Atal, C. K. (1981). *Chemistry and Pharmacology of Vasicine – A New Oxytocic and Abortifacient*. Regional Research Laboratory, Jammu, India.
Dhar, K. L., Jain, M. P., Kaul, S. K. & Atal, C. K. (1981). *Phytochemistry*, **20**, 319–321.
Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Stereochemistry*, Vol. 9, edited by N. L. Allinger & E. L. Eliel, pp. 271–383. New York: John Wiley.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mehta, D. R., Naravane, J. S. & Desai, R. M. (1963). *J. Org. Chem.* **28**, 445–448.
Motherwell, W. D. S. & Clegg, W. (1976). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Pandita, K., Bhatia, M. S., Thappa, R. K., Agarwal, S. G., Dhar, K. L. & Atal, C. K. (1983). *Planta Med.* **48**, 81–82.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Stroud, R. M. (1973). *Acta Cryst.* B**29**, 690–696.
Wheatley, P. J. (1960). *Acta Cryst.* **13**, 80–85.

Acta Cryst. (1996). C**52**, 1493–1496

Bis(*p*-nitrobenzoate) Ester of *cis*-1,1-Dimethylsilacyclohexane-3,4-diol

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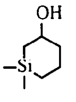
Abstract

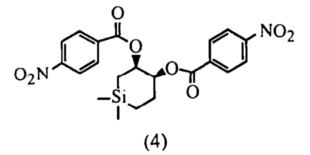
The asymmetric unit of the title structure, 1,1-dimethyl-1-silacyclohexane-3,4-diyl bis(4-nitrobenzoate), consists of four independent $C_{21}H_{22}N_2O_8Si$ molecules which show only minor differences in conformation. The silacyclohexane ring adopts a distorted chair conformation, with the C4 substituent axial and the C3 substituent equatorial.

Comment

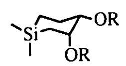
As part of our structural studies on silicon-substituted alcohols and esters (White & Robertson, 1992; White, Green & Kuan, 1995), we attempted to prepare 1,1-dimethylsilacyclohexan-3-ol, (1), by the method outlined below. Unfortunately, treatment of alkene (2) with *m*-chloroperoxybenzoic acid (mCPBA) in dichloromethane gave a complex mixture, which after reduction with lithium aluminium hydride gave the *cis*-diol (3) as the major product. The present structural study was carried out on the bis(*p*-nitrobenzoate) derivative (4) in order to verify the unexpected *cis* stereochemical relationship between the two hydroxy substituents of compound (3).



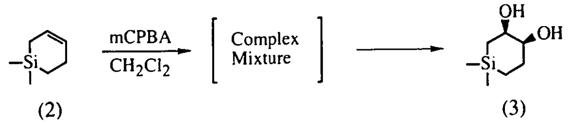
(1)



(4)



(5)



(2) (3)

The asymmetric unit of (4) consists of four independent molecules having similar conformations (Figs. 1–4), although small differences in the orientations of the nitro and carboxyl substituents with respect to the phenyl ring are apparent from the list of selected torsion angles (Table 2). The conformations of the silacyclohexane rings are best described as chair, with distortions from idealized cyclohexane geometry resulting from the longer C—Si bond lengths. The *p*-nitrobenzoate substituent at C3 is in an equatorial position and that at C4 is axial, a conformation that is also observed in solution, as shown by 1D and 2D proton NMR experiments. It is interesting to note that the alternative conformation, (5), having the C3 substituent axial and the C4 substituent equatorial, is predicted by molecular-mechanics calculations to be more stable. The observation that the diester

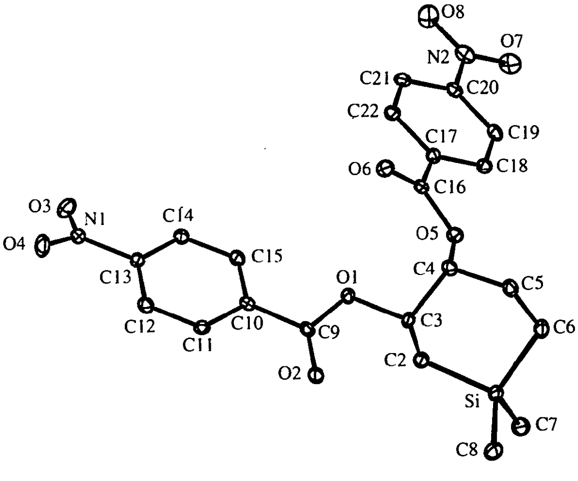


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of molecule 1 of compound (4). Displacement ellipsoids are at the 50% probability level.

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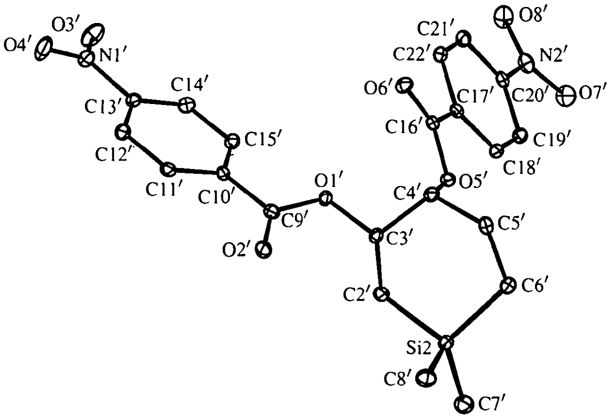

Fig. 2. *ORTEP*II (Johnson, 1976) diagram of molecule 2 of compound (4). Displacement ellipsoids are at the 50% probability level.

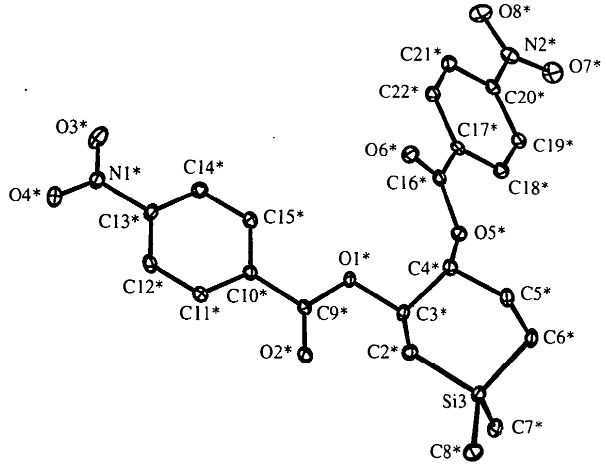

Fig. 3. *ORTEP*II (Johnson, 1976) diagram of molecule 3 of compound (4). Displacement ellipsoids are at the 50% probability level.

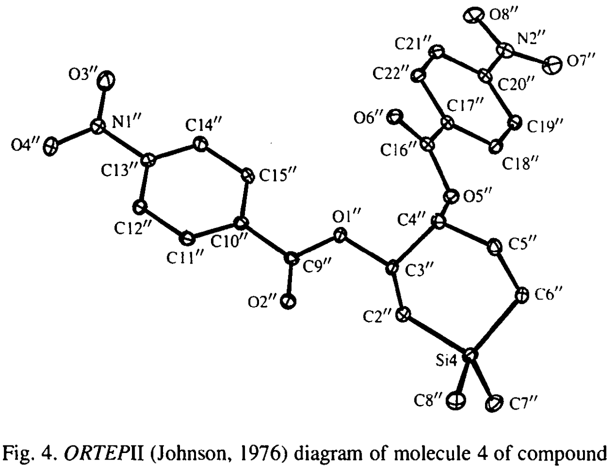

Fig. 4. *ORTEP*II (Johnson, 1976) diagram of molecule 4 of compound (4), an enantiomer of that in the coordinate list. Displacement ellipsoids are at the 50% probability level.

(4) exists in the conformation shown in Fig. 1 can be rationalized in terms of a stabilizing σ_{C-Si}—σ^*_{C-O} interaction between the Si—C2 and C3—O1 bonds. Such an interaction is maximized when the Si—C2—C3—O1 dihedral angle is 180°, which is the case for (4) [mean absolute Si—C2—C3—O1 179°]. The influence of this type of stereoelectronic effect on the conformations of flexible molecules has been demonstrated previously (White & Kuan, 1994). There is no evidence of lengthening of the C3—O1 bond and the mean value for the four molecules of 1.465 Å is not significantly larger than the mean value of 1.463 Å for the C4—O5 bond.

Experimental

Crystals of the title compound were grown from ether/petroleum solution.

Crystal data

$C_{21}H_{22}N_2O_8Si$
$M_r = 458.5$
Monoclinic
Pn
$a = 7.2309\,(9)$ Å
$b = 29.517\,(4)$ Å
$c = 20.717\,(3)$ Å
$\beta = 101.980\,(10)°$
$V = 4325.4\,(10)$ Å^3
$Z = 8$
$D_x = 1.408$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation (Ni filtered)
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 25–35°$
$\mu = 1.415$ mm^{-1}
$T = 130\,(2)$ K
Block
0.3 × 0.3 × 0.1 mm
Colourless

Data collection

Enraf–Nonius CAD-4 MachS diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.69$, $T_{max} = 0.87$
15 806 measured reflections
7839 independent reflections

7518 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0306$
$\theta_{max} = 64.10°$
$h = 0 \rightarrow 8$
$k = -34 \rightarrow 34$
$l = -24 \rightarrow 23$
3 standard reflections
frequency: 150 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0358$
$wR(F^2) = 0.0956$
$S = 1.007$
7836 reflections
1250 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 0.8214P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.415$ e Å^{-3}
$\Delta\rho_{min} = -0.396$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00066 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.01 (2)

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

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

	x	y	z	$U_{\rm eq}$
Molecule 1				
Si	−1.57123 (13)	−0.70137 (3)	−0.98768 (4)	0.0254 (2)
C2	−1.4436 (5)	−0.69442 (10)	−0.89996 (14)	0.0242 (6)
C3	−1.5869 (4)	−0.68513 (10)	−0.85716 (13)	0.0208 (6)
C4	−1.7302 (4)	−0.72247 (9)	−0.85659 (14)	0.0223 (6)
C5	−1.8677 (5)	−0.72660 (10)	−0.92305 (15)	0.0276 (7)
C6	−1.7774 (5)	−0.73834 (11)	−0.98173 (15)	0.0313 (7)
C7	−1.4131 (6)	−0.72650 (12)	−1.0383 (2)	0.0378 (8)
C8	−1.6580 (5)	−0.64454 (12)	−1.0213 (2)	0.0360 (8)
C9	−1.4397 (4)	−0.63482 (10)	−0.77370 (14)	0.0206 (6)
C10	−1.3311 (4)	−0.62997 (9)	−0.70429 (14)	0.0197 (6)
C11	−1.3048 (4)	−0.58629 (10)	−0.67795 (14)	0.0222 (6)
C12	−1.2041 (4)	−0.58016 (10)	−0.61358 (15)	0.0237 (6)
C13	−1.1320 (4)	−0.61802 (10)	−0.57803 (14)	0.0213 (6)
C14	−1.1532 (4)	−0.66139 (10)	−0.60326 (14)	0.0235 (6)
C15	−1.2551 (5)	−0.66757 (10)	−0.66701 (15)	0.0245 (6)
C16	−1.6019 (4)	−0.78108 (10)	−0.78036 (13)	0.0208 (6)
C17	−1.5137 (4)	−0.82709 (10)	−0.77408 (14)	0.0213 (6)
C18	−1.5182 (4)	−0.85549 (10)	−0.82826 (15)	0.0216 (6)
C19	−1.4464 (4)	−0.89888 (10)	−0.8188 (2)	0.0254 (6)
C20	−1.3666 (4)	−0.91314 (10)	−0.7555 (2)	0.0230 (6)
C21	−1.3567 (4)	−0.88526 (10)	−0.70110 (15)	0.0238 (6)
C22	−1.4325 (4)	−0.84215 (10)	−0.71071 (14)	0.0223 (6)
O1	−1.4876 (3)	−0.67744 (7)	−0.78861 (9)	0.0227 (4)
O2	−1.4783 (3)	−0.60307 (7)	−0.81086 (10)	0.0302 (5)
O3	−0.9224 (4)	−0.64212 (8)	−0.48404 (11)	0.0357 (5)
O4	−1.0484 (4)	−0.57597 (8)	−0.48219 (12)	0.0399 (6)
O5	−1.6352 (3)	−0.76622 (6)	−0.84294 (10)	0.0225 (4)
O6	−1.6401 (3)	−0.76115 (7)	−0.73414 (10)	0.0273 (5)
O7	−1.2967 (4)	−0.98367 (8)	−0.79260 (13)	0.0432 (6)
O8	−1.2219 (4)	−0.97059 (8)	−0.68762 (13)	0.0487 (7)
N1	−1.0273 (4)	−0.61152 (8)	−0.50966 (12)	0.0243 (6)
N2	−1.2896 (4)	−0.95904 (9)	−0.74454 (15)	0.0326 (6)
Molecule 2				
Si2	−2.08693 (12)	−1.04180 (3)	−0.99807 (4)	0.0233 (2)
C2′	−2.1194 (4)	−1.05034 (10)	−0.91157 (14)	0.0231 (6)
C3′	−1.9281 (4)	−1.06045 (9)	−0.86626 (13)	0.0197 (6)
C4′	−1.7800 (4)	−1.02350 (9)	−0.86284 (14)	0.0216 (6)
C5′	−1.7188 (4)	−1.01717 (10)	−0.92870 (14)	0.0249 (6)
C6′	−1.8774 (5)	−1.00283 (11)	−0.98686 (14)	0.0273 (7)
C7′	−2.3042 (5)	−1.01717 (12)	−1.0507 (2)	0.0366 (8)
C8′	−2.0289 (5)	−1.09754 (12)	−1.0329 (2)	0.0327 (7)
C9′	−1.9960 (4)	−1.10962 (10)	−0.78399 (14)	0.0213 (6)
C10′	−2.0300 (4)	−1.11281 (9)	−0.71567 (13)	0.0189 (6)
C11′	−2.0240 (4)	−1.15557 (10)	−0.68650 (14)	0.0226 (6)
C12′	−2.0482 (5)	−1.15904 (10)	−0.62179 (14)	0.0255 (6)
C13′	−2.0794 (4)	−1.11985 (11)	−0.58907 (14)	0.0229 (6)
C14′	−2.0934 (4)	−1.07756 (10)	−0.61783 (14)	0.0233 (6)
C15′	−2.0650 (4)	−1.07405 (10)	−0.68171 (14)	0.0222 (6)
C16′	−1.8016 (4)	−0.96570 (9)	−0.78298 (14)	0.0203 (6)
C17′	−1.8738 (4)	−0.91937 (10)	−0.77379 (14)	0.0201 (6)
C18′	−1.9697 (4)	−0.89255 (10)	−0.82578 (14)	0.0219 (6)
C19′	−2.0242 (4)	−0.84912 (11)	−0.81398 (15)	0.0248 (6)
C20′	−1.9853 (4)	−0.83264 (10)	−0.74944 (15)	0.0227 (6)
C21′	−1.8903 (5)	−0.85872 (10)	−0.69730 (15)	0.0259 (7)
C22′	−1.8363 (4)	−0.90196 (10)	−0.70932 (14)	0.0239 (6)
O1′	−1.9542 (3)	−1.06743 (7)	−0.79901 (9)	0.0215 (4)
O2′	−2.0033 (3)	−1.14188 (7)	−0.82085 (10)	0.0296 (5)
O3′	−2.1454 (4)	−1.09041 (9)	−0.49264 (12)	0.0466 (7)
O4′	−2.0620 (5)	−1.15995 (8)	−0.49249 (12)	0.0534 (8)
O5′	−1.8571 (3)	−0.98012 (6)	−0.84603 (9)	0.0207 (4)
O6′	−1.7008 (3)	−0.98670 (7)	−0.73966 (10)	0.0265 (5)
O7′	−2.1109 (4)	−0.76237 (8)	−0.78300 (13)	0.0415 (6)
O8′	−2.0334 (4)	−0.77571 (8)	−0.67804 (12)	0.0395 (6)
N1′	−2.0991 (4)	−1.12354 (10)	−0.51945 (13)	0.0285 (6)
N2′	−2.0461 (4)	−0.78704 (9)	−0.73618 (14)	0.0303 (6)
Molecule 3				
Si3	−0.55735 (12)	−0.45738 (3)	−0.48126 (4)	0.0231 (2)
C2*	−0.4401 (4)	−0.44620 (10)	−0.39343 (14)	0.0237 (6)
C3*	−0.5864 (4)	−0.43691 (9)	−0.35233 (13)	0.0200 (6)
C4*	−0.7288 (4)	−0.47467 (9)	−0.35133 (14)	0.0207 (6)
C5*	−0.8583 (4)	−0.48140 (10)	−0.41900 (14)	0.0253 (6)
C6*	−0.7564 (5)	−0.49633 (10)	−0.47378 (15)	0.0278 (7)
C7*	−0.3849 (5)	−0.48262 (11)	−0.52630 (15)	0.0307 (7)
C8*	−0.6558 (5)	−0.40343 (12)	−0.5219 (2)	0.0343 (8)
C9*	−0.4373 (4)	−0.38624 (10)	−0.26987 (14)	0.0198 (6)
C10*	−0.3285 (4)	−0.38098 (10)	−0.20022 (13)	0.0190 (6)
C11*	−0.2782 (4)	−0.33752 (10)	−0.17745 (15)	0.0239 (6)
C12*	−0.1755 (5)	−0.33087 (10)	−0.1135 (2)	0.0265 (7)
C13*	−0.1268 (4)	−0.36868 (11)	−0.07467 (14)	0.0240 (6)
C14*	−0.1738 (5)	−0.41226 (10)	−0.09596 (15)	0.0257 (6)
C15*	−0.2772 (4)	−0.41851 (10)	−0.15982 (14)	0.0233 (6)
C16*	−0.6221 (4)	−0.53393 (9)	−0.27299 (14)	0.0202 (6)
C17*	−0.5393 (4)	−0.58045 (10)	−0.26583 (14)	0.0210 (6)
C18*	−0.5187 (4)	−0.60638 (10)	−0.32015 (15)	0.0235 (6)
C19*	−0.4480 (4)	−0.64993 (10)	−0.31160 (15)	0.0250 (6)
C20*	−0.3969 (4)	−0.66711 (10)	−0.2480 (2)	0.0238 (6)
C21*	−0.4147 (4)	−0.64179 (10)	−0.19269 (15)	0.0254 (6)
C22*	−0.4877 (4)	−0.59865 (10)	−0.20232 (15)	0.0237 (6)
O1*	−0.4928 (3)	−0.42849 (7)	−0.28350 (9)	0.0213 (4)
O2*	−0.4680 (3)	−0.35483 (7)	−0.30846 (10)	0.0295 (5)
O3*	0.0387 (4)	−0.39639 (9)	0.02555 (11)	0.0436 (6)
O4*	0.0149 (4)	−0.32397 (9)	0.01429 (12)	0.0475 (7)
O5*	−0.6310 (3)	−0.51768 (6)	−0.33392 (9)	0.0222 (4)
O6*	−0.6735 (3)	−0.51438 (7)	−0.22891 (10)	0.0280 (5)
O7*	−0.3225 (4)	−0.73687 (8)	−0.28668 (12)	0.0408 (6)
O8*	−0.2489 (4)	−0.72485 (8)	−0.18143 (12)	0.0415 (6)
N1*	−0.0160 (4)	−0.36238 (10)	−0.00652 (12)	0.0287 (6)
N2*	−0.3172 (4)	−0.71287 (9)	−0.23814 (13)	0.0297 (6)
Molecule 4				
Si4	−0.58990 (12)	−0.20302 (3)	0.00950 (4)	0.0238 (2)
C2″	−0.6225 (4)	−0.19568 (10)	0.09640 (14)	0.0232 (6)
C3″	−0.4320 (4)	−0.18651 (10)	0.14124 (13)	0.0202 (6)
C4″	−0.2859 (4)	−0.22380 (9)	0.14349 (14)	0.0216 (6)
C5″	−0.2239 (5)	−0.22941 (10)	0.07769 (15)	0.0263 (7)
C6″	−0.3826 (5)	−0.24235 (11)	0.01898 (14)	0.0284 (7)
C7″	−0.8087 (5)	−0.22618 (12)	−0.0444 (2)	0.0348 (8)
C8″	−0.5286 (5)	−0.14680 (11)	−0.0222 (2)	0.0340 (8)
C9″	−0.4982 (4)	−0.13891 (9)	0.22578 (14)	0.0197 (6)
C10″	−0.5266 (4)	−0.13745 (9)	0.29548 (13)	0.0194 (6)
C11″	−0.5582 (4)	−0.09578 (10)	0.32247 (14)	0.0221 (6)
C12″	−0.5866 (4)	−0.09349 (10)	0.38662 (14)	0.0225 (6)
C13″	−0.5809 (4)	−0.13347 (10)	0.42172 (14)	0.0235 (6)
C14″	−0.5518 (5)	−0.17526 (10)	0.39606 (15)	0.0263 (7)
C15″	−0.5234 (4)	−0.17719 (10)	0.33238 (14)	0.0231 (6)
C16″	−0.3224 (4)	−0.28191 (10)	0.22147 (14)	0.0223 (6)
C17″	−0.4016 (4)	−0.32782 (9)	0.22811 (14)	0.0202 (6)
C18″	−0.4699 (4)	−0.35567 (10)	0.17355 (14)	0.0237 (6)
C19″	−0.5315 (4)	−0.39883 (10)	0.18260 (14)	0.0235 (6)
C20″	−0.5292 (4)	−0.41395 (10)	0.24610 (15)	0.0226 (6)
C21″	−0.4625 (4)	−0.38693 (10)	0.30133 (15)	0.0252 (6)
C22″	−0.4010 (4)	−0.34405 (10)	0.29157 (14)	0.0238 (6)
O1″	−0.4542 (3)	−0.18048 (7)	0.20942 (9)	0.0223 (4)
O2″	−0.5122 (3)	−0.10615 (7)	0.19011 (10)	0.0278 (5)
O3″	−0.5835 (5)	−0.16574 (9)	0.52346 (12)	0.0527 (8)
O4″	−0.6694 (4)	−0.09589 (8)	0.50912 (11)	0.0329 (5)
O5″	−0.3649 (3)	−0.26720 (6)	0.15846 (9)	0.0228 (4)
O6″	−0.2267 (3)	−0.26175 (7)	0.26713 (10)	0.0264 (5)
O7″	−0.6211 (4)	−0.48581 (8)	0.20876 (12)	0.0402 (6)
O8″	−0.6153 (4)	−0.47058 (8)	0.31143 (11)	0.0380 (6)
N1″	−0.6140 (4)	−0.13158 (9)	0.49008 (12)	0.0279 (6)
N2″	−0.5921 (4)	−0.46002 (9)	0.25604 (13)	0.0282 (6)

Table 2. *Interatomic distances* (Å) *and angles* (°) *for molecule 1 and selected torsion angles* (°) *for all molecules*

Si—C7	1.859 (4)	C13—C14	1.379 (4)
Si—C2	1.871 (3)	C13—N1	1.473 (4)
Si—C6	1.872 (3)	C14—C15	1.384 (4)
Si—C8	1.873 (3)	C16—O6	1.204 (4)
C2—C3	1.522 (4)	C16—O5	1.342 (3)
C3—O1	1.470 (3)	C16—C17	1.495 (4)
C3—C4	1.514 (4)	C17—C22	1.395 (4)
C4—O5	1.463 (3)	C17—C18	1.396 (4)

C4—C5	1.527 (4)	C18—C19	1.381 (4)
C5—C6	1.534 (5)	C19—C20	1.384 (4)
C9—O2	1.208 (4)	C20—C21	1.385 (4)
C9—O1	1.324 (3)	C20—N2	1.465 (4)
C9—C10	1.495 (4)	C21—C22	1.383 (4)
C10—C11	1.397 (4)	O3—N1	1.227 (3)
C10—C15	1.398 (4)	O4—N1	1.218 (3)
C11—C12	1.392 (4)	O7—N2	1.225 (4)
C12—C13	1.380 (4)	O8—N2	1.228 (4)
C7—Si—C2	110.8 (2)	O1—C3—C2	109.6 (2)
C7—Si—C6	113.3 (2)	C4—C3—C2	115.0 (2)
C2—Si—C6	103.83 (14)	O5—C4—C3	110.5 (2)
C7—Si—C8	110.2 (2)	O5—C4—C5	107.2 (2)
C2—Si—C8	108.81 (14)	C3—C4—C5	111.7 (2)
C6—Si—C8	109.7 (2)	C4—C5—C6	115.3 (3)
C3—C2—Si	109.1 (2)	C5—C6—Si	113.3 (2)
O1—C3—C4	107.6 (2)		

Molecule 1	
C6—Si—C2—C3	−44.1 (2)
Si—C2—C3—C4	61.3 (3)
O1—C3—C4—C5	168.5 (2)
C2—C3—C4—C5	−69.0 (3)
C3—C4—C5—C6	61.2 (3)
C4—C5—C6—Si	−49.8 (3)
O5—C16—C17—C18	−17.3 (4)
C14—C13—N1—O4	−161.9 (3)
C19—C20—N2—O7	0.6 (4)
C19—C20—N2—O8	−179.2 (3)
Molecule 2	
O5′—C16′—C17′—C18′	−6.4 (4)
C14′—C13′—N1′—O3′	7.4 (4)
C14′—C13′—N1′—O4′	−170.7 (3)
C19′—C20′—N2′—O7′	−8.2 (4)
C19′—C20′—N2′—O8′	170.1 (3)
Molecule 3	
O5*—C16*—C17*—C18*	−14.1 (4)
C14*—C13*—N1*—O4*	−175.0 (3)
C14*—C13*—N1*—O3*	4.9 (4)
C19*—C20*—N2*—O7*	−10.0 (4)
C19*—C20*—N2*—O8*	170.0 (3)
Molecule 4	
O5″—O16″—C17″—C18″	14.3 (4)
C14″—C13″—N1″—O3″	'1.7 (5)
C14″—C13″—N1″—O4″	− 163.5 (3)
C19″—C20″—N2″—O7″	9.5 (4)
C19″—C20″—N2″—O8″	−169.6 (3)

The title structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). Refinement was performed using *SHELXL*93 (Sheldrick, 1993), with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms. The figures were drawn using *ORTEP*II (Johnson, 1976) and the tables prepared using *SHELXL*93. All calculations were carried out on a VAXstation 4000VLC computer system.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Göttingen, Germany.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

White, J. M., Green, A. J. & Kuan, Y.-L. (1995). *J. Org. Chem.* **60**, 2734–2738.

White, J. M. & Kuan, Y.-L. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1195–1196.

White, J. M. & Robertson, G. B. (1992). *J. Org. Chem.* **57**, 4638–4644.

Acta Cryst. (1996). C**52**, 1496–1499

Methyl 9-Methyl-11-thioxo-8-oxa-10,12-diazatricyclo[7.3.1.0^{2,7}]trideca-2,4,6-triene-13-carboxylate

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Abstract

The title compound, $C_{13}H_{14}N_2O_3S$, represents a conformationally restricted pyrimidine analogue of 1,4-dihydropyridine-type calcium antagonists and was designed to probe the chemical and spatial requirements of the dihydropyridine binding site on the calcium channel. The phenyl ring is fixed in a pseudo-axial and perpendicular orientation with respect to the pyrimidine ring by an O-atom bridge. Each of the two fused six-membered rings assumes an approximate sofa conformation distorted towards a half-chair. The molecules are linked by hydrogen bonds to form chains.

Comment

As a continuation of our study on the structure–activity relationships within 1,4-dihydropyridines (and related compounds) as the most potent class of calcium channel antagonists (Goldmann & Stoltefuss, 1991), we have recently described a diastereoselective synthesis of oxygen-bridged pyrimidines, (1) (Světlik, Hanuš & Bella, 1991). By analogy with sulfur-bridged 1,4-dihydropyridines (Baldwin *et al.*, 1987), the calcium antagonist activity of the molecules (1) was confirmed in both *in vitro* and radioligand-binding experiments (Kettmann, Dřimal & Světlik, 1995). The relative stereochemistry of the molecules (1), especially the α-configuration of the methoxycarbonyl group, has been determined by NMR measurements. To check our conclusions and at the same time to determine the detailed