

Silacyclopropene Ring Structure; X-Ray Crystal Structure of 1,1-Dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene

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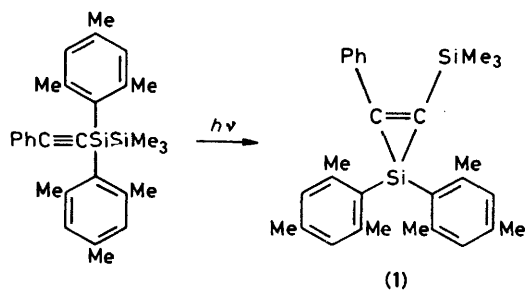
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An X-ray crystal structure analysis of the title compound (1) shows the following notable features of the silacyclopropene ring $\angle \text{CSiC} = 43.5(1)^\circ$, $\angle \text{SiCC} = 69.8(1)$ and $66.7(1)^\circ$, C–C = 1.349(3), and Si–C = 1.800(2) (remarkably short) and 1.839(2) Å; significant deviation of the ring from C_2 symmetry may be due to the effect of substituents on the carbon atoms.

The synthesis of a stable silacyclopropene ring has challenged chemists for many years. We have recently demonstrated that photolysis of 1-phenylethynyl- and 1-trimethylsilylethynyl-1,1-dimesityltrimethylsilane results in the formation of a stable silacyclopropene.¹ We now report the first X-ray crystallographic study of 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (1). Colourless crystals of (1) suitable for X-ray analysis were obtained by recrystallization from ethanol.

Crystal data: $C_{29}H_{36}Si_2$, $M = 440.78$, monoclinic, space group $P2_1/n$, $a = 14.719(7)$, $b = 17.576(7)$, $c = 10.659(4)$ Å, $\beta = 96.70(3)^\circ$, $U = 2739(2)$ Å³, $D_c = 1.069$ g cm⁻³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.35$ cm⁻¹. All unique diffraction maxima with



$2\theta \leq 50^\circ$ were recorded on a four-circle diffractometer using graphite-monochromated Mo- $K\alpha$ radiation. Of the 4832 reflections surveyed 3578 were judged as observed [$I > 3\sigma(I)$]. The structure was solved using MULTAN.² Block-diagonal least-squares refinements with anisotropic temperature factors for non-hydrogen atoms and isotropic for hydrogen atoms converged to a standard R value of 0.052.†

The molecular structure of (1), and important bond lengths and angles, are given in Figure 1. The molecule has an approximate two-fold axis, except for the phenyl and the trimethylsilyl groups. The dihedral angle [$82.4(1)^\circ$] between the plane of the silacyclopropene ring and the plane through Si(1), C(3), and C(12) deviates from 90° , probably owing to steric repulsion between the bulky mesityl groups. A corresponding value of 89.0° is found in dimethyldispiro(bicyclo[4.1.0]heptane-7,2'-silacyclopropane-3''-bicyclo[4.1.0]heptane).³ The silacyclopropene ring and the phenyl ring are almost coplanar, with a dihedral angle of $6.5(1)^\circ$. The devia-

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

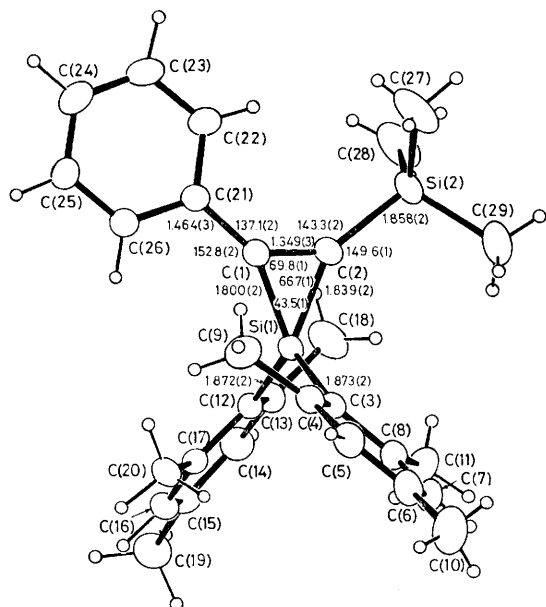


Figure 1. The molecular structure of 1,1-dimesityl-2-phenyl-3-trimethyl-1-silacyclopropene. Important bond angles and non-bonded distances are: C(1)–Si(1)–C(3) 123.2(1), C(1)–Si(1)–C(12) 118.4(1), C(2)–Si(1)–C(3) 117.4(1), C(2)–Si(1)–C(12) 123.5(1), and C(3)–Si(1)–C(12) 113.6(1) $^\circ$; C(1) . . . C(9) 3.426(4), C(2) . . . C(18) 3.337(4), C(3) . . . C(20) 3.311(3), C(11) . . . C(12) 3.374(4), C(9) . . . C(21) 3.890(4), C(9) . . . C(26) 3.808(4), Si(2) . . . C(18) 3.982(3), and C(18) . . . C(28) 3.774(5) Å.

tions of the C(21) and Si(2) atoms from the plane of the silacyclopropene ring are -0.09 and 0.122 Å, respectively, to reduce intramolecular repulsion.

Most of the silacyclopropene ring dimensions, the C(1)–Si(1)–C(2) angle [$43.5(1)^\circ$], the mean value of two Si–C–C angles [$68.3(1)^\circ$], and the C(1)–C(2) [$1.349(3)$ Å] and Si(1)–C(2) [$1.839(2)$ Å] bonds, are compatible with those of silacyclopropene evaluated by the SCF method;⁴ 42.5 , 68.75° , and 1.332 and 1.838 Å respectively. However, the Si(1)–C(1) bond [$1.800(2)$ Å] is much shorter than that obtained by the SCF method.⁴ Significant differences between the Si(1)–C(1) and Si(1)–C(2) bond lengths, and between the Si(1)–C(1)–C(2) and Si(1)–C(2)–C(1) angles may be due to the effect of substituents on the C(1) and C(2) atoms.

The planes of the six-membered rings, C(3)–C(8) and C(12)–C(17), of the mesityl groups are at right angles to one another, $89.4(1)^\circ$.

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