	105
C4a—H4a...O51	2.26	2.735 (5)	110
C7—H7a...O8	2.19	2.647 (7)	109

Symmetry code: (i) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Fig. 1 was prepared using ORTEPII (Johnson, 1976) as implemented in PLATON (Spek, 1994a). An examination of the structure with the SOLV option in PLATON showed that there is a void in the asymmetric unit of volume 16.1 \AA^3 immediately adjacent to the carbonyl O31 atom and it is consequently not surprising that the ORTEPII plot shows that this atom is markedly anisotropic.

Data collection: CAD-4-PC (Enraf-Nonius, 1992). Cell refinement: SET4 and CELDIM (Enraf-Nonius, 1992). Data reduction: DATRD2 in NRCVAX94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: NRCVAX94. Molecular graphics: NRCVAX94, PLATON (Spek, 1994a) and PLUTON (Spek, 1994b). Software used to prepare material for publication: NRCVAX94.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1014). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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S-Methyl (2R,6S,8S)-2,6-Dimethoxy-4-methyl-3,5-dioxatricyclo[5.2.1.0^{4,9}]decane-8-thioate

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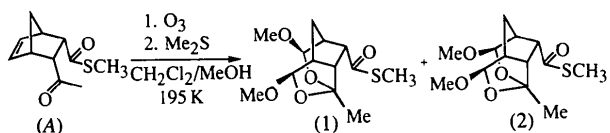
Abstract

The X-ray analysis of the title compound, $\text{C}_{13}\text{H}_{20}\text{O}_5\text{S}$, confirms the *trans* relationship between the two methoxy groups on atoms C(2) and C(6) of the heterocyclic cage. The torsion angles C(15)—S—C(14)—O(8) and C(9)—C(8)—C(14)—O(8) have values of $0.0 (2)^\circ$ and $-15.9 (3)^\circ$, respectively.

Comment

The synthesis and chemistry of heterocyclic cage compounds has received attention in recent years (Metha & Reddy, 1987; Marchand, Reddy, Watson & Kashyap, 1990). The main motivation for these studies has been the desire to compare the reactivity pattern of carbon-cage compounds with their heteroatomic analogues. The synthesis of novel heterocyclic cage compounds by ozonolysis of thioesters followed by reduction with dimethyl sulfide was accomplished by Wu, Huang & Lin (1991). While seeking a protic solvent to improve the heterocyclic cage compound formation, the Diels–Alder

adduct (A), in CH₂Cl₂/MeOH (1:1), was substituted by ozonolysis followed by reduction with Me₂S at 195 K to afford the cage-type hemiacetal solvent adducts (1) and (2) (Wu, 1994).



Because of the difficulties in clarifying the relationship of the configurations of two chiral centres using NMR spectroscopy, the X-ray structure determination of *S*-methyl (2*R*,6*S*,8*S*)-2,6-dimethoxy-4-methyl-3,5-dioxatricyclo[5.2.1.0^{4,9}]decane-8-thioate, (1), was undertaken in order to determine the configuration of the diastereomers. The X-ray analysis confirmed the *trans* relationship between the two methoxy groups on atoms C(2) and C(6) of the heterocyclic cage. An ORTEPII (Johnson, 1976) diagram with atomic numbering is shown in Fig. 1.

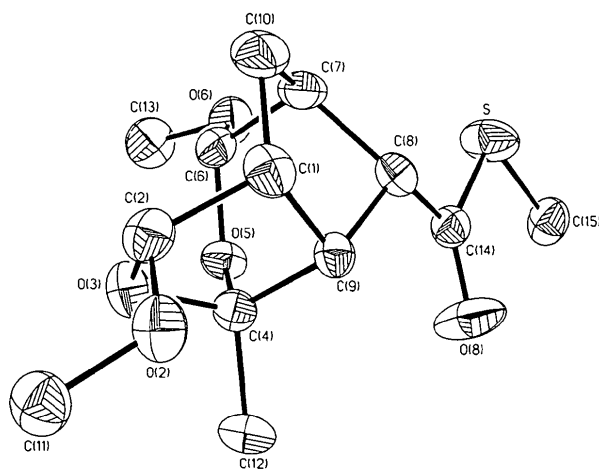


Fig. 1. An ORTEPII (Johnson, 1976) diagram of the title compound with ellipsoids drawn at the 30% probability level.

The C(14)_{sp²}—S and C(15)_{sp³}—S bonds, of lengths 1.755 (4) and 1.775 (4) Å, respectively, are somewhat shorter than the normal C_{sp²}—S and C_{sp³}—S bonds of 1.78 and 1.81 Å, respectively (Kimura, Simonsen, Caldwell & Martin, 1981; Khan, Taylor, Lehn & Dietrich, 1988). In this molecule, atoms C(15), S, C(14) and O(8) are coplanar within 0.001 Å, and atoms C(9), C(8), C(14) and O(8) are coplanar within 0.049 Å. The torsion angles C(15)—S—C(14)—O(8), C(15)—S—C(14)—C(8), C(9)—C(8)—C(14)—S and C(9)—C(8)—C(14)—O(8) have values of 0.0 (2), 174.6 (3), 169.7 (3) and -15.9 (3)°, respectively. The torsion angle O(2)—C(2)—C(6)—O(6) has a value of 103.9 (4)°. The average C—O distance in the heterocyclic rings is 1.42 Å and the average C—C distance is 1.53 Å.

Experimental

Crystals of the title compound were obtained by slow evaporation of a hexane solution into chloroform.

Crystal data

C₁₃H₂₀O₅S
M_r = 288.4
 Monoclinic
*P*2₁/*c*
a = 15.630 (2) Å
b = 7.722 (2) Å
c = 12.986 (2) Å
 β = 113.44 (2)°
V = 1437.9 (3) Å³
Z = 4
D_x = 1.332 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 30 reflections

θ = 7.5–15.0°

μ = 0.238 mm⁻¹

T = 293 K

Cubic

0.3 × 0.3 × 0.2 mm

Colorless

Data collection

Siemens R3m/V diffractometer

2 θ – θ scans

Absorption correction:

ψ scan (SHELXTL-Plus

XEMP; Sheldrick, 1991)

T_{min} = 0.810, *T_{max}* =

0.844

2867 measured reflections

2531 independent reflections

1997 observed reflections

[*F* > 3.0 σ (*F*)]

R_{int} = 0.012

θ_{\max} = 25°

h = -18 → 17

k = -9 → 0

l = 0 → 15

2 standard reflections

monitored every 98

reflections

intensity decay: < 3%

Refinement

Refinement on *F*

R = 0.0556

wR = 0.0918

S = 1.69

1997 reflections

172 parameters

H-atom parameters not

refined

$w = 1/[\sigma^2(F) + 0.0020F^2]$

(Δ/σ)_{max} = 0.001

$\Delta\rho_{\max}$ = 0.69 e Å⁻³

$\Delta\rho_{\min}$ = -0.59 e Å⁻³

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
S	0.8727 (1)	0.0320 (1)	0.9214 (1)	0.079 (1)
O(2)	0.5186 (1)	-0.2852 (3)	1.0876 (2)	0.061 (1)
O(3)	0.6736 (1)	-0.2101 (3)	1.1918 (2)	0.054 (1)
O(5)	0.7965 (1)	-0.0633 (3)	1.1754 (2)	0.048 (1)
O(6)	0.9330 (1)	-0.1669 (3)	1.1779 (2)	0.063 (1)
O(8)	0.7408 (2)	0.1811 (3)	0.9602 (3)	0.099 (2)
C(1)	0.6324 (2)	-0.3185 (4)	1.0118 (3)	0.055 (1)
C(2)	0.6121 (2)	-0.3296 (4)	1.1153 (3)	0.055 (1)
C(4)	0.6978 (2)	-0.0734 (4)	1.1324 (2)	0.044 (1)
C(6)	0.8413 (2)	-0.2125 (4)	1.1548 (2)	0.050 (1)
C(7)	0.7938 (2)	-0.2728 (4)	1.0333 (3)	0.054 (1)
C(8)	0.7313 (2)	-0.1271 (4)	0.9600 (2)	0.047 (1)
C(9)	0.6557 (2)	-0.1254 (4)	1.0076 (2)	0.044 (1)
C(10)	0.7211 (3)	-0.4136 (5)	1.0183 (3)	0.071 (2)
C(11)	0.4912 (2)	-0.2920 (5)	1.1795 (3)	0.068 (2)
C(12)	0.6642 (2)	0.0972 (4)	1.1586 (3)	0.062 (1)
C(13)	0.9896 (2)	-0.1522 (6)	1.2932 (3)	0.074 (2)
C(14)	0.7738 (2)	0.0446 (4)	0.9534 (2)	0.050 (1)
C(15)	0.8958 (2)	0.2540 (5)	0.9075 (3)	0.068 (2)

Table 2. Selected geometric parameters (Å, °)

S—C(14)	1.755 (4)	S—C(15)	1.775 (4)
O(2)—C(2)	1.401 (4)	O(2)—C(11)	1.420 (5)
O(3)—C(2)	1.415 (3)	O(3)—C(4)	1.443 (4)
O(5)—C(4)	1.418 (3)	O(5)—C(6)	1.428 (4)
O(6)—C(6)	1.388 (4)	O(6)—C(13)	1.409 (4)
O(8)—C(14)	1.192 (4)	C(1)—C(2)	1.501 (5)
C(1)—C(9)	1.541 (4)	C(1)—C(10)	1.542 (5)
C(4)—C(9)	1.541 (4)	C(4)—C(12)	1.506 (5)
C(6)—C(7)	1.525 (4)	C(7)—C(8)	1.544 (4)
C(7)—C(10)	1.528 (5)	C(8)—C(9)	1.536 (5)
C(8)—C(14)	1.501 (4)		
C(14)—S—C(15)	101.7 (2)	C(2)—O(2)—C(11)	114.0 (2)
C(2)—O(3)—C(4)	110.6 (2)	C(4)—O(5)—C(6)	114.8 (2)
C(6)—O(6)—C(13)	114.0 (3)	C(2)—C(1)—C(9)	103.0 (3)
C(2)—C(1)—C(10)	115.5 (3)	C(9)—C(1)—C(10)	104.0 (3)
O(2)—C(2)—O(3)	111.6 (3)	O(2)—C(2)—C(1)	109.0 (2)
O(3)—C(2)—C(1)	105.3 (3)	O(3)—C(4)—O(5)	107.8 (2)
O(3)—C(4)—C(9)	106.2 (2)	O(5)—C(4)—C(9)	111.7 (3)
O(3)—C(4)—C(12)	109.3 (3)	O(5)—C(4)—C(12)	106.5 (2)
C(9)—C(4)—C(12)	115.1 (2)	O(5)—C(6)—O(6)	107.2 (2)
O(5)—C(6)—C(7)	111.5 (2)	O(6)—C(6)—C(7)	109.6 (3)
C(6)—C(7)—C(8)	110.1 (2)	C(6)—C(7)—C(10)	112.3 (3)
C(8)—C(7)—C(10)	100.6 (2)	C(7)—C(8)—C(9)	99.1 (3)
C(7)—C(8)—C(14)	119.6 (2)	C(9)—C(8)—C(14)	116.4 (3)
C(1)—C(9)—C(4)	102.8 (2)	C(1)—C(9)—C(8)	103.7 (3)
C(4)—C(9)—C(8)	110.5 (2)	C(1)—C(10)—C(7)	106.0 (3)
S—C(14)—O(8)	121.0 (3)	S—C(14)—C(8)	114.6 (2)
O(8)—C(14)—C(8)	124.2 (3)		

The structure of the title compound was solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1991). All non-H atoms were located from successive Fourier maps. Anisotropic displacement parameters were used for all non-H atoms and fixed isotropic displacement parameters were used for H atoms, which were included using a riding model. The structure was refined with *SHELXTL-Plus XLS*. Analytical scattering factors for neutral atoms were used throughout the analysis.

We would like to thank the National Science Council of the Republic of China for financial support and Professor Hsien-Jen Wu for supplying the crystals.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Diaza-cyclo-tetradecadiene-Bis(pyrido-silafuran) Ring System

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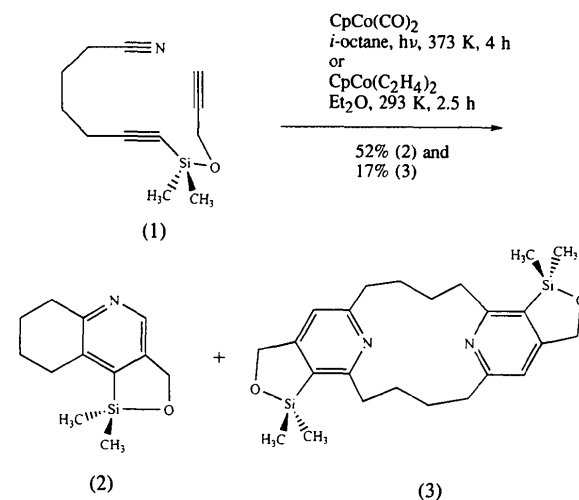
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Abstract

The crystal structure of 8,8,20,20-tetramethyl-9,21-dioxo-25,26-diaza-8,20-disilapentacyclo[16.6.1.1^{6,13}.0^{7,11}.0^{19,23}]-hexacosia-1(25),6,11,13(26),18,23-hexaene, C₂₄H₃₄N₂O₂-Si₂, has been determined at low temperature. The molecule lies on a crystallographic inversion centre.

Comment

In connection with our current work on the cobalt-catalysed intramolecular [2+2+2] cycloaddition of diyne-nitriles to obtain substituted pyridines (Groth, Eckenberg & Huhn, 1993; Huhn, 1994), the cyclization of the diyne-nitrile (1) yielded 52% of the furylquinoline (2) and 17% of the dimeric title compound (3). The relative amount of the dimer was found to be independent of the reaction temperature and the cobalt catalyst.



The crystal structure analysis was performed in order to establish the position of the pyridine N atom within the aromatic ring. All bond lengths and angles are in