

- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- PATEL, G. N., DUESLER, E. N., CURTIN, D. Y. & PAUL, I. C. (1980). *J. Am. Chem. Soc.* **102**, 461–466.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- THOZET, A., RAMILARISOA, H., PERRIN, M., BAVOUX, C. & MEALLIER, P. (1991). *Acta Cryst.* **C47**, 121–123.
- WHULER, A., SPINAT, P. & BROUTY, C. (1984). *Acta Cryst.* **C40**, 693–696.

*Acta Cryst.* (1991). **C47**, 126–129

## Structure of a Highly Crowded Linear Trisilane

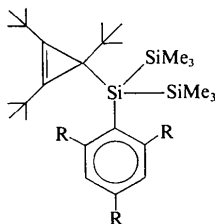
BY M. PONTIER JOHNSON, DHANANJAY B. PURANIK AND MARK J. FINK

*Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA*

(Received 29 July 1989; accepted 6 April 1990)

**Abstract.** Hexamethyl-2-(1,2,3-tri-*tert*-butylcyclopropenyl)-2-(2,4,6-triisopropylphenyl)trisilane, C<sub>36</sub>H<sub>68</sub>Si<sub>3</sub>, *M<sub>r</sub>* = 585.2, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 15.907 (2), *b* = 11.537 (3), *c* = 20.928 (3) Å, β = 94.31 (1)°, *V* = 3830 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.02 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 1.40 cm<sup>-1</sup>, *F*(000) = 1304, *T* = 298 K, *R* = 0.043 for 2115 unique reflections [*I* ≥ 3σ(*I*)]. The molecular geometry of this compound is distinguished by extreme crowding resulting in long Si—Si [2.441 (2) and 2.464 (2) Å] and Si—C [1.973 (4) and 1.988 (4) Å] bonds about the central Si atom. The Si—Si—Si angle is 92.60 (7)°, significantly compressed from a tetrahedral value. A number of short non-bonding contacts between peripheral groups (≤ 3.5 Å) are observed.

**Introduction.** Hexamethyl-2-(1,2,3-tri-*tert*-butylcyclopropenyl)-2-(2,4,6-triisopropylphenyl)trisilane (*R* = isopropyl, shown below), is a photochemical source of highly hindered silylenes and silacyclobutadienes (Puranik & Fink, 1989). This highly crowded molecule is unusual because of the juxtaposition of extremely bulky groups at the central Si atom. An X-ray structure determination was undertaken in order to explore the structural consequences of the steric crowding in this molecule, and to present comparisons with the structures of two closely similar compounds where *R* = H and Me (Puranik, Johnson & Fink, 1989).



**Experimental.** A colorless plate-shaped crystal, 0.40 × 0.40 × 0.17 mm, was obtained from ethanol–hexane; intensity data collected on an Enraf–Nonius CAD-4 diffractometer at 298 K, Mo *K*α radiation (graphite monochromator), lattice parameters from setting of 25 reflections with 4 < θ < 13°; ω–2θ scans, with 1 ≤ 2θ ≤ 50°; scan width (0.8 + 0.2tanθ)°; 0 ≤ *h* ≤ 18, 0 ≤ *k* ≤ 13, –24 ≤ *l* ≤ 24; 6975 total reflections, 6457 unique, 2115 observed with *I* ≥ 3σ(*I*); 2.2% variation in three standard reflections measured every 7200 s; Lorentz–polarization corrections made; absorption corrections based on ψ scans of five reflections near χ = 90 (min. and max. transmission factors are 0.97 and 0.99, respectively); linear decay correction applied to data; *R*<sub>int</sub> = 0.026. The structure was solved by direct methods using *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) in the *Structure Determination Package* (Frenz, 1985); refined on *F* by full-matrix least squares with minimization [Σ(|*F<sub>o</sub>*| – |*F<sub>c</sub>*|)<sup>2</sup>/Σ*w*(*F<sub>o</sub>*)<sup>2</sup>]<sup>1/2</sup>, *w* = 1/σ<sup>2</sup>*F*<sup>2</sup> using the same program. All non-H atoms were refined anisotropically; H atoms were located in a difference map and included as fixed contributions riding on attached C atoms with isotropic thermal parameters 1.3 times those of respective C atoms; the remainder of the H atoms were placed in calculated positions and treated as above. The refinement is not based on a model which includes disorder. The non-H atoms with high thermal parameters, C(15), C(16), C(17), C(29), C(29*A*), C(29*B*), and associated H atoms were removed after final refinement, followed by a reexamination of the difference Fourier map. The Δ*F* map revealed no additional electron density which could be attributed to the presence of disorder of the associated *tert*-butyl or *para*-isopropyl groups in question. Reassignment of the C atoms followed by



2.34 Å (Armitage, 1982). The extreme steric requirements of the aromatic and cyclopropene substituents are also responsible for the small Si—Si—Si bond angle of 92.60 (7)°.

Comparisons of selected bond parameters with two closely analogous cyclopropenyltrisilanes, where R = H and Me, are shown in Table 3. The three trisilanes form a series in which the *ortho* and *para* aromatic substituents become progressively larger. The size of the *ortho* substituent profoundly affects the degree of steric crowding at the central Si atom. It is seen that all bond lengths at Si(1) uniformly increase with the size of the *ortho* substituent. A parallel compression of the Si—Si—Si angle is also found with increasing size of the *ortho* substituents.

The steric crowding at Si(1) also results in some distortion of the aromatic ring in the title compound. The ring C atoms deviate significantly from planarity

Table 3. Comparison of selected bond lengths (Å) and angles (°) for (2,4,6-*R*<sub>3</sub>C<sub>3</sub>H<sub>3</sub>)('Bu<sub>3</sub>C<sub>3</sub>)Si(SiMe<sub>3</sub>)<sub>2</sub>

R	d(Si—aryl)	d(Si—(cyclopropenyl))	d(Si—Si)	θ(Si—Si—Si)
H*	1.893 (5)	1.940 (4)	2.396 (2), 2.398 (2)	102.09 (7)
Me*	1.940 (4)	1.959 (4)	2.426 (2), 2.455 (2)	93.97 (6)
<i>i</i> -Pr	1.973 (4)	1.988 (4)	2.441 (2), 2.464 (2)	92.60 (7)

\* Puranik, Johnson & Fink (1989).

Table 4. Non-bonding contacts (Å) for the title compound

Intramolecular (≤ 3.5 Å)			
C(22)···C(25)	3.291 (9)	C(26)···C(28A)	3.44 (1)
C(24)···C(30)	3.368 (9)	C(27)···C(28)	3.418 (8)
Intermolecular (≤ 4.0 Å)			
C(12)···C(26)	3.891 (9)	C(22)···C(29A)	3.91 (1)
C(19)···C(29A)	3.87 (1)	C(23)···C(29B)	3.84 (1)

( $\chi^2 = 0.32$  relative to the mean plane) and assume a boat-like conformation. Within the ring, longer C—C bond distances are observed to the silicon-bearing carbon. Thus, C(1)—C(2) and C(1)—C(6) are 1.413 (5) and 1.415 (5) Å, respectively, as compared to the analogous distances to the *para* carbon which are 1.380 (6) [C(3)—C(4)] and 1.356 (7) Å [C(4)—C(5)]. The extended bond distances at C(1) are certainly due to repulsive interactions between the large silyl substituent and the *ortho*-isopropyl groups of the aromatic ring.

A number of short intramolecular and intermolecular non-bonding contacts are also evident in the title compound. The shortest intramolecular contacts are between peripheral methyl groups on the *tert*-butyl, trimethylsilyl, and *ortho*-isopropyl groups (Table 4). Some short intermolecular contacts are also present and are listed in Table 4.

It is likely that the high thermal parameters observed for the *para*-isopropyl and one of the vinylic *tert*-butyl groups can be attributed to the packing of the molecules in the crystal. The *para*-isopropyl group (Fig. 2) is oriented in a manner which could allow movement of the group, but not actual rotational disorder. The *tert*-butyl group in question also appears to exhibit movement allowed by packing in the crystal, but again, there is no evidence for true rotational disorder.

We thank the Tulane Committee on Research and the Louisiana Board of Regents for support of this work.

#### References

- ARMITAGE, D. A. (1982). *Comprehensive Organometallic Chemistry*, Vol. 2, edited by G. WILKINSON, F. G. A. STONE & E. W. ABEL. New York: Pergamon.
- FRENZ, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.

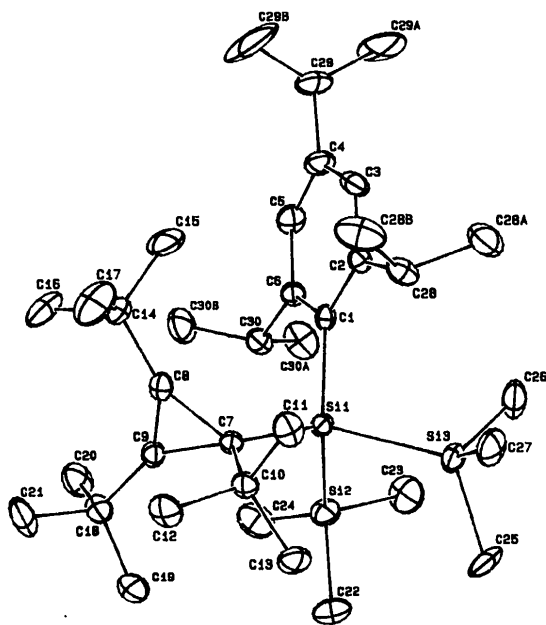


Fig. 1. ORTEP drawing of title compound with atom labeling; thermal ellipsoids are at the 50% probability level.

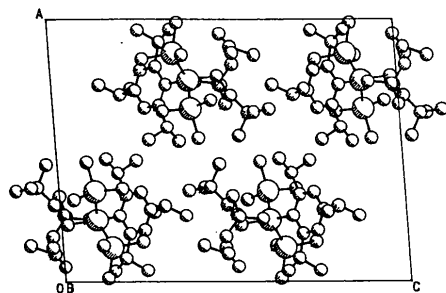


Fig. 2. Packing diagram view along the *b* axis.

- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- PURANIK, D. B. & FINK, M. J. (1989). *J. Am. Chem. Soc.* **111**, 5951–5952.
- PURANIK, D. B., JOHNSON, M. P. & FINK, M. J. (1989). *Organometallics*, **8**, 770–777.
- WEIDENBRUCH, M., BLINTJER, B., PETERS, K. & VON SCHNERING, H. G. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 1129–1131.

*Acta Cryst.* (1991). **C47**, 129–132

## Structure of the Naturally Occurring Sesquiterpene Lactone 8-Epiisolipidiol

BY U. RYCHLEWSKA

*Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*

AND W. KISIEL

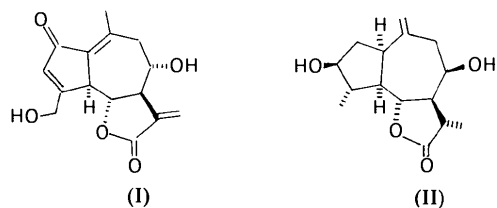
*Department of Phytochemistry, Institute of Pharmacology, Polish Academy of Sciences, Smętna 12, 31-343 Kraków, Poland*

(Received 11 September 1989; accepted 7 March 1990)

**Abstract.** Decahydro-4,8-dihydroxy-3,9-dimethyl-6-methyleneazuleno[4,5-*b*]furan-2(3*H*)-one, C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>,  $M_r = 265.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 5.755$  (1),  $b = 13.891$  (2),  $c = 17.511$  (2) Å,  $V = 1399.9$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.25$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 0.65$  mm<sup>-1</sup>,  $F(000) = 572$ ,  $T = 295$  K,  $R = 0.055$ ,  $wR = 0.070$  for 1685 observed reflections. The three-ring guaianolide system contains an *exo*-methylene-cycloheptane moiety *cis*-fused with the cyclopentane [at C(1)—C(5)] and *trans*-annelated with the  $\alpha$ -methyl- $\gamma$ -lactone [at C(6)—C(7)]. The two five-membered rings are in envelope conformations while the seven-membered ring is about midway between chair and twist-chair forms. The secondary hydroxyl groups are at C(3) and C(8), and are both  $\beta$ -oriented; they participate in intermolecular hydrogen bonds, O(8) both as a donor and an acceptor, and O(3) as a donor only.

**Introduction.** Chemotaxonomic studies are becoming increasingly important in the classification of plants. So far from the plants of the tribe *Lactuceae* (*Compositae* family) predominantly guaiane-type sesquiterpene lactones related to lactucin (I) have been isolated. Recently a series of structurally related 8 $\beta$ -hydroxyguaian-6,12-olides with additional oxygen functions at C(3) have been isolated from *Crepis* species (Barbetti, Casinovi, Santurbano & Longo, 1979; Kisiel, 1983*a, b*, 1984), *Andryala* (Bohlmann & Gupta, 1982; Massanet, Collado, Macias, Luis & Vergara, 1984), *Ixeris* (Nishimura, Miyase, Ueno, Noro, Kuroyanagi & Fukushima, 1985) and

*Prenanthes* (Miyase, Yamada & Fukushima, 1987). The presence of these guaianolides in plants of the tribe *Lactuceae* might be of chemotaxonomical importance, since their C(8) epimers appear mostly in plants of the tribes *Cynareae*, *Vernoniaeae* and *Mutisieae*. 8-Epiisolipidiol (II) was obtained for the first time from *Crepis capillaris* (L.) Wallr. (Kisiel, 1983*a*), and its 8 $\alpha$ -hydroxy analogue was isolated from *Amberboa lippii* D. C. (*Cynareae*) (Gonzalez, Garcia Marrero & Breton, 1970). An initial molecular structure, (II), was proposed for 8-epiisolipidiol based on chemical and spectroscopic methods (Kisiel, 1983*a*). Confirmation of the structure was sought through crystallographic analysis.



**Experimental.** 8-Epiisolipidiol (II) was extracted from the aerial parts of *Crepis capillaris* (L.) Wallr. with ethanol and isolated by silica-gel column chromatography.

A crystal approximately 0.2 × 0.3 × 0.3 mm, obtained from methanol solution, was used for X-ray analysis. Syntex P2<sub>1</sub> diffractometer,  $\theta$ -2 $\theta$  scan, variable scan rate, graphite-monochromated Cu  $K\alpha$  radiation, cell parameters by least-squares refinement