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CRYSTAL STRUCTURE OF TRIS(*Z*-TRIMETHYLSILYLPROP-1-ENYL)-BORANE, $[CH_3CH{=}CSi(CH_3)_3]_3B$

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Summary

The structure of tris(*Z*-trimethylsilylprop-1-enyl)borane was determined by single-crystal X-ray diffraction. Coordination about boron is trigonal planar with an average C–B–C angle of exactly 120.0°. Crystal data: $C_{18}H_{39}BSi_3$, M_r 350.6; space group $P\bar{1}$; a 10.311(3), b 13.693(3), c 19.033(3) Å; α 70.592(17)°, β 85.426(21)°, γ 79.628(21)°; U 2492.4 Å^3; $Z = 4$, D_c 0.934 g cm^{-3}, Mo-K_α radiation, λ 0.71069 Å; μ Mo-K_α 1.83 cm^{-1}; $F(000) = 776$, T 20 °C, $R = 0.061$ calculated from 3422 observed reflections.

Introduction

The $[CH_3CH{=}CSi(CH_3)_3]_3B$ is a white air-stable solid whose preparation has been described elsewhere [1]. The ^{11}B, ^{13}C, and ^{1}H NMR spectra suggested a possible bonding of the central boron atom to the silicon bearing olefinic carbon in each of the vinyl groups. In order to resolve the regio- and stereo-selectivities [2] and to provide definitive characterization of this prototype trivinylborane, we have conducted an X-ray investigation on tris(*Z*-trimethylsilylprop-1-enyl)borane and report herein the results.

Experimental

Large well-formed clear colorless crystals were grown by sublimation onto a glass surface. When mounted in glass Lindemann capillaries in an atmosphere of dry nitrogen, the crystals turned an opaque white. Oscillation and Weissenberg photographs were used to determine the space group ($P1$ or $P\bar{1}$) and preliminary unit cell dimensions. A possible C-centered monoclinic cell with a 13.69, b 35.9, c 10.31 Å, β 100° was ruled out because of lack of symmetry on the diffraction photographs.The

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intensity of the diffracted beam faded significantly with increasing Bragg angle suggesting rather high atomic thermal vibration, as may be expected from such a volatile solid. For this reason a reasonably large crystal of dimensions 1.0 × 1.0 × 0.8 mm was chosen for data collection. Data was collected out to θ 20° on a Nonius

(Continued on p. 5)

TABLE 1

FRACTIONAL COORDINATES OF ATOMS WITH STANDARD DEVIATIONS

	x	y	z	U_{eq}^{a}
Si(1)	0.22163(13)	0.21284(11)	0.80097(8)	0.0741
Si(2)	0.60988(13)	0.33373(11)	0.85258(8)	0.0728
Si(3)	0.22662(15)	0.30484(11)	1.02666(8)	0.0783
C(113)	0.2519(7)	0.2504(6)	0.6993(3)	0.1257
C(111)	0.1230(5)	0.3303(4)	0.8203(3)	0.0949
C(112)	0.1169(6)	0.1075(5)	0.8307(4)	0.1180
C(121)	0.4908(5)	0.4062(4)	0.7773(3)	0.0953
C(122)	0.7506(6)	0.2629(5)	0.8114(4)	0.1130
C(123)	0.6695(7)	0.4342(5)	0.8832(4)	0.1292
C(133)	0.0403(6)	0.3375(5)	1.0271(4)	0.1245
C(131)	0.2873(6)	0.4283(4)	0.9675(3)	0.1008
C(132)	0.2844(8)	0.2689(6)	1.1226(3)	0.1308
B(1)	0.3960(5)	0.2055(4)	0.9229(3)	0.0536
C(114)	0.3778(4)	0.1698(3)	0.85535(24)	0.0569
C(115)	0.4744(5)	0.0964(4)	0.8444(3)	0.0777
C(116)	0.4818(7)	0.0331(5)	0.7921(3)	0.1128
C(124)	0.5286(4)	0.2402(4)	0.93202(24)	0.0586
C(125)	0.5853(5)	0.1885(5)	0.9971(3)	0.0829
C(126)	0.7225(6)	0.1926(6)	1.0212(4)	0.1262
C(134)	0.2847(4)	0.1974(4)	0.98515(24)	0.0588
C(135)	0.2446(5)	0.1042(4)	1.0108(3)	0.0773
C(136)	0.1494(6)	0.0660(5)	1.0759(3)	0.1092
Si(4)	0.20656(15)	0.77125(12)	0.72335(8)	0.0804
Si(5)	−0.10410(14)	0.65184(12)	0.59930(9)	0.0802
Si(6)	0.32458(14)	0.71695(12)	0.48297(8)	0.0820
B(2)	0.1028(5)	0.7901(4)	0.5750(3)	0.0516
C(243)	0.3827(7)	0.7473(6)	0.7513(4)	0.1360
C(242)	0.1029(7)	0.8566(6)	0.7722(4)	0.1283
C(241)	0.1520(7)	0.6412(4)	0.7559(3)	0.1052
C(244)	0.1883(4)	0.8312(4)	0.62033(25)	0.0623
C(245)	0.2357(5)	0.9195(4)	0.5808(3)	0.0807
C(246)	0.3077(7)	0.9855(5)	0.6085(4)	0.1245
C(252)	−0.2073(7)	0.6837(5)	0.5167(4)	0.1305
C(251)	0.0375(6)	0.5485(4)	0.5929(4)	0.1100
C(253)	−0.1976(7)	0.5911(5)	0.6863(4)	0.1273
C(254)	−0.0413(4)	0.7710(4)	0.60245(23)	0.0603
C(255)	−0.1191(5)	0.8496(4)	0.6198(3)	0.0775
C(256)	−0.2649(6)	0.8630(5)	0.6381(4)	0.1199
C(261)	0.3982(6)	0.6355(5)	0.5748(3)	0.1134
C(262)	0.4322(6)	0.8176(5)	0.4365(4)	0.1274
C(263)	0.3252(8)	0.6269(6)	0.4272(4)	0.1534
C(264)	0.1526(4)	0.7822(3)	0.49725(25)	0.0595
C(265)	0.0722(6)	0.8351(4)	0.4405(3)	0.0772
C(266)	0.0984(7)	0.8546(6)	0.3580(3)	0.1165

[a] $U_{eq} = 1/3$ trace $\bar{U}$.

TABLE 2

BOND LENGTHS (Å), BOND ANGLES AND SELECTED TORSION ANGLES (°)

$Z =$	2	3	1	6	4	4	
$n =$	1	1	1	2	2	2	
$x =$	1	2	3	4	5	6	mean σ
Si(x)–C(nx1)	1.872(6)	1.855(6)	1.876(6)	1.856(6)	1.869(7)	1.867(7)	1.866(9)
Si(x)–C(nx2)	1.868(7)	1.865(7)	1.844(8)	1.867(8)	1.854(8)	1.870(7)	1.861(10)
Si(x)–C(nx3)	1.845(7)	1.873(8)	1.893(7)	1.875(8)	1.866(7)	1.874(8)	1.879(14)
Si(x)–C(nx4)	1.879(5)	1.878(5)	1.878(5)	1.868(5)	1.880(5)	1.879(5)	1.877(4)
B(n)–C(nx4)	1.553(7)	1.566(7)	1.574(7)	1.569(7)	1.573(7)	1.560(7)	1.566(7)
C(nx4)–C(nx5)	1.339(7)	1.327(7)	1.335(7)	1.347(7)	1.340(7)	1.337(7)	1.338(6)
C(nx5)–C(nx6)	1.512(4)	1.538(9)	1.527(8)	1.505(9)	1.507(9)	1.513(9)	1.517(13)
C(nx4)–Si(x)–C(nx1)	109.7(3)	110.5(3)	109.8(3)	110.0(3)	110.0(3)	110.0(3)	110.0(2)
C(nx4)–Si(x)–C(nx2)	110.5(3)	111.3(3)	111.8(3)	110.4(3)	111.2(3)	110.5(3)	110.9(6)
C(nx4)–Si(x)–C(nx3)	113.0(3)	111.1(3)	110.7(3)	111.7(3)	111.7(3)	111.3(3)	111.58(7)
C(nx1)–Si(x)–C(nx2)	106.8(3)	197.4(3)	109.3(3)	108.2(3)	107.5(3)	107.4(3)	107.8(9)
C(nx1)–Si(x)–C(nx3)	107.0(3)	106.9(3)	106.0(3)	106.2(3)	105.8(3)	107.1(3)	106.5(6)
C(nx2)–Si(x)–C(nx3)	109.5(3)	109.5(3)	109.1(3)	110.4(3)	110.3(3)	110.3(3)	109.9(6)
Si(x)–C(nx4)–C(nx5)	122.0(4)	123.3(4)	122.9(4)	122.4(4)	122.7(4)	122.2(4)	122.6(5)
Si(x)–C(nx4)–B(n)	122.2(4)	122.0(3)	122.6(3)	122.3(3)	121.1(3)	121.3(3)	121.9(6)
C(nx5)–C(nx4)–B(n)	115.1(4)	114.2(4)	114.2(3)	114.9(4)	115.8(4)	116.0(4)	115.0(8)
C(nx6)–C(nx5)–C(nx4)	129.9(5)	128.0(5)	128.0(5)	128.5(5)	129.4(5)	128.8(5)	128.8(8)
C(nx4)–B(n)–C(nZ4)	120.2(4)	120.2(4)	119.2(4)	120.1(4)	120.3(4)	120.1(4)	120.0(4)
C(nx2)–Si(x)–C(nx4)–B(n)	−100.1(4)	−101.5(4)	−107.2(4)	−103.7(4)	−99.7(4)	−102.2(4)	−102.4(28)
Si(x)–C(nx4)–B(n)–C(nZ4)	−136.8(4)	−138.0(4)	−136.6(4)	−139.7(4)	−138.2(4)	−139.0(4)	−138.1(12)
C(nx6)–C(nx5)–C(nx4)–B(n)	170.7(5)	172.0(5)	173.3(5)	172.7(6)	171.3(6)	171.4(5)	171.9(10)

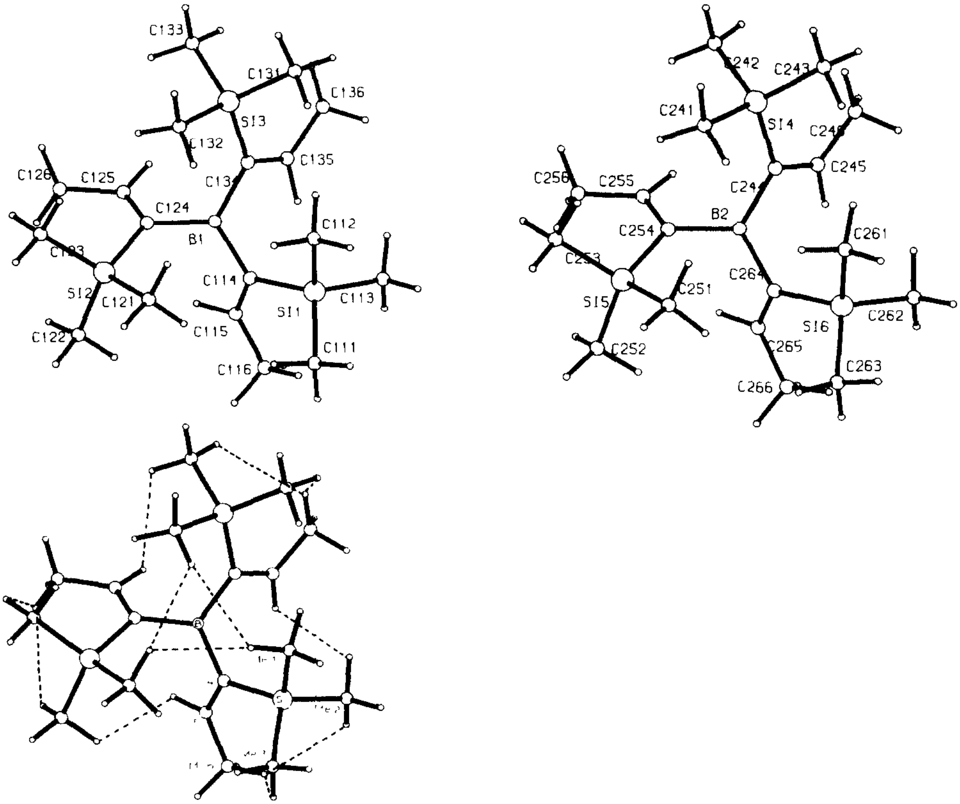

Fig. 1 (a, b) Labelled drawings of the two crystallographically independent molecules in the asymmetric unit viewed along their approximate three fold axes. (c) Labelling for the six conformationally independent trimethylsilylpropenyl groups. Dashed lines indicate short non-bonded H ..H interactions.

TABLE 3
AVERAGE BOND LENGTHS IN CRYSTALS OF RELATED COMPOUNDS

Compound	Bond length (Å)			Reference
	Si–Me	Si–C(sp^2)	C=C	
Tetrakis(trimethylsilyl)-ethylene	1.871	1.914	1 368	4
1,1-bis(*t*-butyldimethyl-silyl)-2,2-bis(trimethyl-silyl)ethylene	1.871	1.920	1.370	5
trans-1,2-bis(trimethyl-silyl)-1,2-bis(methylthio)-ethylene	1.864	1.905	1.351	6
Tricarbonyl-[4-methoxy--4-η^6-phenyl-2,3-bis-(trimethylsilyl)-1,3--butadiene-1-one]chromium	1.844	1.881	1.334	7
Tris(*Z*-trimethylsilylprop--1-enyl)borane	1.866	1.877	1.338	This work

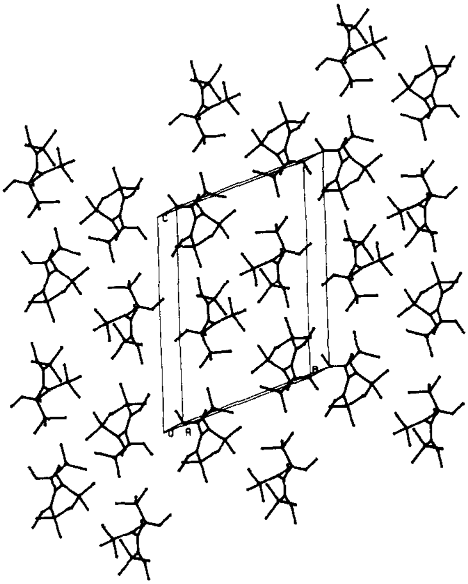

Fig. 2. Unit cell packing diagram viewed along *a*.

CAD-4 diffractometer using Mo-K_α, graphite monochromated radiation. Of the 4629 unique measured reflections, 3422 had $I > 2.5\sigma(I)$. No absorption correction was applied. There was significant (12%) decay of reflected intensity which was corrected by using a drift curve obtained from monitoring two intensity control reflections. The structure was solved using direct methods (SHELX 84, G. Sheldrick 1983) [3]. A number of hydrogen atoms were visible in subsequently calculated difference Fourier maps; however, only the six clearly visible methyl hydrogen atoms were refined, all other methyl hydrogen atoms were input in idealized positions and refined as a rigid group, (C–H 1.08 Å, H–C–H 109.4°). In the final cycles of blocked matrix least squares all nonhydrogen atoms were refined anisotropically and the average shift over estimated error for any of the 509 parameters was less than 0.2. The highest peak in the final difference Fourier map was less than 0.4 e Å^{-3}. The weighting scheme which gave the best analysis of variance in ranges of $|F|$ and in θ was $w = 1/(\sigma^2(F) + 0.0035F^2)$ and gave a final R of 0.061 and R' of 0.083.

Fractional coordinates are given in Table 1. Bond length, angles and torsion angles are given in Table 2.

Discussion

The two crystallographically independent molecules in the asymmetric unit adopt almost identical conformations. There are no statistically significant differences between any of the chemically (and conformationally) equivalent bond lengths, bond angles, and torsion angles of the six independent trimethylsilylpropenyl side arms (Table 2). Non-crystallographic molecular three-fold rotation axes pass through the boron atoms to provide a propeller arrangement as shown in Fig. 1a and 1b. Subsequent discussion is based on the average parameters of the six equivalent side arms using the labelling scheme shown in Fig. 1c.

In contrast with what is generally found for C–C bonds, the length of the bonds from silicon to carbon do not vary regularly with hybridization at the carbon atom. In simple molecules with no possibility of crowding, the Si–C(sp^2) bond length [4] of around 1.85 Å is a little shorter than the Si–C(sp^3) bond. Crowded molecules like this, however, show a different pattern. The 18 independent Si–Me bond lengths in this molecule have an average value of 1.866(12) Å, and the average Si–C(4) bond at 1.877(14) Å is slightly, though not significantly, larger. The lengthening of the Si–C(sp^2) bond is much more pronounced in other comparable but more crowded compounds (Table 3) [4–7]. There is also a correlation between lengthening of the Si–C(sp^2) bond and lengthening of the C=C bond.

The lengthening of C=C bond may be related to the significant twist away from the expected *cis* or *trans* planar configuration. In ref. 5, the C–C=C–C torsion angle is 45° while in this work the average C–C=C–B angle is much less distorted at 171.9°. This distortion may be a result of non-bonded interactions between hydrogen atoms on Me(6) which are between 2.04 and 2.48 Å away from hydrogen atoms on Me(2) and Me(3) of the same silyl propenyl group (Fig. 1c). The average angles for C(1)–Si–C(2) and C(1)–Si–C(3) are 107.8(9) and 106.5(6)°, respectively, and are a consequence of the mutual interaction (as shown in Fig. 1c) between atoms on the three Me(1) groups in the range of 2.4 to 2.5 Å and also contacts between hydrogen atoms on Me(1) and Me(3) of an adjacent silylpropenyl arm of about 2.5 Å.

C(4) is essentially planar with the three relevant angles summing to 359.5°. The interaction between Me(6) and the silyl methyl group Me(2) and Me(3) results in a narrowing of C(5)–C(4)=B to 115.0° and a very significant widening of the C(6)–C(5)–C(4) angle to 128.8°.

Coordination about boron is trigonal planar with an average C–B–C angle of exactly 120.0°. The threefold propeller conformation of the molecules is a result of a constant interplanar angle between the boron coordination plane and the silylpropenyl groups. This is defined by the torsion angle about the B–C(4) bond of $-138.1°$ ($\pm 2.5°$) for all six groups.

The packing diagram (Fig. 2) shows the molecules arranged in parallel layers with the boron coordination planes of the independent molecules almost coplanar. (The interplanar angle is 1°). There is a clearly different environment around the two molecules, though in both cases the only notable intermolecular contacts are between hydrogen atoms. Each of the independent molecules is involved in ten H...H contacts less than 2.6 Å.

Listings of observed and calculated structure factor amplitudes and tables of nearest intermolecular contacts are available upon request from the authors.

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