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THE CRYSTAL STRUCTURE OF 2-[3,4,5,6-TETRAKIS(TRIMETHYLSILYL)-1-CYCLOHEXEN-1-YL]HEPTAMETHYLTRISILANE*

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SUMMARY

The crystal structure of 2-[3,4,5,6-tetrakis(trimethylsilyl)-1-cyclohexen-1-yl]-heptamethyltrisilane has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter methods. The crystals are orthorhombic, space group $Pna2_1$ with unit cell parameters $a=24.081\pm0.008$, $b=9.839\pm0.007$, $c=15.973\pm0.009$ Å, $\rho_o=0.967$, $\rho_c=0.984$ g/cm^3 for $Z=4$. Block-diagonal anisotropic least-squares refinement led to a conventional R of 0.07 for 1225 observed reflections. The molecular structure is composed of a tetrasubstituted cyclohexene ring with the carbon–carbon double bond vinylic to the trisilane moiety. The average Si–Si bond distance is 2.35 ± 0.01 Å, and the average Si–C(sp^3) bond distance is 1.88 ± 0.04 Å.

INTRODUCTION

Although the structures of inorganic silicon compounds as well as a number of organic siloxanes and silsesquioxanes have been studied extensively, relatively little structural information is available for organosilicon compounds which contain

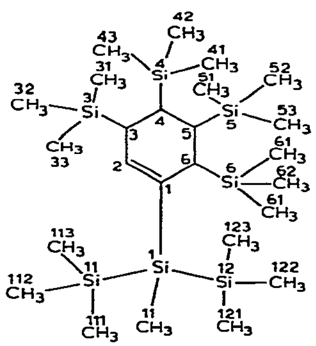

Fig. 1. The molecular structure of TTCH. The ring carbons are numbered from 1 through 6 and the silicon atoms which are bonded to them have the same number as the carbon to which they are attached. Substituents on each silicon atom are identified by moving the silicon number one digit to the left.

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Si–Si bonds. Gas phase electron diffraction was used to investigate the structures of disilane[1] and hexamethyldisilane[2], but the only compound of this type to be investigated by single-crystal X-ray diffraction techniques prior to the present study was bis(tetramethyldisilanylene) dioxide*, $[(CH_3)_4Si_2O]_2$[3]. The title compound, 2-[3,4,5,6-tetrakis(trimethylsilyl)-1-cyclohexen-1-yl]heptamethyltrisilane, hereafter referred to as TTCH, is of interest because of the trisilane moiety. The molecular configuration and the numbering scheme used in this investigation are seen in Fig. 1. TTCH was obtained as the major product[4] in the reaction of phenylmethyldichlorosilane and chlorotrimethylsilane with metallic lithium in tetrahydrofuran, and was unambiguously characterized only after this structural investigation.

EXPERIMENTAL

A sample of TTCH, m.p. 121°, was kindly supplied by Professor Gilman of this department. After recrystallization from a 1/1 solution of methanol and ethyl acetate, many small, colorless crystals were obtained and were used without further purification. Weissenberg and precession photographs made with Cu-K_α and Mo-K_α radiation, respectively, indicated orthorhombic symmetry. Systematic absences observed for $0kl$ reflections with $k+l$ odd, and for $h0l$ reflections with h odd, limited the choice of space groups to $Pna2_1$ or $Pnma$. Accurate unit cell parameters were obtained from a least-squares refinement based on the 2θ values for 16 reflections which had been carefully measured on a General Electric diffractometer using Cr-K_α radiation. The α_1 and α_2 components were unresolved. Hence the wavelength used was the weighted mean of α_1 and α_2, $\lambda=2.291$ Å. The unit cell parameters and their standard deviations based on the elements of the least-squares inverse matrix are $a=24.081\pm0.008$, $b=9.839\pm0.007$, $c=15.973\pm0.009$ Å, and $V=3784$ Å^3. The density as measured by flotation in a methanol/glycerol mixture was 0.967 g/cm^3; the density calculated with $Z=4$ was 0.984 g/cm^3. A General Electric XRD-5 X-ray unit equipped with a single-crystal orienter and scintillation counter was used with Mo-K_α radiation ($\lambda=0.7107$ Å) in the moving-crystal-moving-counter mode ($\theta, 2\theta$ coupling) to measure intensities. A 100-sec scan covering 1.67° in 2θ was used for each reflection. The take-off angle was 1.0°. The backgrounds for individual reflections were obtained from a plot of background *vs.* 2θ. One crystallographically independent octant of data was measured within a 2θ sphere of 45° ($\sin\theta/\lambda=0.538$) beyond which no reflections were observed to have intensities significantly above the background. These data, after correction for noncharacteristic radiation streaks[5] and Lorentz-polarization factors, were reduced to structure factors. The crystal used for intensity measurements had approximate dimensions 0.2 × 0.2 × 0.4 mm. The minimum and maximum transmittances were 91% and 97% based on $\mu=2.50$ cm^{-1}. Consequently no absorption correction was made. In an attempt to account for systematic as well as random errors, standard deviations were assigned to the intensity data according to the formula:

$$\sigma(I)=[C_T+C_B+C_S+(0.04C_T)^2+(0.04C_B)^2+(0.06C_S)^2]^{\frac{1}{2}}$$

where C_T, C_B, and C_S are, respectively, the total counts, background counts, and

* 2,2,3,3,5,5,6,6-octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane.

TABLE 1

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS[a,b]

ATOM	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
SI 1	-0.0173(2)	0.4391(6)	0.3002(4)	14(1)	134(7)	60(3)	11(9)	-4(3)	4(4)
SI 11	-0.0854(2)	0.2947(6)	0.3541(-)	16(1)	157(8)	101(4)	-8(12)	9(4)	-14(5)
SI 12	-0.0302(2)	0.6653(5)	0.3455(5)	21(1)	114(7)	66(3)	-2(10)	1(4)	2(5)
SI 3	0.1297(2)	0.1504(6)	0.4857(4)	25(1)	124(7)	66(4)	27(10)	-12(4)	-8(5)
SI 4	0.2050(2)	0.5079(6)	0.5019(4)	19(1)	143(7)	62(3)	-31(10)	-15(4)	-3(5)
SI 5	0.2005(2)	0.6148(6)	0.2787(5)	17(1)	160(8)	74(4)	43(11)	10(1)	-4(5)
SI 6	0.1301(2)	0.2862(6)	0.2092(4)	18(1)	169(9)	58(3)	-32(10)	-1(4)	24(5)
C 1	0.0554(6)	0.3917(16)	0.3328(11)	18(3)	115(21)	37(9)	-39(26)	-18(9)	34(14)
C 2	0.0619(6)	0.3504(16)	0.4112(12)	6(3)	133(24)	59(11)	8(30)	-22(9)	21(14)
C 3	0.1180(6)	0.3369(18)	0.4571(13)	14(3)	147(25)	72(12)	-29(32)	-1(11)	-7(15)
C 4	0.1697(6)	0.4194(16)	0.4142(11)	17(3)	95(22)	50(10)	54(28)	-20(10)	-17(14)
C 5	0.1486(6)	0.5090(16)	0.3394(11)	13(3)	124(21)	43(9)	-11(28)	-6(9)	1(14)
C 6	0.1047(6)	0.4360(17)	0.2817(14)	10(3)	118(22)	81(13)	-18(34)	16(11)	16(14)
C 11	-0.0746(8)	0.4398(25)	0.1813(14)	27(5)	310(44)	56(13)	-62(42)	-16(13)	16(24)
C 31	0.2062(8)	0.1025(19)	0.4837(17)	32(5)	140(26)	116(18)	38(43)	-34(18)	13(19)
C 32	0.0999(11)	0.1218(27)	0.5892(17)	54(8)	235(40)	76(15)	94(45)	27(19)	14(30)
C 33	0.0934(8)	0.0335(20)	0.4144(19)	25(4)	142(29)	128(19)	29(42)	-4(15)	12(19)
C 41	0.1702(10)	0.6748(24)	0.5245(15)	41(6)	232(38)	76(16)	-68(42)	-11(16)	23(26)
C 42	0.2820(7)	0.5208(29)	0.4790(16)	12(3)	400(50)	87(15)	33(50)	-22(13)	-42(22)
C 43	0.1999(9)	0.4151(23)	0.6029(14)	30(5)	233(37)	65(13)	-19(39)	-29(14)	-2(23)
C 51	0.2652(7)	0.5210(24)	0.2431(16)	13(3)	277(39)	106(17)	56(45)	12(13)	14(19)
C 52	0.2235(10)	0.7722(22)	0.3355(17)	48(6)	165(32)	103(17)	20(44)	53(20)	-64(24)
C 53	0.1659(8)	0.6967(26)	0.1798(16)	24(5)	308(45)	87(17)	100(48)	-1(14)	51(25)
C 61	0.0714(9)	0.1635(22)	0.1983(16)	34(5)	193(35)	92(16)	-92(43)	-12(17)	16(22)
C 62	0.1873(9)	0.1820(19)	0.2461(15)	32(5)	130(26)	85(15)	-54(34)	2(14)	10(19)
C 63	0.1477(9)	0.3565(30)	0.1009(15)	29(5)	406(55)	58(14)	-36(49)	30(14)	68(28)
C 111	-0.1553(10)	0.3457(30)	0.3133(33)	27(5)	310(51)	297(48)	175(89)	-31(27)	-84(27)
C 112	-0.0673(17)	0.1144(30)	0.3257(29)	98(15)	224(46)	232(41)	175(75)	158(42)	-202(44)
C 113	-0.0956(13)	0.2938(37)	0.4675(20)	62(10)	459(73)	87(19)	-119(65)	41(25)	-97(45)
C 121	-0.1044(9)	0.7195(25)	0.3359(19)	33(5)	237(39)	117(19)	48(48)	4(19)	37(25)
C 122	-0.0965(9)	0.6859(23)	0.4564(14)	38(6)	217(35)	59(12)	-62(37)	-16(14)	44(24)
C 123	0.0147(9)	0.7800(23)	0.2772(17)	31(5)	206(34)	93(19)	68(43)	19(17)	27(23)

[a] $10^4 \sigma$ is given in parentheses.
[b] β's are $\times 10^4$ and have the form $\exp[-(h^2\cdot\beta_{11}+k^2\cdot\beta_{22}+l^2\cdot\beta_{33}+k\cdot l\cdot\beta_{23}+h\cdot l\cdot\beta_{13}+h\cdot k\cdot\beta_{12})]$.

streak counts. The quadratic terms correspond to estimated errors of 4% in intensity and background measurements, and 6% in the streak correction. The estimated standard deviation for each structure factor was obtained by the method of finite differences[5] $\sigma(F) = ([I+\sigma(I)]^{\frac{1}{2}} - I^{\frac{1}{2}})(Lp)^{-\frac{1}{2}}$ where Lp is the Lorentz-polarization factor. Of the 1423 measured reflections, 198 had $F < 3\sigma(F)$ and were excluded from the refinement.

(*continued* p. 71)

TABLE 2

OBSERVED AND CALCULATED STRUCTURE FACTORS

Each group of data is headed with the value for k. Within each group of data are listed h, l, $10\,F_o$, $10\,\sigma(F_o)$, and $10\,F_c$ respectively. Reflections for which F_o is negative are unobserved and were not included in the refinement.

h	l	$10\,F_o$	$10\,\sigma(F_o)$	$10\,F_c$
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 2

OBSERVED AND CALCULATED STRUCTURE FACTORS

Each group of data is headed with the value for k. Within each group of data are listed h, l, 10 F_o, 10 $\sigma(F_o)$, and 10 F_c respectively. Reflections for which F_o is negative are unobserved and were not included in the refinement.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 3

DISTANCES (Å) AND ANGLES (°) WITH STANDARD DEVIATIONS IN PARENTHESES

Non-methyl bond distances and angles

Bond	Value	Angle	Value	Angle	Value
Si_1-Si_{11}	2.335(7)	$Si_{11}-Si_1-Si_{12}$	111.6(0.2)	$Si_4-C_4-C_3$	105.4(0.9)
Si_1-Si_{12}	2.361(8)	$Si_{11}-Si_1-C_1$	115.6(0.5)	$Si_4-C_4-C_5$	117.3(0.9)
Si_1-C_1	1.884(17)	$Si_{12}-Si_1-C_1$	105.7(0.5)	$C_3-C_4-C_5$	110.6(1.2)
Si_3-C_3	1.912(19)	$Si_1-C_1-C_2$	116.5(1.0)	$Si_5-C_5-C_4$	119.1(0.9)
Si_4-C_4	1.856(17)	$Si_1-C_1-C_6$	120.7(1.0)	$Si_5-C_5-C_6$	113.2(0.9)
Si_5-C_5	1.893(17)	$C_6-C_1-C_2$	120.4(1.3)	$C_5-C_5-C_6$	113.9(1.6)
Si_6-C_6	1.971(18)	$C_1-C_2-C_3$	125.4(1.3)	$Si_6-C_6-C_5$	118.4(0.9)
C_1-C_2	1.325(22)	$Si_3-C_3-C_4$	117.7(1.0)	$Si_6-C_6-C_1$	110.3(0.9)
C_2-C_3	1.544(24)	$Si_3-C_3-C_2$	107.3(1.0)	$C_5-C_6-C_1$	110.1(1.2)
C_3-C_4	1.635(24)	$C_2-C_3-C_4$	115.1(1.2)		
C_4-C_5	1.569(23)				
C_5-C_6	1.577(23)				
C_6-C_1	1.504(24)				

Bond distances involving methyl groups

Bond	Value	Bond	Value	Bond	Value
Si_1-C_{11}	1.908(23)	Si_4-C_{43}	1.857(23)	Si_6-C_{63}	1.911(25)
Si_3-C_{31}	1.903(23)	Si_5-C_{51}	1.899(23)	$Si_{11}-C_{111}$	1.873(35)
Si_3-C_{32}	1.824(27)	Si_5-C_{52}	1.878(25)	$Si_{11}-C_{112}$	1.882(39)
Si_3-C_{33}	1.840(24)	Si_5-C_{53}	1.971(24)	$Si_{11}-C_{113}$	1.811(33)
Si_4-C_{41}	1.878(25)	Si_6-C_{61}	1.889(24)	$Si_{12}-C_{121}$	1.873(27)
Si_4-C_{42}	1.895(24)	Si_6-C_{62}	1.814(24)	$Si_{12}-C_{122}$	1.871(23)
				$Si_{12}-C_{123}$	1.906(23)

Bond angles involving methyl groups

Angle	Value	Angle	Value	Angle	Value
$C_{11}-Si_1-C_1$	112.0(0.9)	$C_{41}-Si_4-C_{43}$	103.6(1.0)	$C_{62}-Si_6-C_{63}$	109.3(1.0)
$C_{11}-Si_1-Si_{11}$	107.7(0.7)	$C_{42}-Si_4-C_{43}$	105.4(1.0)	$Si_1-Si_{12}-C_{121}$	111.7(0.8)
$C_{11}-Si_1-S_{12}$	106.8(0.7)	$C_5-Si_5-C_{51}$	115.3(0.9)	$Si_1-Si_{12}-C_{122}$	110.6(0.7)
$C_3-Si_3-C_{31}$	112.1(0.9)	$C_5-Si_5-C_{52}$	113.6(0.9)	$Si_1-Si_{12}-C_{123}$	107.9(0.7)
$C_3-Si_3-C_{32}$	107.9(1.0)	$C_5-Si_5-C_{53}$	111.2(0.9)	$C_{121}-Si_{12}-C_{122}$	109.7(1.1)
$C_3-Si_3-C_{33}$	112.4(0.9)	$C_{51}-Si_5-C_{52}$	107.7(1.0)	$C_{122}-Si_{12}-C_{123}$	107.8(1.0)
$C_{31}-Si_3-C_{32}$	111.0(1.1)	$C_{51}-Si_5-C_{53}$	107.6(1.0)	$C_{121}-Si_{12}-C_{123}$	109.0(1.1)
$C_{31}-Si_3-C_{33}$	107.2(1.0)	$C_{52}-Si_5-C_{53}$	100.3(1.0)	$Si_1-Si_{11}-C_{111}$	109.9(1.1)
$C_{32}-Si_3-C_{33}$	106.1(1.0)	$C_6-Si_6-C_{61}$	110.4(0.9)	$Si_1-Si_{11}-C_{112}$	108.8(1.2)
$C_4-Si_4-C_{41}$	110.6(0.9)	$C_6-Si_6-C_{62}$	117.9(0.9)	$Si_1-Si_{11}-C_{113}$	111.9(1.0)
$C_4-Si_4-C_{42}$	109.5(0.9)	$C_6-Si_6-C_{63}$	109.3(0.9)	$C_{111}-Si_{11}-C_{112}$	112.1(1.6)
$C_4-Si_4-C_{43}$	113.3(0.9)	$C_{61}-Si_6-C_{62}$	105.3(1.0)	$C_{111}-Si_{11}-C_{113}$	110.3(1.5)
$C_{41}-Si_4-C_{42}$	114.5(1.1)	$C_{61}-Si_6-C_{63}$	103.7(1.0)	$C_{112}-Si_{11}-C_{113}$	103.7(1.6)

Since the general multiplicity of the centrosymmetric space group, *Pnma*, is 8, four molecules of TTCH could occupy one unit cell in this space group only if each possessed either a center of symmetry or a mirror plane. The improbability of either symmetry in TTCH molecules indicated the noncentrosymmetric space group $Pna2_1$. The successful solution of the structure verified this space group assignment. Six of the seven silicon atoms were located by conventional, three-dimensional superposition and Fourier techniques. Because of the large number of apparently equal peaks in the three-dimensional electron density map, the final silicon atom, Si_5, could not be distinguished from the many, as yet unassigned, carbon peaks. A centrosymmetric projection of the Fourier map along the c-axis, however, clearly yielded the x and y coordinates of Si_5. The z coordinate was readily obtained by searching the three-dimensional map along the line defined by x and y. Subsequent three-dimensional Fourier syntheses revealed the locations of all of the carbon atoms. Calculations were performed on IBM/360 models 50 and 65 computers using a series of unpublished programs developed at Iowa State University, the Oak Ridge least-squares program[6], and the block-diagonal least-squares program of the National Research Council of Canada[7]. Scattering factors for neutral silicon and carbon atoms were those of Hanson *et al.*[8] Only the x and y parameters of Si_{11} were varied in the least-squares refinement in order to fix the origin of the polar unit cell. The full-matrix isotropic refinement converged to a conventional R, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.116. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ in which the weight, w, was $1/\sigma^2(F)$. The anisotropic refinement of 287 positional and temperature factors necessitated use of the block-diagonal approximation. In the final stages of refinement a modified weighting function was used in order to remove the dependence of $< w(|F_o| - |F_c|)^2 >$ on F_o. The modified weighting function was $w = 1/[\sigma^2(F) + 0.005F^2]$. Convergence was achieved with a conventional R factor of 0.07 and a weighted R factor, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w \cdot F_o^2]^{\frac{1}{2}}$, of 0.10. The standard deviation of a reflection of unit weight was 1.009. A consideration of the isotropic and anisotropic R factors permits rejection at the 0.005 level of the hypothesis that all atoms vibrate isotropically[9]. A difference map was calculated in an attempt to determine the positions of the hydrogens. However, due to the large thermal vibrations in the molecule, the hydrogen atoms could not be located. Final positional and thermal parameters along with their estimated standard deviations are listed in Table 1. The neglect of interatomic correlations in the block-diagonal approximation leads to underestimation of the standard deviations. Experience in this laboratory has shown that the block-diagonal standard deviations and quantities calculated from them should be multiplied by 1.2 for comparison with full-matrix values. Calculated structure factors are compared with the observed values in Table 2.

RESULTS AND DISCUSSION

The molecular structure of TTCH is shown in Fig. 2 which was prepared by the computer utilizing Johnson's ORTEP program[10]. TTCH absorbs in the ultraviolet with a maximum at 241 mμ[11] whereas trisilanes usually absorb at 215 mμ[12]. Such a shift toward the visible is common in the spectra of silanes which have phenyl or vinyl substituents and has been explained in terms of p_π–d_π interactions with the unoccupied $3d$ orbitals on silicon[13–14]. Accordingly the carbon–carbon double bond in TTCH was placed vinylic to the trisilane moiety by Gilman *et al.*[4]. The carbon–carbon double bond of the cyclohexene system is unambiguously located between C_1 and C_2 on the basis of interatomic distances. Thus the structure proposed by Gilman *et al.*[4] is verified.

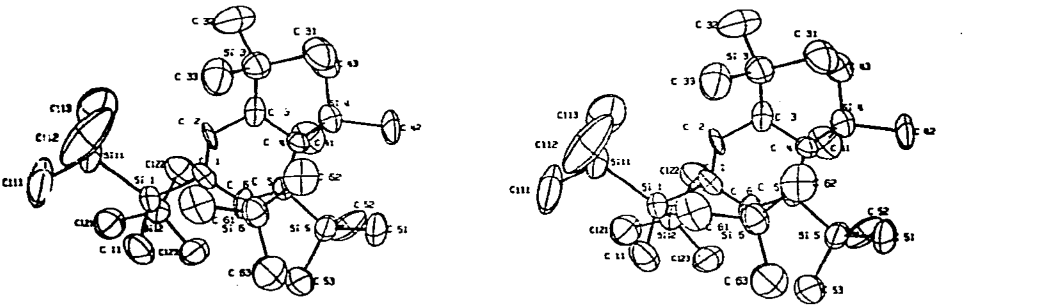

Fig. 2. Stereoscopic representation of TTCH. Anisotropic thermal vibration is indicated by 50% probability ellipsoids.

The bond distances and angles in TTCH are listed in Table 3. Anisotropic thermal vibration is indicated in Fig. 2 by the ellipsoids which are drawn to a scale such that the atomic centers are found within them 50% of the time. Root-mean-square amplitudes of thermal vibration along the principal axes 1–3 of the ellipsoids are presented in Table 4. There are 23 crystallographically independent Si–C(sp^3) bonds in TTCH all of which should be chemically equivalent. However, a rather large scatter is observed in these Si–C bond lengths. The range is 1.81–1.97 Å with the mean and root-mean-square deviation 1.88 ± 0.04 Å. Such a wide variation is not uncommon in organosilicon compounds[3,15] and, in this case, may be attributed to the large amplitudes of thermal vibration. The mean Si–Si distance is 2.35 ± 0.01 Å which is in agreement with the value of 2.3517 ± 0.0001 Å in metallic silicon[16]. With respect to

TABLE 4

ROOT-MEAN-SQUARE AMPLITUDE OF VIBRATION (Å × 10^3)

Atom	1	2	3	Atom	1	2	3
Si_1	200	252	282	C_{33}	250	280	406
Si_{11}	207	280	362	C_{41}	277	330	382
Si_{12}	235	250	291	C_{42}	160	335	450
Si_3	238	255	310	C_{43}	237	331	344
Si_4	216	259	302	C_{51}	191	337	399
Si_5	216	265	327	C_{52}	200	340	445
Si_6	218	262	310	C_{53}	238	310	426
C_1	178	190	297	C_{61}	260	311	386
C_2	94	261	289	C_{62}	227	308	348
C_3	200	259	312	C_{63}	204	324	461
C_4	178	198	301	C_{111}	229	390	637
C_5	188	231	252	C_{112}	218	393	703
C_6	155	246	328	C_{113}	300	377	535
C_{11}	240	292	401	C_{121}	285	347	402
C_{31}	241	293	407	C_{122}	248	293	383
C_{32}	256	359	421	C_{123}	281	288	386

the approximate plane of the ring, the four trimethylsilyl groups are bonded β, α, β, β, to ring carbons C_3, C_4, C_5, and C_6, respectively. The torsion angles about the three $C(sp^3)$–$C(sp^3)$ bonds within the cyclohexene ring are listed in Table 5. Methyl groups on adjacent silyl groups are meshed as follows. C_{11} is between C_{61} and C_{63}; C_{51}, between C_{62} and C_{63}; C_{52}, between C_{41} and C_{42}; and C_{43}, between C_{31} and C_{32}. In this way intramolecular nonbonded repulsions are minimized. TTCH is obviously a racemate as is required by the presence of improper symmetry elements in the space group. The molecular packing is apparently governed entirely by steric factors

TABLE 5

TORSION ANGLES

Bond	Torsion angle (°)
C_3–C_4	84.8
C_4–C_5	59.3
C_5–C_6	69.5

because there exists no possibility for hydrogen bonding.

The shortest intermolecular distances were 3.86 Å between C_{11} and C_{122} (molecule at $\bar{x}$, $\bar{y}$, $\frac{1}{2}+z$) and 3.88 Å between C_{53} and C_{113} (molecule at $\bar{x}$, $\bar{y}$, $\frac{1}{2}+z$).

REFERENCES

1 L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.*, 60 (1938) 1836.
2 L. O. Brockway and N. R. Davidson, *J. Amer. Chem. Soc.*, 63 (1941) 3287.
3 T. Takano, N. Kasai and M. Kakudo, *Bull. Chem. Soc. Jap.*, 36 (1963) 585.
4 H. Gilman, R. L. Harrell, C. L. Smith and K. Shiina, *J. Organometal. Chem.*, 5 (1966) 387.
5 D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, 86 (1964) 1660.
6 W. R. Busing, K. O. Martin and H. A. Levy, *A Fortran Crystallographic Least-Squares Program*, Oak Ridge National Laboratory, ORNL-TM-305.
7 F. R. Ahmed, S. R. Hall, M. E. Pippy and C. P. Saunderson, *NRC Crystallographic Programs for the IBM/360 System*, National Research Council, Ottawa, Canada.
8 H. P. Hanson, F. Herman, J. D. Lea and S. Skillman, *Acta Crystallogr.*, 17 (1964) 1040.
9 W. C. Hamilton, *Acta Crystallogr.*, 18 (1965) 502.
10 C. K. Johnson, *ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory, ORNL-3794.
11 R. L. Harrell, Ph.D. Dissertation, Iowa State University, 1966.
12 H. Gilman, W. H. Atwell, P. K. Sen and C. L. Smith, *J. Organometal. Chem.*, 4 (1965) 163.
13 D. N. Hague and R. H. Prince, *J. Chem. Soc.*, (1965) 4690.
14 H. Gilman and D. R. Chapman, *J. Organometal. Chem.*, 5 (1966) 392.
15 T. Higuchi and A. Shimada, *Bull. Chem. Soc. Jap.*, 39 (1966) 1316.
16 M. E. Straumanis and E. Z. Aka, *J. Appl. Phys.*, 23 (1952) 330.