Crystal and Molecular Structure of α-Form of 2,4,6-Trimethyl-1,3,5-trithiane*

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The crystal structure of α-form of 2,4,6-trimethyl-1,3,5-trithiane (α-TTA) has been determined by the X-ray method. The crystal data are $a=9.768$, $b=12.306$, $c=8.521$ Å, and $\beta=116.33°$. The space group is Cc with four molecules in a unit cell. The structure was deduced from interpretation of the 3D-Patterson series, and refined by 3D-Fourier and least-squares method to the final R factor of 0.040 for 1371 reflections. The molecule has a six-membered ring where three sulfur atoms and three carbon atoms are linked alternatively, forming a chair-form. Two methyl groups are in the equatorial positions and one methyl group in the axial. The mean values of the bond distances are 1.818 Å for S–C and 1.519 Å for C–C_{eq}. The distance is 1.541 Å for C–C_{ax}. The mean values of the bond angles are 101.89° for C–S–C, 107.60° for S–C–C_{eq}, 113.25° for S–C–C_{ax}, and 112.92° for S–C–S.

Studies on organic synthesis show that TTA has two isomers. One isomer is called the α-form (mp 102 °C), where two methyl groups are in the equatorial positions and a third one is axial. The other is called the β-form (mp 126 °C), where all the methyl groups are equatorial.

The crystal structure of the β-form has been reported by Valle *et al.*[1] and Hirokawa *et al.*,[2] but not that of the α-form. We have determined the crystal and molecular structure of the α-form from the viewpoint of molecular geometry or the packing of molecules in the crystal. The results are given below.

Experimental

Colorless prisms elongated along the a-axis were obtained by slow evaporation of α-TTA from acetone solution. The crystals are built upon a monoclinic unit cell.

Crystal Data. The cell dimensions were determined by the least-squares method using various sets of high angle reflections on a diffractometer. Systematic absence, $h+k$ odd in hkl and l odd in $h0l$, restricted the possible space group to either Cc or C2/c. Consideration on the number of molecules in the unit cell and the symmetric feature of the molecule favored the former. This was supported by the statistical test of intensity-distribution, and confirmed by the packing of the molecules. The crystal data are given in Table 1.

TABLE 1. CRYSTAL DATA

The experimental errors, given in parentheses, refer to the last figures.

Molecular formula	$C_6H_{12}S_3$
Formula weight	180.4
Mp	102 °C
Crystal system	Monoclinic
a	9.768 (4) Å
b	12.306 (7)
c	8.521 (4)
β	116.33(3)°
Systematic absences	hkl, $h+k=2n$
	$h0l$, $l=2n$
Space group	Cc
V	918.0(3) Å^3
Z	4
D_m	1.299 g cm^{-3}
D_x	1.305
μ (Mo $K\alpha$)	7.31 cm^{-1}
Crystal dimension	0.5 mm $\phi\times$0.8 mm
λ (Mo $K\alpha$)	0.7107 Å

Intensity Data. A prismatic crystal was ground to a cylinder of 0.5 mm in diameter and 0.8 mm in length. It was mounted on a four-circle diffractometer (Rigaku AFC-III) with Mo $K\alpha$ from a graphite monochrometer, and intensities were collected for the independent 1403 reflections within $2\theta<60°$, using the ω-2θ scan technique with a scanning speed of 4° min^{-1} in 2θ. Thirty-two reflections whose $|F|$'s were less than $2\sigma(|F|)$ were designated unobserved, where $\sigma(|F|)$ is the standard deviation of $|F|$ due to counting statistics. After corrections for background and Lorentz-polarization factor, the intensities were reduced to structure amplitudes. No corrections were made for absorption or extinction.

Structure Determination

The location of three sulfur atoms in the general positions was derived from synthesized 3D-Patterson series. The first 3D-Fourier series were synthesized, using phases determined by the atomic coordinates of the three sulfur atoms. The synthesized electron-density maps showed extra peaks in addition to the peaks due to the three sulfur atoms. Some of these extra peaks were considered to be significant as the constituent-atoms of the molecule. These were added to the successive Fourier-works. After three cycles of the procedure, the location of all the carbon atoms was determined. The possibility of centrosymmetric arrangement was discarded because of the mode of the packing of the molecules in the unit cell.

The structure was refined by syntheses of 3D-Fourier and 3D-difference series, where structure factors were calculated with isotropic B values for all the atoms. Location of the hydrogen atoms was roughly obtained from the 3D-difference maps. They were refined after the heavier atoms were fixed, assuming the tetrahedral angle for each carbon atom and a bond length of 1.09 Å for each C–H bond. Further refinements were made with a block-diagonal least-squares program on a computer CDC-6600 in Century Research Center Co.,

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Table 2. Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$) of the non-hydrogen atoms
The estimated standard deviations given in parentheses, refer to the last decimal position. The anisotropic temperature factor is of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	42(2)	1881(1)	−30(2)	129(1)	65(1)	120(1)	−6(1)	52(1)	−9(1)
S(2)	189(2)	3584(1)	2601(2)	208(2)	48(1)	211(2)	0(1)	129(2)	−9(1)
S(3)	−859(2)	1304(1)	2850(2)	140(2)	63(1)	189(2)	−18(1)	94(2)	−6(1)
C(4)	1127(6)	2985(4)	1373(6)	116(6)	56(3)	156(8)	−8(4)	65(6)	2(4)
C(5)	302(6)	2461(4)	4029(6)	148(7)	69(3)	135(7)	−6(4)	73(6)	−5(4)
C(6)	72(6)	858(4)	1529(7)	162(8)	48(3)	182(9)	−15(4)	91(7)	−18(4)
C(7)	1282(8)	3873(5)	232(9)	209(11)	73(4)	246(12)	−14(6)	146(10)	31(6)
C(8)	−300(9)	2870(5)	5295(9)	283(14)	93(5)	231(13)	−13(7)	190(12)	−27(7)
C(9)	1673(8)	373(5)	2607(9)	201(11)	70(4)	234(15)	35(6)	116(11)	22(7)

Table 3. Atomic coordinates ($\times 10^3$) of the hydrogen atoms
The average refined values for the isotropic temperature factor are 2.5 Å^2.

	x	y	z	Bonding atom
H(10)	224	270	226	C(4)
H(11)	147	221	474	C(5)
H(12)	−63	24	72	C(6)
H(13)	140	353	−87	C(7)
H(14)	33	443	−18	C(7)
H(15)	233	434	100	C(7)
H(16)	−151	272	478	C(8)
H(17)	25	225	638	C(8)
H(18)	22	364	585	C(8)
H(19)	158	−22	349	C(9)
H(20)	212	10	171	C(9)
H(21)	238	105	338	C(9)

Tokyo, using anisotropic thermal parameters for the non-hydrogen atoms with B values of the hydrogen atoms fixed at isotropic values. After six cycles of this procedure convergence was attained with $R=0.040$. The final parameters with standard deviations resulting from the procedure are given in Tables 2 and 3.***

Discussion

Molecular Geometry and Conformation. The structural and conformational features are shown in Fig. 1, together with atomic numbering and thermal vibration ellipsoids[3] scaled to 50% probability, excluding the hydrogen atoms. Intramolecular interatomic distances and angles involving the non-hydrogen atoms are given in Table 4, being also shown in Fig. 2(a) and (b). The standard deviations of these measurements are 0.001 Å for distances and 0.01—0.05° for angles. S–C lengths are in the range 1.810—1.824 Å with a mean of 1.818 Å, showing a slight alternative shortening along the sides of the six-membered ring. These values together with the bond angles of the sulfur atoms (101.89° as a mean) are comparable to those for organic compounds which have ring-membered sulfur atoms.[1,2,4-7]

*** The complete F_o-F_c data are deposited as Document No. 7722 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

A significant difference can be seen between the lengths of C–C_{eq} (from a ring-membered carbon to a methyl carbon in the equatorial position) and C–C_{ax} (axial); a mean of 1.519 Å is given to C–C_{eq} and 1.541 Å to C–C_{ax}. This might correspond to the difference in the bond angles for the ring-membered carbon atoms; a mean of 107.60° for S–C–C_{eq} and a mean of 113.25° for S–C–C_{ax}. A similar difference can be seen in the distance from a sulfur atom to a ring-membered carbon atom which is in a diagonal position of the ring; a mean of 3.431 Å for S···C whose carbon atom is linked with the equatorial methyl group, and 3.466 Å for S···C where the carbon atom is linked with the axial methyl group. The conformation of a methyl group may affect the molecular dimensions of a ring-membered carbon atom linked with it.

Table 4. Intramolecular interatomic distances (l) and angles (ϕ) involving the non-hydrogen atoms
Estimated standard deviations are given in parentheses.

	l/Å		ϕ/°
S(1)–C(4)	1.810(1)	C(6)–S(1)–C(4)	102.81(3)
S(2)–C(4)	1.824(1)	C(4)–S(2)–C(5)	100.31(3)
S(2)–C(5)	1.812(1)	C(5)–S(3)–C(6)	102.54(3)
S(3)–C(5)	1.821(1)	C–S–C(mean)	101.89
S(3)–C(6)	1.817(1)	S(1)–C(4)–S(2)	112.77(3)
S(1)–C(6)	1.821(1)	S(2)–C(5)–S(3)	112.90(3)
S–C(mean)	1.818	S(3)–C(6)–S(1)	113.09(3)
C(4)–C(7)	1.514(1)	S–C–S(mean)	112.92
C(5)–C(8)	1.524(1)	S(1)–C(4)–C(7)	108.27(5)
C–C_{eq}(mean)	1.519	S(2)–C(4)–C(7)	107.12(5)
C(6)–C(9)	1.541	S(2)–C(5)–C(8)	107.16(5)
		S(3)–C(5)–C(8)	107.86(5)
S(1)···S(2)	3.026(0)	S–C–C_{eq}(mean)	107.60
S(2)···S(3)	3.027(0)	S(3)–C(6)–C(9)	113.76(5)
S(3)···S(1)	3.035(0)	S(1)–C(6)–C(9)	112.73(5)
S···S(mean)	3.029	S–C–C_{ax}(mean)	113.25
C(4)···C(5)	2.791(1)	S(1)···S(2)···S(3)	60.20(1)
C(5)···C(6)	2.837(1)	S(2)···S(3)···S(1)	59.88(1)
C(6)···C(4)	2.838(1)	S(3)···S(1)···S(2)	59.93(1)
C···C(mean)	2.822	S···S···S(mean)	60.00
S(1)···C(5)	3.428(1)	C(4)···C(5)···C(6)	60.52(2)
S(3)···C(4)	3.433(1)	C(6)···C(4)···C(5)	60.53(2)
S···C(mean)	3.431	C(5)···C(6)···C(4)	58.93(2)
S(2)···C(6)	3.466(1)	C···C···C(mean)	60.00

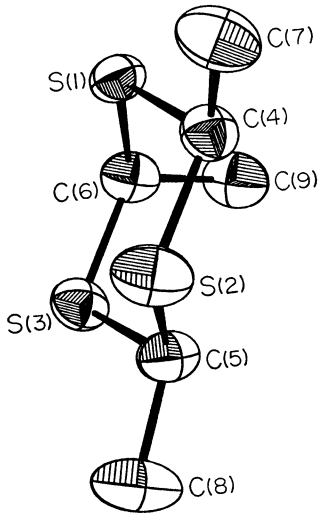

Fig. 1. The thermal vibration ellipsoids of non-hydrogen atoms drawn by ORTEP.[3]

Table 5. Torsion angles (ϕ)
Torsion angle A(i)–A(j)–A(k)–A(l) is viewed down A(j)–A(k) with a clockwise rotation of A(i) to A(l) taken to be positive.

Ring torsion angles	ϕ/°
C(6)–S(1)–C(4)–S(2)	−65.4
C(5)–S(2)–C(4)–S(1)	67.0
C(4)–S(2)–C(5)–S(3)	−67.0
C(6)–S(3)–C(5)–S(2)	65.6
C(5)–S(3)–C(6)–S(1)	−62.2
C(4)–S(1)–C(6)–S(3)	62.4
Mean (absolute value)	64.9
Exocyclic torsion angles	
C(6)–S(1)–C(4)–C(7)	176.3
C(5)–S(2)–C(4)–C(7)	−174.0
C(4)–S(2)–C(5)–C(8)	174.4
C(6)–S(3)–C(5)–C(8)	−176.2
Mean (absolute value)	175.2
C(5)–S(3)–C(6)–C(9)	68.2
C(4)–S(1)–C(6)–C(9)	−68.5
Mean (absolute value)	68.3

The triangle formed by these three sulfur atoms is regular, the averaged length being 3.029 (±0.006) Å and the averaged apex angle 60.00 (±0.12)°. Another triangle formed by three ring-membered carbon atoms is also regular, with length 2.822 (±0.031) Å and angle 60.00 (±1.07)°. These triangles are approximately parallel to each other, showing that the ring has a chair-form. Shifts of three sulfur atoms from the plane containing three ring-membered carbon atoms are −0.635 Å for S(1), −0.712 Å for S(2), and −0.637 Å for S(3), where signs indicate whether or not the atoms are on the same side of the plane.

A torsion angle of these two triangles is calculated to be 60.4° (from S(1) to C(6)), which is given as a dihedral

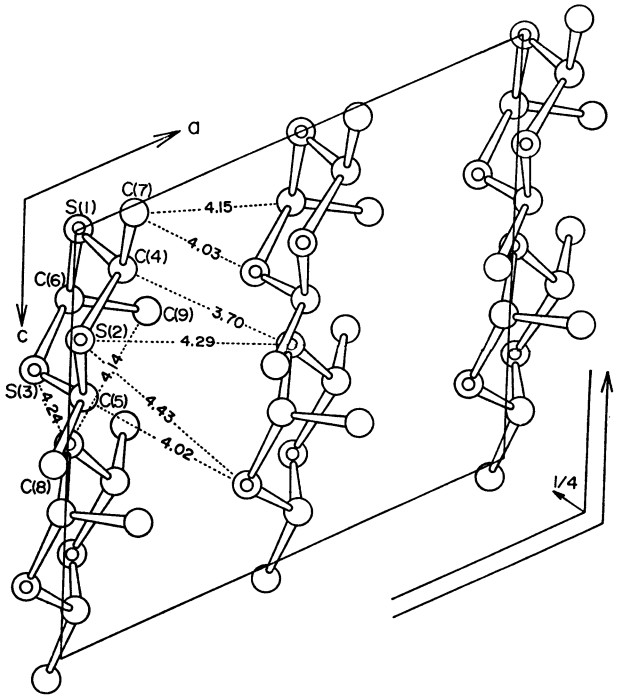

Fig. 3. The molecular packing viewed down b, showing all intermolecular distances (the non-hydrogen atoms) of less than 4.50 Å.

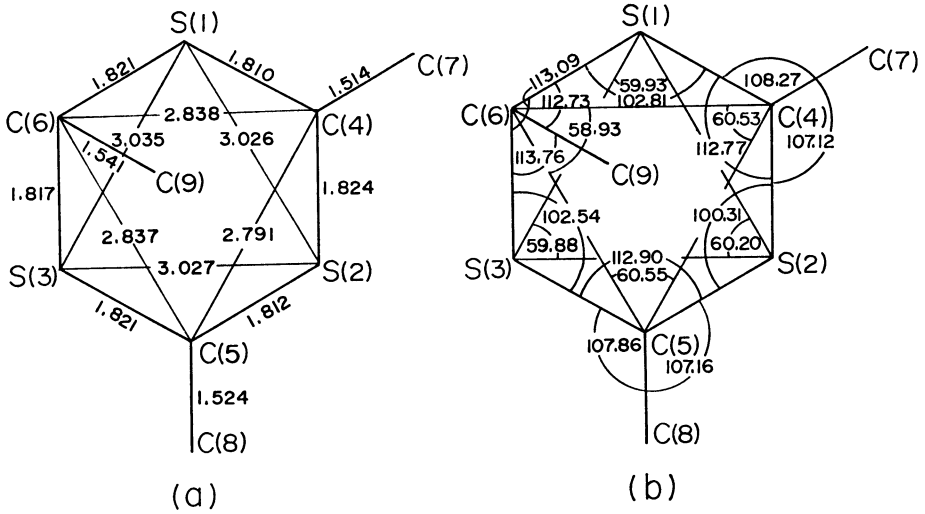

Fig. 2. Intramolecular interatomic distances (a) and angles (b).

angle around the line connecting the centers of the triangles.

Shifts of the three methyl carbon atoms from the plane formed by the three ring-membered carbon atoms are −0.283 Å for C(7), −0.389 Å for C(8), and +1.531 Å for C(9), showing that C(7) and C(8) are equatorial and C(9) is axial.

Torsion angles in the molecule are given in Table 5, where an angle for A(i)–A(j)–A(k)–A(l) is viewed down A(j)–A(k) with a clockwise rotation of A(i) to A(l) to be positive. The conformation of the chair-form is clearly seen from the alternative change of sign assigned to each torsion angle. The averaged value of the endocyclic torsion angles is 64.9° in absolute value.

The conformation of each methyl group is also clear; a mean of 175.2° for C···C_{eq} and a mean of 68.3° for C···C_{ax} rotation.

Molecular Packing. The molecular packing in the unit cell together with intermolecular interatomic distances less than 4.50 Å are shown in Fig. 3. The shortest contact of 3.70 Å is seen between C(4) and S(1) operated by the n-glide plane. No significant contact other than this can be seen. The molecules are held together in the crystal by the weak van der Waals contacts, corresponding to a low melting point.

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