helpful discussions. In addition, MMT is grateful to the Chemistry Department at the University of Canterbury for providing facilities during his sabbatical stay.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A *cis,trans,cis,cis*-[4.5.5.5]Fenestrane Derivative

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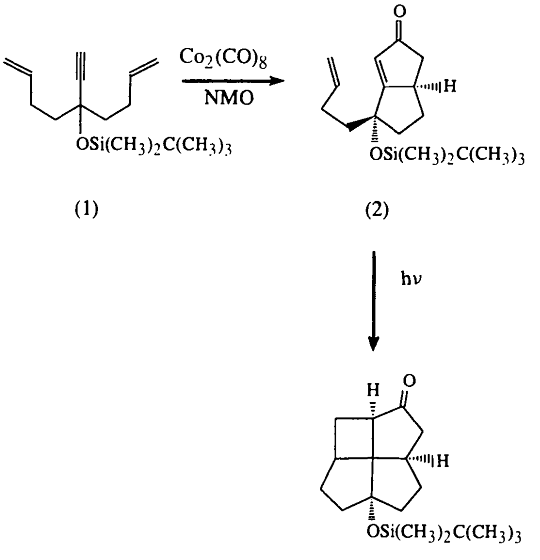
Abstract

The title compound, *rel*-(1*R*,4*R*,7*S*,10*R*)-7-(*tert*-butyldimethylsilyloxy)tetracyclo[5.4.1.$0^{4,12}$.$0^{10,12}$]dodecan-2-one, $C_{18}H_{30}O_2Si$, has been prepared and its structure determined. The geometry of the central $C(C)_4$ substructure of the fenestrane skeleton shows a considerable distortion from an ideal tetrahedral arrangement towards planarity. Values of 127.0 (2) and 131.1 (2)° are observed for the bond angles at the bridgehead atoms of the *trans*-bicyclo[3.3.0]octane subunit.

Comment

Fenestranes are of considerable interest because of the planarizing distortions observed in several cases. The planarizing distortions in the central $C(C)_4$ subunit of this class of compound can be enhanced *inter alia* by construction of *trans*-fused bicyclo[3.3.0]octane subunits (Luef & Keese, 1993). In a systematic search for fenestranes having large distortions, the title compound, (3), was prepared by a $Co_2(CO)_8$-induced cyclocarbonylation reaction of (1) (Thommen, 1995), followed by a photo-induced olefin–enone cycloaddition.



(3)

The structure of (3) shows remarkable features both around the central C atom and in the *trans*-fused bicyclo[3.3.0]octane substructure (Table 2). The architecture of fenestrane (3) induces a deformation of the tetrahedral angles in the central $C(C)_4$ substructure towards planarity. The angles C4—C12—C10 and C1—C12—C7 have values of 120.2 (2) and 131.1 (2)°, respectively, which are similar to those observed in the two previously studied [4.5.5.5]fenestranes containing a *trans*-fused [3.3.0]octane substructure (Hirschi, Luef, Gerber & Keese, 1992; Wang, Thommen & Keese, 1996). The largest deviations observed so far are 129.2 (5) and 128.3 (6)° in the all-*cis* [4.4.4.5]fenestrane series (Rao, George, Wolff & Agosta, 1985). The C3—C4—C5 bond angle at the bridgehead of the *trans*-bicyclo[3.3.0]octane substructure is 127.0 (2)°. Compared with the average bond angles of 126 (4) and 127 (6)° found for corresponding bridgehead angles in 19 *trans*-bicyclo[3.3.0]octane subunits retrieved (Hirschi, Luef, Gerber & Keese, 1992) from the Cambridge Structural Database (Allen *et al.*, 1987), C3—C4—C5 is typical but C1—C12—C7, with a value of 131.1 (2)°, is rather large.

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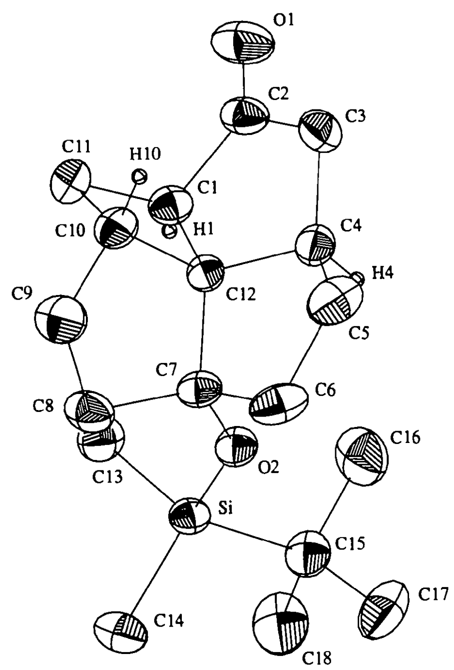

Fig. 1. The molecular structure of (3) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 30% probability levels and bridgehead H atoms are drawn as small circles of arbitrary radii.

Experimental

The title compound, (3), was prepared by treating 5-(*tert*-butyldimethylsilyloxy)-5-ethynyl-1,8-nonadiene, (1), with one equivalent of $Co_2(CO)_8$ in CH_2Cl_2/tetrahydrofuran (1:1). Subsequent treatment of the cobalt–hexacarbonyl complex with *N*-methylmorpholine *N*-oxide at room temperature gave enone (2) along with the other diastereoisomer. Irradiation of (2) with UV light afforded compound (3) in 89% isolated yield. Recrystallization from hexane at 253 K gave pure colourless crystals (m.p. 331 K).

Crystal data

$C_{18}H_{30}O_2Si$
$M_r = 306.51$
Monoclinic
$P2_1/n$
$a = 11.212\,(2)$ Å
$b = 8.4300\,(8)$ Å
$c = 19.384\,(2)$ Å
$\beta = 90.810\,(11)°$
$V = 1831.9\,(4)$ Å^3
$Z = 4$
$D_x = 1.111$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 18 reflections
$\theta = 8.70–18.60°$
$\mu = 0.131$ mm^{-1}
$T = 293\,(2)$ K
Elongated flat prism
0.37 × 0.35 × 0.27 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scan (Enraf–Nonius, 1985)
$T_{min} = 0.977$, $T_{max} = 0.999$
4038 measured reflections
3212 independent reflections

2318 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0175$
$\theta_{max} = 24.97°$
$h = -13 \rightarrow 13$
$k = -1 \rightarrow 10$
$l = -1 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 16.7%

Refinement

Refinement on F^2
$R(F) = 0.0421$
$wR(F^2) = 0.1246$
$S = 1.062$
3212 reflections
282 parameters
H atoms refined with group U_{iso}
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 0.4327P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.174$ e Å^{-3}
$\Delta\rho_{min} = -0.267$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.5624 (2)	0.3295 (3)	0.13043 (11)	0.0513 (5)
C2	0.5096 (2)	0.4765 (3)	0.09607 (11)	0.0570 (6)
C3	0.3739 (3)	0.4688 (3)	0.09632 (14)	0.0676 (7)
C4	0.3495 (2)	0.3505 (3)	0.15328 (11)	0.0546 (6)
C5	0.2434 (2)	0.2430 (5)	0.15893 (14)	0.0786 (9)
C6	0.2912 (2)	0.1126 (4)	0.20807 (13)	0.0689 (8)
C7	0.4306 (2)	0.1170 (3)	0.20759 (10)	0.0461 (5)
C8	0.4875 (3)	−0.0378 (3)	0.18449 (13)	0.0669 (7)
C9	0.4609 (4)	−0.0417 (3)	0.10677 (14)	0.0783 (9)
C10	0.4687 (2)	0.1306 (3)	0.08381 (11)	0.0560 (6)
C11	0.5933 (3)	0.2030 (4)	0.07618 (14)	0.0705 (7)
C12	0.4518 (2)	0.2355 (2)	0.14968 (9)	0.0398 (4)
C13	0.7268 (2)	0.1846 (4)	0.28883 (15)	0.0642 (7)
C14	0.5812 (3)	−0.0629 (3)	0.3619 (2)	0.0705 (7)
C15	0.5471 (2)	0.2891 (3)	0.39833 (11)	0.0599 (6)
C16	0.5512 (4)	0.4588 (4)	0.3700 (2)	0.0908 (10)
C17	0.4232 (3)	0.2598 (5)	0.4266 (2)	0.0954 (11)
C18	0.6389 (4)	0.2736 (5)	0.4573 (2)	0.0986 (12)
O1	0.5678 (2)	0.5832 (2)	0.07199 (9)	0.0834 (6)
O2	0.46929 (12)	0.1734 (2)	0.27314 (6)	0.0501 (4)
Si	0.57961 (5)	0.14323 (7)	0.32776 (3)	0.0449 (2)

Table 2. *Selected geometric parameters (Å, °)*

C1—C12	1.522 (3)	C6—C7	1.564 (3)
C1—C2	1.523 (3)	C7—C8	1.523 (3)
C1—C11	1.541 (3)	C7—C12	1.524 (3)
C2—C3	1.523 (4)	C8—C9	1.532 (4)
C3—C4	1.516 (3)	C9—C10	1.523 (4)
C4—C5	1.500 (4)	C10—C11	1.533 (4)
C4—C12	1.504 (3)	C10—C12	1.567 (3)
C5—C6	1.546 (4)		
C5—C4—C12	102.7 (2)	C1—C12—C7	131.1 (2)
C5—C4—C3	127.0 (2)	C4—C12—C10	120.2 (2)
C12—C4—C3	104.1 (2)	C1—C12—C10	89.1 (2)
C4—C12—C1	107.5 (2)	C7—C12—C10	104.6 (2)
C4—C12—C7	105.2 (2)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure:

SHELXL93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dicyano(7,7-dimethyl-2,5-di-*p*-tolyl-3,4-diazabicyclo[4.1.0]hepta-2,4-dien-3-ium-3-yl)methanide and (4-Benzoyl-5,5-dimethyl-2-phenyl-1-azacyclopenta-1,3-dien-1-ium-1-yl)dicyanomethanide, Two Stable Azomethine Ylides

JOSEF BREU,[a]* KLAUS-JÜRGEN RANGE,[a] PETER RIEBEL,[b] ANDREAS WEBER[b] AND JÜRGEN SAUER[b]

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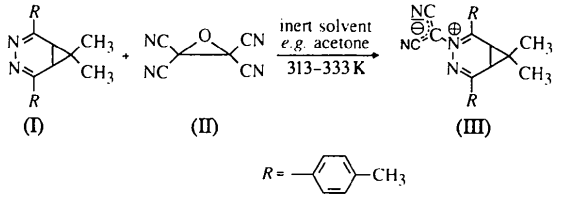
Abstract

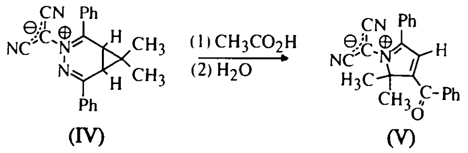
The azomethine ylide moieties of dicyano(7,7-dimethyl-2,5-di-*p*-tolyl-3,4-diazabicyclo[4.1.0]hepta-2,4-dien-3-ium-3-yl)methanide, $C_{24}H_{22}N_4$, and (4-benzoyl-5,5-dimethyl-2-phenyl-1-azacyclopenta-1,3-dien-1-ium-1-yl)dicyanomethanide, $C_{22}H_{17}N_3O$, show normal bond distances and angles in comparison with related structures reported previously. The dipolar N—C distances of 1.430 (4) and 1.401 (3) Å are appreciably shortened compared with the C—N$^+$ bond lengths [1.485 (9) Å] found in *N*-substituted pyridinium compounds, which is consistent with previous observations. Both title compounds pack in such a way that the ylide dipoles are arranged above each other but pointing in opposite directions.

Comment

3,4-Diazanorcaradienes, (I), show high reactivity in Diels–Alder reactions with inverse electron demand (Sauer, 1992, 1994). In order to lower the LUMO (lowest unoccupied molecular orbital) energy of these diazadienes, the introduction of a substituent at the N atom of the diene system was attempted. Reaction of diazanorcaradiene (I) with tetracyanoethylene oxide, (II), yielded the stable betaine (III) (Riebel, Weber, Troll, Sauer & Breu, 1996).



These betaines, which are also cationic 2,3-diazadienes and azomethine ylides, underwent a facile and unexpected rearrangement to form another stable betaine, (V), as shown for the reaction of the diphenyl derivative (IV) to (V). In compound (V), the combination of a cyclic azadiene and a 1,3-dipole is again found (Riebel, Weber, Troll, Sauer, Breu & Nöth, 1996). In order to characterize this reaction unambiguously, the X-ray structure determinations of compounds (III) and (V) were undertaken.



The molecular structures of (III) and (V) are represented in Figs. 1 and 2, respectively. There is only one diazanorcaradiene structure (Krieger, Fritchie & Blumburg, 1969) deposited in the Cambridge Structural Database (Allen *et al.*, 1987), however, crystal decomposition prevented an accurate determination of the molecular parameters and no coordinates were reported. Whereas for 2,5-di-*p*-bromophenyl-1,6-diphenyl-

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