A Reinvestigation of the Crystal and Molecular Structure of the β-Form of 2,4,6-Trimethyl-1,3,5-Trithiane

Kiyotane SEKIDO,* Jun ITOH,† Teruo NOGUCHI,† and Sakutaro HIROKAWA

Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239

†*Koa Oil Co., Ltd., Ōtemachi, Tokyo 100*

(Received April 28, 1980)

Synopsis. The crystal structure of the title compound has been reinvestgated and refined to a final *R* factor of 0.057 for 1286 independent reflections. The six-membered ring takes a chair-form. All the three methyl groups are in the equatorial position. The mean values are 1.818 Å and 1.513 Å for the S–C and C–C distances respectively, and 101.3° and 108.5° for the C–S–C and S–C–S angles respectively.

The structure analysis of β-TTA has been reported by Valle *et al.*[1] and by the present authors.[2] The intensity data used in these works were collected by the photographic method, however, so the molecular geometry obtained was not accurate. Recently, the structure analysis of α-TTA using three-dimensional intensities collected by the counter-technique was reported by the present authors.[3] The crystal structure of β-TTA was, therefore, reinvestigated for comparison with that of α-TTA.

Experimental

The single crystals of β-TTA used in the analysis were obtained by the slow evaporation of an acetone solution. They are transparent prisms elongated along a principal axis, having approximately square cross sections.

The cell constants were determined by the least-squares method using various sets of high-angle reflections on a diffractometer. The crystal data are as follows: $C_6H_{12}S_3$, *F. W.* =180.4, orthorhombic, space group $P2_12_12_1$, $a=13.437(13)$, $b=4.740(5)$, $c=14.688(15)$Å, $V=935.4(1.6)$Å^3, $D_m=1.274$ g cm^{-3}, $D_c=1.280$ g cm^{-3}, μ(Mo K_α)$=7.17$ cm^{-1}.

A prismatic crystal of $0.3\times0.5\times0.8$ mm was mounted on a four-circle diffractometer (Rigaku AFC-III) with Mo K_α from a graphite monochrometer, and the intensities were collected for the independent 1614 reflections within $2\theta<60°$, using the ω-2θ scan technique with a scanning speed of 4° min^{-1} in 2θ, while 324 reflections with $|F_o|<3\sigma(F)$ were designated as unobserved. Corrections for background and the Lorentz-polarization factor were made, but corrections for the absorption or the extinction were omitted.

The atomic parameters determined in the previous work[2] were used as input into the block-diagonal least-squares program on a computer CDC-6600 in the Century Reserch Center Co., Tokyo. At the stage of $R=0.096$, the hydrogen atoms were located, 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 block-diagonal least-squares using anisotropic thermal parameters for the non-hydrogen, and isotropic *B* values for the hydrogen, atoms. After six cycles, convergence was attained with $R=0.057$. The final coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 1.**

TABLE 1. ATOMIC COORDINATES($\times10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS

	x	*y*	*z*	B_{eq}/Å^2
S(1)	2237(2)	1602(5)	711(1)	5.34
S(2)	3937(1)	3904(4)	1863(1)	4.58
S(3)	2032(1)	1755(5)	2759(1)	4.94
C(4)	3573(6)	1789(17)	889(5)	4.92
C(5)	3379(5)	1995(16)	2813(5)	4.42
C(6)	1866(5)	−318(15)	1728(5)	4.75
C(7)	4070(7)	2988(25)	53(6)	7.20
C(8)	3663(7)	3549(21)	3675(5)	5.90
C(9)	775(6)	−1088(22)	1628(6)	6.13

Results and Discussion

The thermal vibration ellipsoids[4] scaled to a 50% probability, together with the atomic numbering, are shown in Fig. 1. The intramolecular interatomic distances and angles involving the non-hydrogen atoms are given in Table 2. The mean S–C length is 1.818 Å, the C–S–C angles are 100.2—102.6° (mean 101.3°), and the S–C–S angles are 112.3—114.1° (mean 113.5°). The mean values reported previously were: S–C, 1.814 Å; C–S–C, 98.9°; S–C–S, 114.7° in the unsubsituted 1,3,5-trithiane,[5] 1.818 Å, 101.89°, 113.09° in α-TTA.[3]

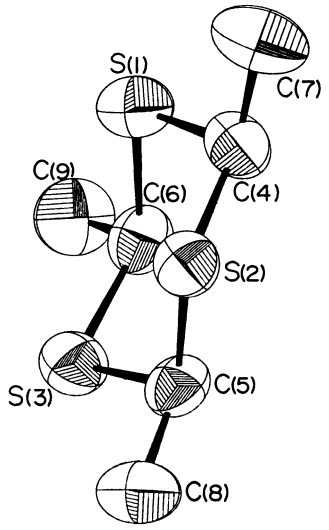

Fig. 1. The thermal vibration ellipsoids of non-hydrogen atoms drawn by ORTEP.[4]

The triangle formed by three sulfur atoms is regular, the averaged length being 3.040 Å (3.029 Å in α-TTA).

** The complete tables of the anisotropic thermal parameters, the F_o–F_c data, the least-squares planes, and the torsion angles are deposited as Document No. 8138 at the Office of the Editor of the Bulletin, the Chemical Society of Japan.

Table 2. 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)	1.816(8)	C(6) – S(1) – C(4)	100.2(3)
S(2) – C(4)	1.815(8)	C(4) – S(2) – C(5)	102.6(3)
S(2) – C(5)	1.823(7)	C(5) – S(3) – C(6)	101.1(3)
S(3) – C(5)	1.816(7)	S(1) – C(4) – S(2)	114.0(4)
S(3) – C(6)	1.820(8)	S(2) – C(5) – S(3)	114.1(4)
S(1) – C(6)	1.818(8)	S(3) – C(6) – S(1)	112.3(3)
C(4) – C(7)	1.508(12)	S(1) – C(4) – C(7)	109.9(6)
C(5) – C(8)	1.514(10)	S(2) – C(4) – C(7)	108.3(6)
C(6) – C(9)	1.518(10)	S(2) – C(5) – C(8)	107.2(5)
S(1)···S(2)	3.045(3)	S(3) – C(5) – C(8)	108.5(5)
S(2)···S(3)	3.053(3)	S(3) – C(6) – C(9)	109.2(5)
S(3)···S(1)	3.022(3)	S(1) – C(6) – C(9)	107.8(5)
C(4)···C(5)	2.840(10)	S(1)···S(2)···S(3)	59.4(1)
C(5)···C(6)	2.807(10)	S(2)···S(3)···S(1)	60.2(1)
C(6)···C(4)	2.789(10)	S(3)···S(1)···S(2)	60.4(1)
S(1)···C(5)	3.452(7)	C(4)···C(5)···C(6)	59.2(3)
S(3)···C(4)	3.440(7)	C(6)···C(4)···C(5)	59.8(3)
S(2)···C(6)	3.434(7)	C(5)···C(6)···C(4)	61.0(3)

The other triangle formed by three ring-membered carbon atoms is also regular, with a length of 2.812 Å (2.833 Å in α-TTA).

The C–C bond distances are in the range of 1.508—1.518 Å, with a mean of 1.513 Å, shorter than the previously reported values (1.58 Å by Valle *et al.*[1] and 1.572 Å by the present authors[2]). However, it agrees with the lengths of C–C_{eq} (from a ring-membered carbon to a methyl carbon in the equatorial position) in α-TTA (1.514 and 1.524 Å). The S–C–C bond angles are in the range of 107.2—109.9°, with a mean of 108.5°, in accordance with the value of α-TTA (107.60°).

The conformation of the chair-form can clearly be seen from the alternative change of sign assigned to each torsion angle. The averaged value of the endocyclic torsion angles is 65.0° (in absolute values), showing a good agreement with the 64.9° in α-TTA. The calculated exocyclic torsion angles (174.4° as a mean in absolute values) show that all three methyl groups are co-ordinated in an equatorial. In α-TTA they are

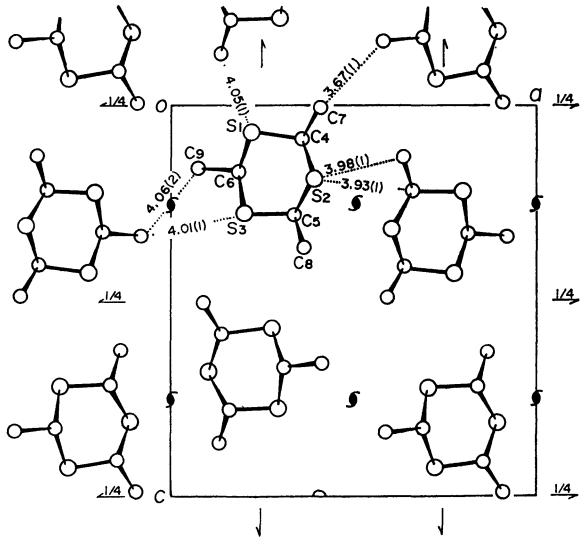

Fig. 2. The molecular packing viewed down **b**, showing all intermolecular distances (the non-hydrogen atoms) of less than 4.10 Å.

175.2° as a mean for the C···C_{eq}, and 68.3° for the C···C_{ax}, rotation.

The molecular packing, together with intermolecular interatomic distances less than 4.10 Å, are shown in Fig. 2. The shortest contact is 3.67 Å between C(7) and C(9) at $(1/2+x, 1/2-y, \bar{z})$. Since this is shorter than the van der Waals contact between two methyl groups, the rotations of the methyl groups may be hindered.

References

1) G. Valle, V. Busetti, and M. Mammi, *Acta Crystallogr., Sect. B*, **25**, 1631 (1969).
2) S. Hirokawa, K. Sekido, A. Suzuki, and T. Noguchi, *Memoirs of the Defense Academy, Jpn.*, XIV, No. 3, 89 (1974).
3) K. Sekido, H. Ono, T. Noguchi, and S. Hirokawa, *Bull. Chem. Soc. Jpn.*, **50**, 3149 (1977).
4) C. K. Johnson, *ORTEP*, ORNL-3794, Oak Ridge National Laboratory, Tennessee (1965).
5) G. Valle, V. Busetti, M. Mammi, and G. Carazzolov, *Acta Crystallogr., Sect. B*, **25**, 1432 (1969).