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Structure of 3,4-Bis(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene

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Abstract. $C_{14}H_{24}Si_2$, $M_r = 248.5$, orthorhombic, $Pna2_1$, $a = 23.296$ (5), $b = 9.447$ (2), $c = 7.227$ (2) Å, $V = 1590.5$ Å³, $F(000) = 544$, $\rho_{calc} = 1.04$ Mg m⁻³ ($Z = 4$), $\mu(Cu K\alpha) = 1.75$ mm⁻¹. Final $R = 0.065$ for 1595 reflections. Systematic absences for $0kl$, $k + l = 2n + 1$, and $h0l$, $h = 2n + 1$, establish the space group as either $Pna2_1$ or $Pnma$. The former was shown to be correct in the structure determination.

Introduction. The title compound (Hillard & Vollhardt, 1977), which was of interest as a precursor in our investigation of substituted *o*-xylylene compounds, was recrystallized from ether–methanol at 253 K as colorless crystals, m.p. 317 K. The purpose of determining the structure was threefold: first, the title compound is a unique example of a strained aromatic in which the strain is due to the small fused ring as well as to the bulky *ortho* substituents; second, the structure constitutes the first crystal structure report of an *ortho*-bis(trimethylsilyl)benzene; third, it permits comparison of the steric effect of *ortho-tert*-butyl groups with that of *ortho*-trimethylsilyl groups.

The cell constants were obtained by a least-squares fit to the automatically centered settings for 15 reflections on a Syntex $P2_1$ automated diffractometer equipped with a graphite monochromator (Cu $K\alpha$, $\lambda = 1.54178$ Å). Data collection was started on a crystal of approximate dimensions $0.75 \times 0.45 \times 0.35$ mm using the θ - 2θ scan mode for the h,k,l octant out to 2θ of 142° . The variable scan option was used at 4 – 29.3°

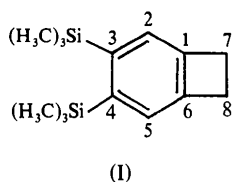
min⁻¹. The background scan time/total scan time was set at 0.5. Three standard reflections were monitored every 57 reflections. After 1128 reflections had been collected, the standards had dropped by about 33%. A second crystal ($0.70 \times 0.45 \times 0.30$ mm) was mounted and data collection was resumed using the same data-collection parameters, except that the variable scan rate was increased to 8 – 29.3° min⁻¹. Roughly 500 reflections were retaken with the second crystal to average in the first crystal. The standards of the second crystal had deteriorated about 13% at the end of the data collection. After the data were corrected for crystal decay and Lorentz and polarization effects, the data were averaged. Of the 1644 unique reflections, 1595 were considered observed at the $1.96\sigma(I)$ level and were used in the data refinement.

The structure was solved by the *MULTAN* program (Germain, Main & Woolfson, 1971). The E statistics indicated that the space group might be noncentrosymmetric. The molecule was not expected to exhibit symmetry in the crystal because of the variety of relative orientations available to the six methyl groups about the Si–CH₃ bonds. Successful refinement in the noncentrosymmetric case gave $Pna2_1$ for the space group. Most of the H atom positions were located in difference maps, allowing all H positions to be calculated using standard techniques. Full-matrix least-squares refinements on the positions and anisotropic thermal parameters of the non-hydrogen atoms and the isotropic thermal parameters of the ring H atoms converged to the agreement factors: $R = 0.065$, $R_w = 0.080$, and $[\sum w(|F_{obs}| - |F_{calc}|)^2 / (m - n)]^{1/2}$, where m is the number of observations and n is the number of

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variables, was 1.82.* The scattering curves were taken from the analytical expression in *International Tables for X-ray Crystallography* (1974). The positions of the methyl H atoms were fixed, and they were assigned a fixed isotropic thermal parameter of 9.0 \AA^2 . The observed C—H distances fell within an exceptionally narrow range. The final difference map showed no peak greater than 26% of an ideal H atom.

Discussion. The structural formula is shown in (I), and a stereoscopic view of a single molecule, together with the atom numbering used in the analysis, is given in Fig. 1. Positional parameters as well as bond lengths and angles are listed in Tables 1 and 2.†



The molecular geometry of this compound is consistent with those of other bicyclo[4.2.0]octa-1,3,5-trienes (Mak & Trotter, 1964; MacDonald, Lawrence & Cava, 1965; Hardgrove, Templeton & Templeton, 1968; Lawrence & MacDonald, 1969; Allen & Trotter, 1970*a,b*; Crawford & Marsh, 1973; Thummel, Korp, Bernal, Harlow & Soulen, 1977; Korp, Thummel & Bernal, 1977; Webber, Petcher & Loosli, 1977; Winter & Straub, 1978; Hart, Jeffares, Teuerstein & Ward, 1978; Thummel & Nutakul, 1978; Straub, Döring & Winter, 1979; Korp & Bernal 1979; Ward, 1980; Hart, Teuerstein, Jeffares, Kung & Ward, 1980). The average Si—C(methyl) bond lengths are in agreement with recently published values (Hursthouse & Malik, 1979). However, the Si—C(ring) bonds are some-

* The function minimized was $\sum w|F_o| - |F_c|^2$, $w = \{[\sigma(F_o)]^2 + [0.04|F_o|^2]^{-1}\}$; $R = \sum |F_{obs}| - |F_{calc}| / \sum |F_{obs}|$; $R_w = [\sum w|F_{obs}| - |F_{calc}|^2 / \sum w|F_{obs}|^2]^{1/2}$.

† Lists of structure factors, anisotropic thermal parameters, bond distances and angles including H atoms, and a stereoscopic view of the packing in (I) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35655 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

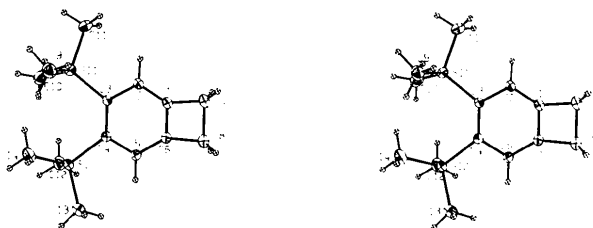


Fig. 1. Stereoscopic view of a single molecule of $C_{14}H_{24}Si_2$.

Table 1. Final atomic coordinates for (I) in fractions of the unit-cell edge

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} (a_i \cdot a_j)$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
Si(1)	0.40191 (4)	0.02662 (9)	0.0000*	3.98 (4)
Si(2)	0.32130 (4)	0.36481 (10)	0.0821 (3)	3.98 (4)
C(1)	0.5208 (1)	0.3433 (4)	0.0355 (6)	3.73 (14)
C(2)	0.4934 (1)	0.2146 (3)	0.0237 (6)	3.76 (13)
C(3)	0.4324 (1)	0.2109 (3)	0.0281 (5)	3.25 (12)
C(4)	0.4013 (1)	0.3403 (4)	0.0447 (7)	3.37 (13)
C(5)	0.4312 (2)	0.4704 (3)	0.0525 (6)	3.75 (13)
C(6)	0.4907 (2)	0.4694 (3)	0.0461 (5)	3.59 (15)
C(7)	0.5791 (2)	0.4169 (5)	0.0384 (7)	4.89 (18)
C(8)	0.5448 (2)	0.5594 (5)	0.0496 (6)	4.54 (16)
C(9)	0.3717 (2)	0.0050 (6)	-0.2388 (9)	6.27 (25)
C(10)	0.3496 (3)	-0.0227 (5)	0.1825 (12)	6.99 (30)
C(11)	0.4609 (2)	-0.1085 (4)	0.0144 (10)	6.03 (23)
C(12)	0.3045 (2)	0.3396 (5)	0.3321 (9)	5.81 (22)
C(13)	0.3009 (2)	0.5516 (5)	0.0179 (13)	7.11 (28)
C(14)	0.2728 (2)	0.2530 (7)	-0.0631 (12)	7.29 (31)
H(2)	0.5163	0.1259	0.0117	
H(5)	0.4097	0.5612	0.0622	
H(7A)	0.6030	0.3962	0.1508	
H(7B)	0.6028	0.4053	-0.0748	
H(8A)	0.5509	0.6144	0.1657	
H(8B)	0.5500	0.6225	-0.0600	
H(9A)	0.3598	-0.1086	-0.2544	
H(9B)	0.4015	0.0314	-0.3352	
H(9C)	0.3373	0.0672	-0.2575	
H(10A)	0.3294	0.0413	0.2515	
H(10B)	0.3699	-0.0839	0.2719	
H(10C)	0.3186	-0.0800	0.1179	
H(11A)	0.4838	-0.0931	0.1309	
H(11B)	0.4889	-0.1051	-0.0915	
H(11C)	0.4397	-0.2018	0.0081	
H(12A)	0.3217	0.2482	0.3723	
H(12B)	0.2620	0.3425	0.3500	
H(12C)	0.3207	0.4182	0.4087	
H(13A)	0.3073	0.5767	-0.1147	
H(13B)	0.3274	0.6235	0.0883	
H(13C)	0.2609	0.5760	0.0537	
H(14A)	0.2700	0.2807	-0.2127	
H(14B)	0.2330	0.2601	-0.0147	
H(14C)	0.2864	0.1533	-0.0590	

* The z coordinate of Si(1) was held constant to define the origin in that direction.

what elongated, as is the $C_{ar}-C_{ar}$ ring bond between the two $Si(Me)_3$ groups. In general, the phenomenon of bond elongation observed in *ortho*-di-*tert*-butyl-substituted aromatic rings has been attributed to steric interaction between the bulky groups (Visser & Vos, 1971*a,b*; Stam, 1972). The distortions observed for (I) are logically due to similar steric interactions since no such distortions were observed in *p*-bis(trimethylsilyl)benzene (Menczel & Kiss, 1975).

The bicyclo ring system is planar, with all C atoms lying within four e.s.d.'s of the best plane. The two Si atoms, however, lie off the plane by an average of 0.167 \AA , with one above and one below. The twisting of the trimethylsilyl groups to avoid each other is also

Table 2. Bond distances (Å) and angles (°)

Si(1)—C(3)	1.891 (3)	C(1)—C(6)	1.384 (5)
Si(1)—C(9)	1.875 (6)	C(1)—C(7)	1.526 (5)
Si(1)—C(10)	1.854 (8)	C(2)—C(3)	1.421 (5)
Si(1)—C(11)	1.878 (5)	C(3)—C(4)	1.426 (5)
Si(2)—C(4)	1.897 (3)	C(4)—C(5)	1.415 (5)
Si(2)—C(12)	1.864 (7)	C(5)—C(6)	1.387 (5)
Si(2)—C(13)	1.886 (5)	C(6)—C(8)	1.520 (5)
Si(2)—C(14)	1.869 (7)	C(7)—C(8)	1.568 (6)
C(1)—C(2)	1.376 (5)		
C(3)—Si(1)—C(9)	109.9 (2)	C(6)—C(1)—C(7)	93.3 (3)
C(3)—Si(1)—C(10)	113.7 (2)	C(3)—C(2)—C(1)	119.0 (3)
C(3)—Si(1)—C(11)	110.1 (2)	C(4)—C(3)—Si(1)	127.3 (3)
C(9)—Si(1)—C(10)	112.4 (3)	C(4)—C(3)—C(2)	119.3 (3)
C(9)—Si(1)—C(11)	104.6 (2)	Si(1)—C(3)—C(2)	113.3 (2)
C(10)—Si(1)—C(11)	105.7 (3)	C(5)—C(4)—Si(2)	111.9 (3)
C(4)—Si(2)—C(12)	109.2 (2)	C(5)—C(4)—C(3)	119.8 (3)
C(4)—Si(2)—C(13)	109.1 (2)	Si(2)—C(4)—C(3)	128.1 (3)
C(4)—Si(2)—C(14)	116.4 (2)	C(6)—C(5)—C(4)	119.0 (3)
C(12)—Si(2)—C(13)	107.7 (3)	C(8)—C(6)—C(1)	93.6 (3)
C(12)—Si(2)—C(14)	110.2 (3)	C(8)—C(6)—C(5)	145.5 (3)
C(13)—Si(2)—C(14)	103.8 (3)	C(1)—C(6)—C(5)	120.9 (3)
C(2)—C(1)—C(6)	121.9 (3)	C(8)—C(7)—C(1)	86.4 (3)
C(2)—C(1)—C(7)	144.7 (4)	C(6)—C(8)—C(7)	86.6 (3)

observable in the Si(1)—C(3)—C(4)—Si(2) torsion angle of 10.7°. The disposition of the methyl groups on the Si atoms is such that steric interactions are minimized. No strong intermolecular forces are observed.

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17β-Hydroxy-17α-methyl-4,9,11-estratrien-3-one

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Abstract. C₁₉H₂₄O₂, *M_r* = 284, monoclinic, *P*2₁, *Z* = 4, *a* = 7.533 (1), *b* = 19.043 (3), *c* = 10.891 (1) Å, β = 93.07 (9)°, *V* = 1560.1 Å³, *d_x* = 1.21 Mg m⁻³. The final *R* value is 0.03 for 2011 independent reflexions

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measured on a Siemens diffractometer using the five-points method. The conformations of the two independent molecules are very different, particularly on the *A* side of the steroid.

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