

2,2,4,4-Tetra-*tert*-butyl-1,3,5,2,4-benzotrioxadisilepine-7-carbaldehydeL. C. R. Andrade,^a J. A. Paixão,^{a*} M. J. M. de Almeida,^a
C. Siquet^b and F. Borges^c^aCEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-516 Coimbra, Portugal, ^bREQUIMTE, Departamento de Química Física, Faculdade de Farmácia, Universidade do Porto, Portugal, and ^cUnidade de Química Física Molecular, Departamento de Química Orgânica, Faculdade de Farmácia, Universidade do Porto, Portugal
Correspondence e-mail: jap@pollux.fis.uc.pt

Received 5 December 2005

Accepted 22 December 2005

Online 21 January 2006

The molecule of the title compound, C₂₃H₄₀O₄Si₂, features an approximate non-crystallographic C₂ symmetry axis. The aldehyde group is disordered over two positions with similar occupancies. The geometry of the isolated molecule was studied by *ab initio* quantum mechanical calculations employing a molecular orbital Hartree–Fock method. The calculations reproduce well the equilibrium geometry but slightly overestimate the value of the Si–O bond lengths of the trioxadisilepine ring.

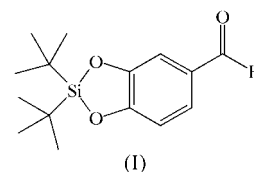
Comment

In conjunction with an ongoing project aimed at the synthesis of phenolic antioxidant agents (Silva *et al.*, 2001; Borges *et al.*, 2003), we are interested in the problem of suitable protection/deprotection protocols, which is one of the major challenges in organic synthetic chemistry.

Many of the methods for a successful total synthesis of a phenol-containing product depend not only on the correct strategy but also on the right choice of protecting groups to prevent side reactions. Most of the protective groups developed for alcohol protection are also applicable to the phenol function. In this context, protection of hydroxy groups by the formation of silyl ethers has been recognized as one of the most versatile since its introduction by Corey & Venkateswarlu (1972). Such protection is often selected either because of its ease of introduction or its general stability to basic and mildly acidic conditions (Sharma *et al.*, 2003). In addition, a large number of deprotection methods are available for its removal (Crouch, 2004).

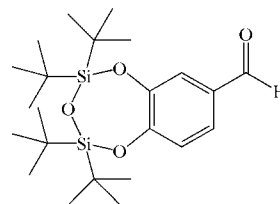
Silicon-based protecting groups have also been employed for catechol protection, the diethers being obtained by the methods described to protect the hydroxy group. Di-*tert*-butyldichlorosilane (tBu₂SiCl₂, DTBS) was one of the reagents used as a convenient protection for diol-like moieties (Trost & Caldwell, 1981; Trost *et al.*, 1983; Evans *et al.*, 1990). Therefore,

this reagent was used in a synthetic strategy in which the starting material 3,4-dihydroxybenzaldehyde would be protected by the formation of a dioxasilole five-membered ring, (I).



(I)

However, the results of spectroscopic analysis were not in agreement with this expected O-protected derivative, hence the need for elucidation of the structure through X-ray analysis. This revealed the formation of the title compound, (II), which possesses a trioxadisilepine seven-membered ring. This type of heterocyclic ring has already been obtained using catechol as starting material (Hanson *et al.*, 1986). An ORTEPII (Johnson, 1976) plot of (II) is shown in Fig. 1.



(II)

Most bond lengths are within the expected ranges (Allen *et al.*, 1987), with mean Csp³–Csp³, Csp³–Si4, C_{ar}–O2 and C_{ar}–C_{ar} (not including C6–C7) distances of 1.533 (9), 1.892 (4), 1.363 (5) and 1.382 (5) Å, respectively. Being part of the heptane ring, the C6–C7 bond length [1.402 (3) Å] is significantly longer than the average C_{ar}–C_{ar} distance. Two types of Si–O bonds can be distinguished in the heptane ring, *viz.* two Si–O(–C) bonds, with a common length of 1.651 (2) Å, and two Si–O(–Si) bonds, with an average value of 1.640 (3) Å. The structure refinement of (II) shows disorder in the aldehyde group, with interchange of the H and O

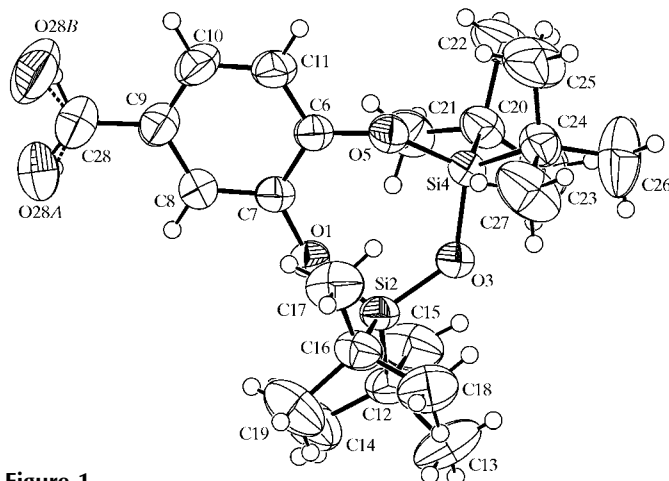


Figure 1

The molecular structure of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

positions; the refined occupancies are 0.568 (8) and 0.432 (8), respectively. This is probably the reason why very short C=O distances [1.118 (6) and 1.176 (7) Å] are observed in this group for both orientations. Large Si—O—C bond angles, of 137.83 (17) and 139.40 (17)°, confirm the proposal of Cragg & Lane (1984) that such values are characteristic of oxasilacycloalkanes. These values are greater than those found for several similar structures (Hanson *et al.*, 1986), including 2,2,4,4-tetraphenyl-2,4-disila-1,3,5-trioxa-6,7-benzocycloheptane, with an identical heptane ring. On the other hand, the Si—O—Si bond angle of 132.40 (17)° found for (II) is slightly smaller than the reported value of 134.9°. The three O atoms of the heptane ring are coplanar with the benzene group, the least-squares plane having a maximum deviation of 0.03 (2) Å. Atoms Si2 and Si4 are symmetrically displaced above [0.5799 (19) Å for Si2] and below [0.5307 (18) Å for Si4] this plane. Excluding the aldehyde group, an approximate non-crystallographic binary axis exists running from atom O3 towards the middle of the C6—C7 bond.

Owing to the absence of any strong donor group, cohesion of this crystal structure is mainly achieved by weak van der Waals interactions. No close contacts with suitable geometry to classify as weak hydrogen-bond interactions were found.

We have also performed quantum chemistry calculations of the optimized geometry of the isolated molecule to check whether such a calculation could accurately reproduce the conformation of the trioxadisilolepine ring. The *ab initio* calculations were performed with the program GAMESS (Schmidt *et al.*, 1993), using the Roothaan Hartree–Fock molecular orbital (MO) method. An extended 6-31G(*d,p*) basis set was used with tight conditions for convergence of both the self-consistent field (SCF) cycles and the maximum energy and density gradients at the final optimized geometry (10⁻⁵ atomic units). The code was executed in parallel on a cluster of 12 Pentium IV workstations running Linux.

The calculated equilibrium geometry of the molecule is well reproduced by the quantum mechanical calculations, with overall good agreement between the observed and calculated valence and torsion angles (Table 1). However, we have found that the calculations tend to slightly overestimate the Si—O bond lengths.

Experimental

3,4-Dihydroxybenzaldehyde, di-*tert*-butyldichlorosilane and 1-hydroxybenzotriazole were obtained from Sigma (Sintra, Portugal). All other reagents and solvents were of analytical grade and were purchased from Merck (Lisbon, Portugal). 3,4-Dihydroxybenzaldehyde (0.5 g, 3.62 mmol) was dissolved in a mixture of acetonitrile (3 ml) and triethylamine (1 ml). The aldehyde was then added to a reaction flask, flushed with nitrogen, containing di-*tert*-butyldichlorosilane (2 ml, 9.38 mmol) and 1-hydroxybenzotriazole (50 mg, 0.37 mmol) in solution in acetonitrile (3 ml) at 333 K. The reaction mixture was stirred for 2 h at 333 K. Diethyl ether (15 ml) was then added and the organic phase was washed with HCl (2 M, 3 × 10 ml), water (3 × 10 ml) and brine (3 × 10 ml). The organic phase was dried over Na₂SO₄ and evaporated. The crude product was purified by column chromatography (petroleum ether/diethyl ether, 2:1) to give 630 mg (yield 57%) of (II) (m.p. 366–368 K). ¹H NMR (CDCl₃, 300 MHz):

δ 9.83 (*s*, 1H), 7.44 (*d*, 1H, *J* = 2.02 Hz), 7.41 (*dd*, 1H, *J* = 2.12 and 8.13 Hz), 7.01 (*d*, 1H, *J* = 8.13 Hz), 1.10 (*s*, 36H). ¹³C NMR (CDCl₃, 75 MHz): δ 190.93 (CHO), 146.51, 151.88 (COSi), 131.34 (CCHO), 121.90, 122.03, 125.22 (C₆H₃), 27.92 [C(CH₃)₃], 21.41 [C(CH₃)₃]. MS (*m/z*): 436 (molecular peak), 379, 337, 295, 253 (base peak), 223.

Crystal data

C₂₃H₄₀O₄Si₂
M_r = 436.73
 Triclinic, *P* $\bar{1}$
a = 8.8451 (5) Å
b = 9.751 (3) Å
c = 16.1106 (10) Å
 α = 98.127 (8)°
 β = 90.392 (5)°
 γ = 107.899 (10)°
V = 1307.2 (4) Å³
Z = 2
D_x = 1.110 Mg m⁻³

Cu *K*α radiation
 Cell parameters from 25 reflections
 θ = 8.3–23.8°
 μ = 1.42 mm⁻¹
T = 291 (2) K
 Prism, colourless
 0.32 × 0.22 × 0.12 mm

Data collection

Enraf–Nonius MACH3 diffractometer
 ω –2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.773, *T_{max}* = 0.845
 5292 measured reflections
 5079 independent reflections
 3922 reflections with *I* > 2σ(*I*)

R_{int} = 0.020
 θ_{max} = 72.3°
h = –10 → 10
k = –12 → 11
l = 0 → 19
 3 standard reflections
 frequency: 180 min
 intensity decay: 0.1%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.048
wR(*F*²) = 0.148
S = 1.06
 5079 reflections
 285 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.8484P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0027 (4)

Table 1

Calculated and observed geometrical parameters (Å, °).

	Calculated	Observed
C6—C7	1.403	1.402 (3)
Si2—O1	1.669	1.6508 (19)
Si2—O3	1.661	1.6422 (17)
Si4—O3	1.657	1.6383 (17)
Si4—O5	1.674	1.6513 (19)
Si2—O3—Si4	131.96	132.40 (11)
Si2—O1—C7	138.93	137.83 (17)
Si4—O5—C6	139.70	139.40 (17)
C7—O1—Si2—O3	–62.83	–59.1 (3)
O1—Si2—O3—Si4	20.94	21.13 (18)
Si2—O3—Si4—O5	21.81	20.80 (19)
O3—Si4—O5—C6	–59.95	–56.7 (3)
Si4—O5—C6—C7	36.63	34.8 (4)
O1—C7—C6—O5	–4.21	–4.5 (4)

All H atoms were refined as riding on their parent atoms [C—H = 0.93 and 0.96 Å, and *U*_{iso}(H) = 1.2*U*_{eq}(C) and 1.5*U*_{eq}(methyl C)]. The disordered aldehyde group was refined using two components constrained to add to 100% occupancy.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge computing time provided by the Computational Physics Center of FCTUC at the CENTOPEIA parallel cluster. This work was supported by Fundação para a Ciência e Tecnologia. CS thanks FCT (SFRH/BD/7005/2001) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1028). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Borges, F., Lima, J. L. F. C., Pinto, I., Reis, S. & Siquet, C. (2003). *Helv. Chim. Acta*, **86**, 3081–3087.
- Corey, E. J. & Venkateswarlu, A. (1972). *J. Am. Chem. Soc.* **94**, 6190–6191.
- Cragg, R. H. & Lane, R. D. (1984). *J. Organomet. Chem.* **267**, 1–71.
- Crouch, R. D. (2004). *Tetrahedron*, **60**, 5833–5871.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Evans, D. A., Kaldor, S. W., Jones, T. K., Clardy, J. & Stout, T. J. (1990). *J. Am. Chem. Soc.* **112**, 7001–7031.
- Hanson, A. W., McCulloch, A. W. & McInnes, A. G. (1986). *Can. J. Chem.* **64**, 1450–1457.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Schmidt, M. W., Baldrige, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. J., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S., Windus, T. L., Dupuis, M. & Montgomery, J. A. (1993). *J. Comput. Chem.* **14**, 1347–1363.
- Sharma, G. V. M., Srinivas, B. & Krishna, P. R. (2003). *Tetrahedron Lett.* **44**, 4689–4691.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Silva, A. M. S., Santos, C. M. M., Cavaleiro, J. A. S., Tavares, H. R., Borges, F. & Silva, F. A. M. (2001). *Magnetic Resonance in Food Science – A View to the Future*, pp. 110–116. Cambridge, England: Royal Society of Chemistry.
- Spek, A. L. (1997). *HELENA*. University of Utrecht, The Netherlands.
- Trost, B. M. & Caldwell, C. G. (1981). *Tetrahedron Lett.* **22**, 4999–5002.
- Trost, B. M., Caldwell, C. G., Murayama, E. & Heissler, D. (1983). *J. Org. Chem.* **48**, 3252–3265.