Acta Cryst. (1973). **B29**, 1815

The Boat-Chair Conformation in Crystalline 1,3,5,7-Tetrathiocane*

By Gerard W. Frank & Peter J. Degen†

Department of Chemistry,‡ University of California, Los Angeles, California 90024, *U.S.A.*

(*Received* 2 *March* 1973; *accepted* 12 *April* 1973)

The crystal structure of cyclic 1,3,5,7-tetrathiocane, $(CH_2S)_4$, with three crystallographically independent molecules in the asymmetric unit has been refined with X-ray diffractometer data. The space group is $P2_1/c$, with $a=20{\cdot}340$, $b=8{\cdot}747$, $c=13{\cdot}466$ Å, $\beta=99{\cdot}80°$ and $Z=12$ molecules per unit cell. The structure was solved by application of Sayre's relation and full-matrix least-squares refinement converged to an R value on F_o of 0·053. All molecules have a nearly identical boat-chair conformation with sulfur atoms in a square-planar arrangement and an approximate mirror plane of symmetry passing between two carbons on opposite sides of the ring. The average S–C bond length after thermal motion correction is 1·817 Å and all deviations from this average are small. The average C–S–C angle is 103°. The average S–C–S angle for carbon atoms lying on the pseudo mirror plane is 119° and for carbons off the plane is 117°. Intramolecular H–H contacts as short as 2·25 Å are found. All molecules are characterized by the same rigid-body thermal motion.

Introduction

The conformations of cyclic hydrocarbons and their oxygen-, nitrogen- and sulfur-substituted analogs have been studied from a theoretical standpoint, and experimentally using a variety of techniques. The conformations of such compounds and the nature of their nonbonded contacts are of wide interest in relation to chemical properties such as polymerization and complexing of ions. With regard to cyclooctane, energy calculations by Hendrickson (1967) predicted the boat-chair to be the conformer of lowest strain energy. Crystallographic studies on substituted cyclooctanes have shown in some cases, however, the crown form, as, for example, in metaldehyde (Pauling & Carpenter, 1936), in *N,N'*-dimethyl-1,5-diaza-3,7-dithiacyclooctane (Grandjean & Leclaire, 1967), and 1,3,5,7-tetraoxocane (Chatani, Uchida, Tadokoro, Hayashi, Nishii & Okamura, 1968). On the other hand, Frank, Degen, & Anet (1972) reported a boat-chair conformation for the present molecule, 1,3,5,7-tetrathiocane, in the crystalline state, as well as a non-crown conformation in solution. A non-crown conformation has also been found in two crystal forms of 1,3,5,7,9-pentathiocyclodecane (Valle, Piazzesi & del Pra, 1972). Fig. 1 illustrates the boat-chair conformation of 1,3,5,7-tetrathiocane.

The effect of substituents on ring conformation and the strain energies associated with the various conformers will be related to the interatomic distances and angles in such molecules. The present refinement of the three crystallographically independent molecules in the crystal structure of 1,3,5,7-tetrathiocane has provided an accurate determination of the geometry about the carbon and sulfur atoms, and shows the subtle effect of conformation on the interatomic angles, in particular.

Experimental

Intensity data were collected from a crystal in the shape of an elongated plate, with approximate dimensions 0·8 × 0·5 × 0·2 mm. The crystal was sealed in a glass capillary (wall thickness = 0·01 mm) since previous work had indicated that the crystals sublime during the course of data collection. The crystal was mounted with its elongated dimension, which was parallel to the crystallographic c axis, along the spindle axis. X-ray intensities were measured on a Syntex $P\bar{1}$ automated four-circle diffractometer, with graphite crystal-monochromated Mo $K\alpha$ radiation. The incident beam collimator had a diameter of 1 mm. The unit-cell parameters were refined by least-squares calculations from 2θ measurements at room temperature corresponding to the Mo $K\alpha$ (0·71069 Å) peaks for 26 independent reflections. These parameters are only slightly different from those reported by Russo, Mortillaro, De Checchi, Valle & Mammi (1965) from photographic data. The density of the crystals was measured by flotation, and the essential crystal data are presented in Table 1.

Table 1. *Crystal data*

Space group: $P2_1/c$; $Z=12$ molecules/cell
$a=20{\cdot}340$ (5), $b=8{\cdot}747$ (3), $c=13{\cdot}466$ (5) Å; $\beta=99{\cdot}80$ (3)°
$V=2360$ Å^3; $d_{\text{calc}}=1{\cdot}555$; $d_{\text{obs}}=1{\cdot}56$ g cm^{-3}.

All reciprocal lattice points in the hkl and $\bar{h}kl$ octants were examined out to a maximum $(\sin\theta)/\lambda$ value of 0·703 Å^{-1} ($2\theta_{\max}=60°$). Intensities of equivalent reflections in all octants were sampled and found to agree

---

* This work is supported in part by National Science Foundation grants GP-8223, GP-10949, GP-32324X and GP-28248.

† Present address: Central Research Laboratories, The Minnesota Mining & Manufacturing Company, St. Paul, Minnesota 55101, U.S.A.

‡ Contribution No. 3122.

within 2%. Integrated intensities were measured with the θ–2θ scan technique using a variable 2θ scan rate of from 2 to 24° per min, depending on the magnitude of the intensity. The scan width was approximately 2·2° in 2θ and left and right backgrounds were counted for a total time of one-half the peak scan time.

The number of independent reciprocal lattice points thus examined was 7170. Data were reduced using the following Lorentz–polarization factor:

$$\mathrm{Lp}^{-1}=(\sin 2\theta_{\mathrm{cryst}})/(\cos^2 2\theta_{\mathrm{mono}}+\cos^2 2\theta_{\mathrm{cryst}})$$

(after Azaroff, 1955) which is the expression appropriate to a geometry in which the respective θ–2θ planes of the monochromating and diffracting crystals are at right angles to each other.

Absorption of X-rays by the crystal has the value $\mu=10{\cdot}7\ \mathrm{cm}^{-1}$. For the specimen used in data collection the value of $\exp(-\mu R_{\mathrm{min}})/\exp(-\mu R_{\mathrm{max}})=1{\cdot}36$. No correction for anisotropic absorption of X-rays was applied since the absorption characteristics of the glass capillary could not be adequately assessed. Moreover, the fact that the long dimension of the crystal and the spindle axis were parallel reduces the variation in optical path as the crystal is reoriented.

A value of $\sigma(F)$ based on counting statistics and other errors in measurements, such as coincidence errors, was calculated for each $|F_{hkl}|$ according to the expression:

$$\sigma(F)=\frac{\mathrm{Lp}^{-1}}{2F_o}\,(\text{Scan intensity}+\text{Background}+[0{\cdot}04I_o]^2)^{1/2}$$

Reflections for which $|F_{hkl}|$ was less than $4\sigma(F)$ were considered to be unobserved and not used in least-squares refinement of the structure. The number of observed reflections by this criterion was 4509.

Structure refinement

The atomic positions reported by Frank *et al.* (1972) provided a starting set for the refinement carried out on the present data. These positions had been determined by the application of Sayre's (1952) relation in the computer program by Long (1965) using 400 reflections with E-values greater than 1·7. An E-map based on the set of signs with the highest consistency index yielded the coordinates of all sulfur atoms. A Fourier map phased on the sulfurs showed all carbon atoms. Full-matrix least-squares refinement was carried out using carbon and sulfur atomic scattering factors taken from *International Tables for X-ray Crystallography* (1962), and the contribution of each reflection was weighted by $[1/\sigma(F)]^2$. The R value, defined by $R=\sum||F_o|-|F_c||/\sum|F_o|$ converged to 0·092. Positions for the 24 hydrogen atoms in the asymmetric unit were calculated at this point, assuming a carbon–hydrogen bond length of 1·0 Å and tetrahedral geometry about the carbon atoms. Hydrogen atoms were included in subsequent structure factor calculations, using the scattering factors of Stewart, Davidson & Simpson (1965). Since, on average, the hydrogen atoms account for only 0·5% of the scattering, their coordinates were not refined. The hydrogen isotropic B was set at 6·0 Å^2. Additional refinement cycles gave an R value of 0·060.

Table 2. *Refined positions of sulfur and carbon atoms; calculated hydrogen positions*

A, *B*, *C* designate rings; *a*, *e* designate axial and equatorial hydrogens. E.s.d. values in parentheses.

	x	*y*	*z*
S(2*A*)	−0·01526 (5)	0·1530 (1)	0·20558 (7)
S(4*A*)	0·13517 (5)	0·1748 (1)	0·19932 (7)
S(6*A*)	0·16616 (5)	0·2144 (1)	0·43194 (7)
S(8*A*)	0·01547 (5)	0·2035 (1)	0·43953 (7)
S(2*B*)	0·49158 (5)	0·1516 (1)	0·13842 (8)
S(4*B*)	0·45565 (5)	0·2209 (2)	0·34601 (8)
S(6*B*)	0·30568 (5)	0·2437 (1)	0·25053 (7)
S(8*B*)	0·34154 (5)	0·1772 (1)	0·03945 (7)
S(2*C*)	0·66234 (5)	0·2817 (1)	0·14063 (7)
S(4*C*)	0·81429 (5)	0·2354 (1)	0·16349 (7)
S(6*C*)	0·80516 (5)	0·2657 (1)	−0·06793 (7)
S(8*C*)	0·65290 (5)	0·3200 (1)	−0·09247 (7)
C(1*A*)	−0·0288 (2)	0·1020 (5)	0·3312 (3)
C(3*A*)	0·0621 (2)	0·0548 (5)	0·1970 (3)
C(5*A*)	0·1350 (2)	0·2931 (5)	0·3091 (3)
C(7*A*)	0·0955 (2)	0·1067 (5)	0·4601 (3)
C(1*B*)	0·4198 (2)	0·0739 (5)	0·0559 (3)
C(3*B*)	0·4780 (2)	0·0810 (5)	0·2599 (3)
C(5*B*)	0·3883 (2)	0·3245 (5)	0·2700 (3)
C(7*B*)	0·3062 (2)	0·1119 (5)	0·1464 (3)
C(1*C*)	0·6301 (2)	0·3835 (5)	0·0255 (3)
C(3*C*)	0·7455 (2)	0·3610 (5)	0·1731 (3)
C(5*C*)	0·7915 (2)	0·1543 (5)	0·0388 (3)
C(7*C*)	0·7360 (2)	0·3977 (5)	−0·0879 (3)
H(1*Aa*)	−0·018	−0·020	0·343
H(1*Ae*)	−0·082	0·109	0·332
H(3*Aa*)	0·072	−0·031	0·258
H(3*Ae*)	0·055	−0·016	0·129
H(5*Aa*)	0·084	0·335	0·308
H(5*Ae*)	0·162	0·400	0·300
H(7*Aa*)	0·091	−0·001	0·417
H(7*Ae*)	0·106	0·066	0·538
H(1*Ba*)	0·411	−0·043	0·081
H(1*Be*)	0·433	0·055	−0·019
H(3*Ba*)	0·440	−0·009	0·248
H(3*Be*)	0·523	0·019	0·296
H(5*Ba*)	0·402	0·347	0·196
H(5*Be*)	0·386	0·440	0·301
H(7*Ba*)	0·332	0·006	0·176
H(7*Be*)	0·225	0·072	0·120
H(1*Ca*)	0·644	0·505	0·036
H(1*Ce*)	0·575	0·386	0·017
H(3*Ca*)	0·749	0·463	0·127
H(3*Ce*)	0·752	0·408	0·250
H(5*Ca*)	0·739	0·121	0·028
H(5*Ce*)	0·817	0·044	0·037
H(7*Ca*)	0·744	0·487	−0·030
H(7*Ce*)	0·737	0·462	−0·158

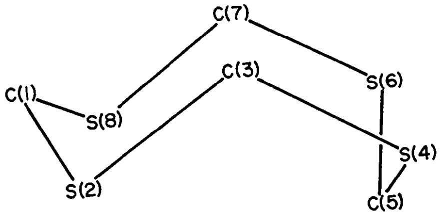

Fig. 1. The boat-chair conformation of 1,3,5,7-tetrathiocane. Drawn to scale.

It was observed that a number of intense, low-angle reflections had large positive values for $[|F_c|-|F_o|]$, which was attributed to secondary extinction. A correction was applied to the reflections (after Zachariasen, 1967), using:

$$|F_{corr}|=|F_o|[1+\beta C I_o]^{1/2}\,.$$

C was determined empirically to have the value $0{\cdot}71\times10^{-6}$. The largest correction thus derived for any reflection was a factor of 1·32, this being for the 020 reflection. The 020 and 600 reflections deserve special note. Both were too intense to be measured accurately under the given experimental conditions. Their intensities were estimated from a set of data collected from a smaller crystal. They were given zero weight in the present refinement.

The final R value was 0·053, based on the 4509 reflections included in refinement, and 0·097 for all 7170 measured reflections. Refined carbon and sulfur atom positions are listed in Table 2, with the calculated hydrogen positions. Refined anisotropic thermal parameters for carbon and sulfur are listed in Table 3. The observed values of $|F_{hkl}|$ and those calculated from the refined structure are given in Table 4. The quoted estimated standard deviations in the position and thermal parameters were derived from the inverse of the least-squares matrix. The averaged estimated standard deviations in sulfur and carbon positions are, respectively, 0·001 and 0·004 Å.

Description of the structure

Molecular packing and space group symmetry

Fig. 2 is a stereoview of the unit-cell contents along the b axis. It is evident that in all rings, the planes formed by the four sulfur atoms lie perpendicular to the b axis, or nearly so. The curious fact that rings A, B and C have nearly identical conformations, yet are crystallographically independent, raised the question of possible pseudo-symmetry elements in the crystal structure. It can be seen, however, that the pseudo mirror planes which characterize the point symmetry of each ring do not bear any special relationship to the symmetry elements of the crystal lattice. While close inspection reveals that ring A and the ring generated from C by the operation of the c glide (C_3 in Fig. 2). are similarly oriented, and can be related by a pseudo translation vector which is approximately perpendicular to **b**, this vector does not correspond to a lattice translation; neither is ring B related to any other rings in the unit cell by this vector.

Bond lengths and angles

Figs. 3 and 4 illustrate the bond lengths and angles for the three rings in the asymmetric unit, and Table 5 lists various averaged values of these lengths and angles. The estimated standard deviation in a typical carbon–sulfur bond length is about 0·004 Å, which is the approximate uncertainty in the carbon atom position. The deviations of individual bond lengths from the overall average of 1·817 Å for the 24 bonds are not significant in terms of the precision of the structure. The forces due to conformational strain and molecular packing show themselves primarily in the deviations of the bond angles. The expected standard deviations in C–S–C and S–C–S angles are about the same, or 0·2°, which again reflects chiefly the precision in the positions of the carbon atoms. Deviations of individual C–S–C and S–C–S angles from their respective averages in Table 5 are clearly large relative to the expected

Table 3. *Anisotropic thermal parameters* ($\times 10^5$) *with e.s.d's in parentheses*

Values correspond to the expression $B=\exp\,[-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(2*A*)	161 (2)	1275 (14)	529 (5)	36 (9)	72 (6)	23 (16)
S(4*A*)	183 (2)	1630 (16)	486 (5)	−45 (10)	228 (5)	−118 (16)
S(6*A*)	195 (2)	1433 (15)	496 (5)	−151 (10)	1 (6)	100 (16)
S(8*A*)	227 (2)	1189 (13)	533 (5)	143 (10)	252 (6)	−7 (15)
S(2*B*)	170 (2)	1463 (15)	757 (6)	−136 (10)	314 (6)	−354 (18)
S(4*B*)	252 (3)	1528 (16)	543 (5)	327 (11)	−18 (7)	−330 (17)
S(6*B*)	175 (2)	1230 (13)	588 (5)	−109 (9)	271 (5)	−386 (15)
S(8*B*)	224 (2)	1316 (14)	432 (5)	93 (10)	134 (6)	190 (15)
S(2*C*)	200 (2)	1498 (15)	516 (5)	−74 (11)	168 (6)	229 (16)
S(4*C*)	219 (2)	1687 (16)	420 (5)	420 (11)	−51 (6)	−282 (16)
S(6*C*)	237 (2)	1609 (16)	479 (5)	−55 (11)	211 (6)	−78 (17)
S(8*C*)	233 (2)	1225 (13)	473 (5)	−45 (11)	−63 (6)	−29 (16)
C(1*A*)	166 (8)	1223 (56)	508 (20)	−88 (38)	149 (21)	163 (62)
C(3*A*)	184 (9)	1110 (53)	573 (22)	−1 (38)	165 (22)	−389 (62)
C(5*A*)	199 (8)	879 (46)	438 (19)	−167 (35)	145 (19)	83 (54)
C(7*A*)	196 (9)	1027 (50)	471 (20)	48 (37)	124 (26)	226 (60)
C(1*B*)	205 (9)	1116 (55)	443 (19)	61 (37)	229 (20)	−116 (57)
C(3*B*)	221 (10)	1154 (56)	562 (24)	342 (40)	−4 (26)	−164 (66)
C(5*B*)	155 (9)	800 (45)	509 (20)	−17 (33)	55 (21)	−131 (55)
C(7*B*)	170 (9)	986 (48)	465 (19)	−194 (34)	203 (19)	−210 (55)
C(1*C*)	172 (9)	1245 (56)	539 (22)	145 (39)	26 (23)	47 (67)
C(3*C*)	174 (8)	1126 (51)	368 (18)	69 (37)	13 (20)	−296 (55)
C(5*C*)	237 (9)	864 (48)	417 (19)	170 (38)	78 (23)	−147 (54)
C(7*C*)	281 (11)	997 (53)	501 (22)	−90 (42)	138 (16)	219 (62)

Table 4. F_o *and* F_c *values*

Table 4 (*cont.*)

H	F_o	F_c
[illegible]	[illegible]	[illegible]

standard deviation. Deviations in the C–S–C bond angles do not show any clear pattern related to the mirror plane point symmetry which would obtain in an idealized boat-chair molecule. However, in all three molecules of the asymmetric unit, the S–C–S bond angles about C(1) and C(5) are larger than those about C(3) and C(7). C(1) and C(5) would lie on the mirror plane through an idealized boat-chair. Such an enlargement of the bond angles about these two atoms due to intramolecular conformational strain has been predicted for the boat-chair conformer of cyclooctane by Hendrickson (1967). Other bond angle and torsion angle deviations from ring to ring and within each ring may probably be attributed to intermolecular packing forces.

Non-bonded intramolecular contacts

A qualitative idea of the molecular strain resulting from van der Waals forces between non-bonded atoms within the ring may be obtained by comparing the

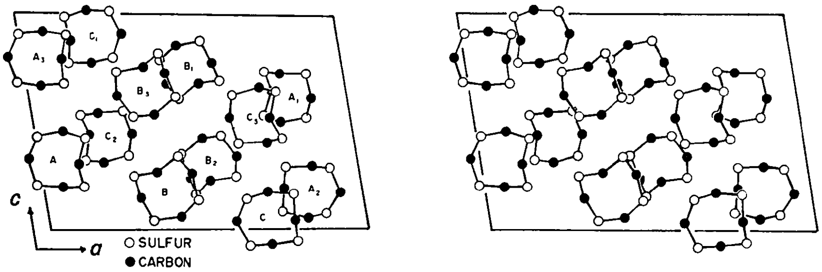

Fig. 2. Stereo packing diagram viewed along the *b* axis. Subscripts denote rings generated by symmetry operations: 1 = center of symmetry; 2 = twofold screw axis along *b*; 3 = *c* glide.

distance between such atoms with the sums of accepted values for the van der Waals radii. In the present work, these values have been taken to be 1·7 and 1·2 Å, respectively, for carbon and hydrogen (Pauling, 1960) and 1·65 Å for sulfur (Donohue, 1950). No unusually short C–C or S–S contacts were found in 1,3,5,7-tetrathiocane, as can be seen from the averaged cross-ring distances listed in Table 5. On the other hand, several H–H distances are about 2·25 Å, or almost 0·2 Å shorter than the sum of two van der Waals radii for hydrogen.

It would be of interest to know the strain energy of the boat-chair conformation, at least relative to other possible conformers, in particular, the crown which has been found in other substituted cyclooctanes. Such a comparison is difficult in the absence of information about twisting and bending energies in covalent bonds to sulfur. One can, however, compare the number and lengths of the non-bonded contacts observed in boat-chair 1,3,5,7-tetrathiocane with those in a hypothetical, idealized crown conformer of the same molecule. Such a conformer is illustrated in Fig. 5. The coordinates have been constructed on the assumption of 4*mm* point symmetry, a C–S bond of 1·817 Å, a C–H bond length of 1·1 Å, and values for the C–S–C, S–C–S, and H–C–H angles of 103°, 118° and 103°, respectively.

The four sulfurs of such a crown lie on the corners of a square 3·1 Å on a side, much as they do in the ob-

Table 5. *Intramolecular geometry with e.s.d. values in parentheses*

	Ring *A*	Ring *B*	Ring *C*	All rings
Average C–S bond	1·818 (4) Å	1·817 (6) Å	1·817 (7) Å	1·817 (5) Å
Average C–S–C angle	102·4 (6)°	102·4 (9)°	103·1 (9)°	102·6 (9)°
Average S–C–S angle	118 (2)	118 (1)	118 (1)	118 (1)
Average angle about C(1) and C(5)				119·1 (4)
Average angle about C(3) and C(7)				116·9 (6)
Torsion angles (about bonds between indicated atoms):				
C(1)–S(2): S(8)–C(1)				82 (2)°
S(2)–C(3); C(7)–C(8)				109 (2)
C(3)–S(4); S(6)–C(7)				49 (2)
S(4)–C(5); C(5)–S(6)				81 (2)
Non-bonded contact distances between indicated atoms on same ring:				
C(1)–C(5)				3·80 (3) Å
C(3)–C(7)				3·55 (3)
S(2)–S(6); S(4)–S(8)				4·40 (1)
H(1*a*)–H(2*a*); H(2*a*)–H(4*a*); H(4*a*)–H(1*a*)				2·25
H(3*a*)–C(3); H(3*a*)–C(7); H(1*a*)–C(3); H(1*a*)–C(7)				2·80
H(2*a*)–C(1); H(4*a*)–C(1)				2·60

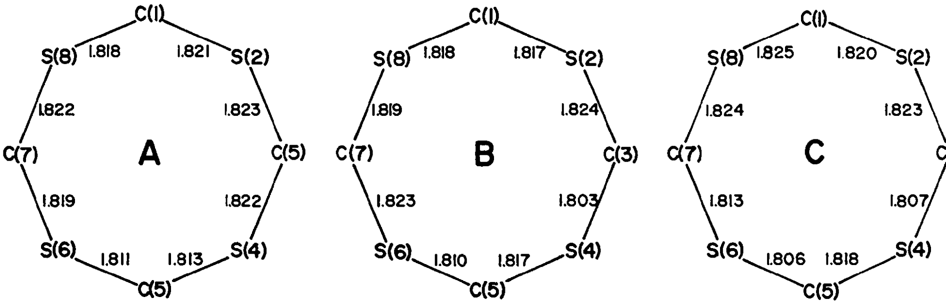

Fig. 3. Bond distances in 1,3,5,7-tetrathiocane. Pseudo symmetry plane passes through C(1) and C(5).

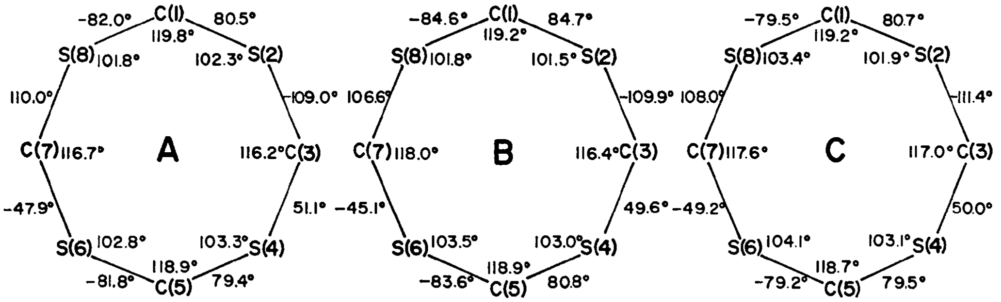

Fig. 4. Bond angles and torsion angles in 1,3,5,7-tetrathiocane.

served boat-chair conformer. Thus S–S non-bonded contacts are quite the same in both conformers. There are short C–H contacts (of about 2·7 Å) in both conformers, 4 in the boat–chair, 8 in the crown. These, however, are not short enough to contribute significantly to the repulsive energy in either conformation. Lastly, concerning H–H contacts of about 2·25 Å, there are four such in the crown and only three in the boat–chair. In energy calculations for cyclooctane conformers (Hendrickson, 1967) such H–H interactions are the largest contributors among the non-bonded contacts, and are always repulsive. It may be inferred from this that in 1,3,5,7-tetrathiocane, the strain energy of the boat–chair conformation is probably, but only slightly, less than that in the crown. The length of the C–S bond suggests that twisting energies in sulfur-substituted rings would be less than those in cyclooctane, and the energy differences between various conformers smaller in 1,3,5,7-tetrathiocane than in cyclooctane.

Molecular thermal motion

An analysis of the anisotropic thermal parameters according to the 21-element rigid-body model of Schomaker & Trueblood (1968) was made for each molecule in the asymmetric unit. The similarity in the thermal behavior of all three rings can be seen in the eigenvalues for the translation, libration, and correlation tensors which are listed in Table 6 with those for the moment of inertia tensors. The e.s.d. between the values of the mean-square displacements of atoms due to thermal motion (the U_{ij}'s) calculated from the rigid-body model and those calculated from the observed β_{ij} values in Table 3 is 0·0024 Å^2 for each ring. The e.s.d. values for the observed U_{ij} values themselves are 0·0006 Å^2 for sulfur atoms, and 0·002 Å^2 for carbon atoms. Thus, each ring vibrates rigidly by and large, with little motion of individual atoms relative to each other.

Fig. 6 is a stereo *ORTEP* drawing which shows the thermal ellipsoids in ring *A*, and is typical of the other rings as well. The libration tensors for each ring show two larger and one smaller eigenvalue. This is true also of the moment of inertia tensors. The largest angle between eigenvectors which correspond to the axes of minimum libration and minimum moment of inertia are nearly parallel, the largest $\mathbf{L}_3$–$\mathbf{I}_3$ angle being 29° in ring *B*. This accords with the expectation that libration should impart to the molecule a larger motion along the direction parallel to the minimum moment of inertia.

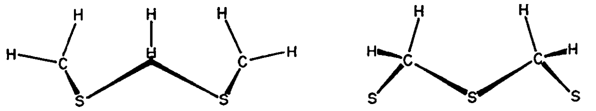

Fig. 5. Idealized crown conformer of 1,3,5,7-tetrathiocane (hypothetical construction). Left: one C, two S eclipsed. Right: one S, two C eclipsed.

Table 6. *Rigid-body thermal motion tensors*

		Principal axes	Direction cosines*		
Moment of inertia†					
Ring *A*	I_1	390	0·3592	0·1625	0·9190
	I_2	385	−0·9238	−0·0775	0·3749
	I_3	31	0·1321	−0·9837	0·1223
Ring *B*	I_1	391	0·7822	0·0022	0·6230
	I_2	384	−0·5981	0·2826	0·7499
	I_3	30	0·1744	0·9592	−0·2224
Ring *C*	I_1	390	0·7412	−0·2387	0·6274
	I_2	387	0·6370	−0·0448	−0·7696
	I_3	31	0·2119	0·9700	0·1188
Libration tensor					
Ring *A*	L_1	22°^{2}	−0·1998	0·0396	−0·9790
	L_2	21	−0·9380	−0·3133	0·1482
	L_3	6	0·3013	−0·9471	−0·1106
Ring *B*	L_1	32	−0·2909	0·6976	0·6547
	L_2	20	−0·9188	−0·0125	−0·3945
	L_3	5	0·2669	0·7164	−0·6447
Ring *C*	L_1	31	−0·4137	0·3884	0·8234
	L_2	26	−0·7659	0·3437	−0·5433
	L_3	7	0·4944	0·8557	−0·1525
Translation tensor‡					
Ring *A*	T_1	0·040Å^2	0·3510	0·1509	0·9321
	T_2	0·031	−0·8722	−0·3212	0·3617
	T_3	0·021	0·3560	−0·9333	0·0089
Ring *B*	T_1	0·038	−0·4372	−0·2193	−0·8721
	T_2	0·030	0·7695	−0·5937	−0·2359
	T_3	0·020	−0·4662	−0·7742	0·4280
Ring *C*	T_1	0·038	−0·7949	0·2719	0·5439
	T_2	0·032	0·4797	−0·2764	0·8312
	T_3	0·018	0·3765	0·9225	0·0917
Correlation tensor§					
Ring *A*	S_1	0·0015 rad. Å	0·7740	0·4784	−0·3929
	S_2	0·0004	0·1827	−0·7949	−0·5859
	S_3	−0·0019	−0·6165	0·3635	−0·7046
Ring *B*	S_1	0·0019	0·4254	−0·1169	0·8974
	S_2	0·0001	0·4526	0·8861	−0·0989
	S_3	−0·0020	−0·7823	0·4528	0·4279
Ring *C*	S_1	0·0025	0·3554	−0·9349	−0·0419
	S_2	−0·0001	−0·5798	−0·1827	−0·7935
	S_3	−0·0024	0·7339	0·3040	−0·6063
		Ring *A*	Ring *B*	Ring *C*	
I_3–L_3 angle		17°	29°	24°	

* Along orthogonal directions parallel to crystallographic **a**, **b** and **c*** axes.

† Principal axes set to arbitrary scale.

‡ Transformed after symmetrization of S-tensor and shift of origin to effective center of libration.

§ After symmetrization. Trace set to zero.

The bond distances presented in Fig. 1 have been corrected for the foreshortening due to libration, according to Cruickshank (1961). The average C–S bond length was 1·809 Å before correction, and 1·817 Å after.

Full matrix least-squares refinement was performed with the computer program of P. K. Gantzel, R. A. Sparks, and K. N. Trueblood (UCLA-LS1). Stereoscopic drawings were made with the *ORTEP* program written by C. K. Johnson (ORNL Report 3794, revised). The authors are indebted to Professors K. N. Trueblood and F. A. L. Anet for helpful suggestions and criticisms.

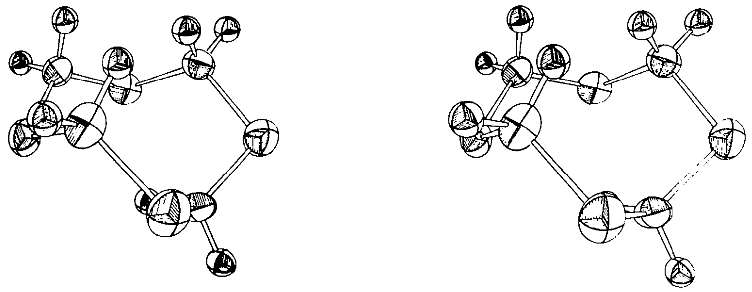

Fig. 6. Stereo *ORTEP* drawing of ring *A*, showing thermal ellipsoids, staggered view.

References

AZAROFF, L. V. (1955). *Acta Cryst.* **8**, 701–704.

CHATANI, Y., UCHIDA, T., TADOKORO, H., HAYASHI, K., NISHII, M. & OKAMURA, S. (1968). *J. Macromol. Sci.* B**2**, 567–590.

CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896–897.

DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 2701–2705.

FRANK, G. W., DEGEN, P. J. & ANET, F. A. L. (1972). *J. Amer. Chem. Soc.* **94**, 4792–4793.

GRANDJEAN, D. & LECLAIRE, A. (1967). *C. R. Acad. Sci. Paris. Ser. C.* **265**, 795–796.

HENDRICKSON, J. B. (1967). *J. Amer. Chem. Soc.* **89**, 7036–7043.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202 ff. Birmingham: Kynoch Press.

LONG, R. (1965). Ph. D. Thesis. Department of Chemistry Univ. of California, Los Angeles.

PAULING, L. & CARPENTER, D. C. (1936). *J. Amer. Chem. Soc.* **58**, 1274–1278.

PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd Ed., p. 260. Ithaca: Cornell Univ. Press.

RUSSO, M., MORTILLARO, L., DE CHECCHI, C., VALLE, G. & MAMMI, M. (1965). *Polymer. Lett.* **3**, 501–504.

SAYRE, D. (1952). *Acta Cryst.* **5**, 60–65.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VALLE, G., PIAZZESI, A. & DEL PRA, A. (1972). *Cryst. Struct. Commun.* **1**, 289–296.

ZACHARIASEN, W. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1973). B**29**, 1822

The Crystal Structure of Acetophenone at 154°K

BY Y. TANIMOTO, H. KOBAYASHI,* S. NAGAKURA AND Y. SAITO

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

(*Received* 20 *March* 1973; *accepted* 10 *April* 1973)

The crystal and molecular structure of acetophenone, $C_6H_5COCH_3$, has been determined by three-dimensional X-ray data collected by diffractometry at 154°K. The crystals are monoclinic, space group $P2_1/n$ with cell dimensions: $a=10{\cdot}256$ (1), $b=8{\cdot}678$ (2), $c=8{\cdot}558$ (1) Å, $\beta=121{\cdot}00$ (1)° and $Z=4$. The structure was solved by the symbolic addition procedure and refined by the block-diagonal least-squares method to give $R=0{\cdot}038$ for the 1237 observed reflexions. The molecule is nearly planar. The methyl carbon atom deviates from the plane of the benzene ring by 0·121 Å. The C=O bond length is 1·216 (2) Å. The molecules are packed by van der Waals forces.

Introduction

Analysis of the Zeeman splitting pattern of the acetophenone crystal requires a knowledge of the crystal structure (Tanimoto, Kobayashi, Nagakura & Azumi, 1972). Acetophenone was subjected to X-ray crystal analysis at 154°K in order to obtain accurate structural parameters.

Experimental

Crystals were obtained by standing an ethanol solution in a refrigerator. A small spherical crystal of about 0·5 mm in diameter was used. The cooling device is broadly similar to that described by Post, Schwartz & Fankuchen (1951). The crystal specimen was cooled by a flow of cold nitrogen gas surrounded by a jacket of dry nitrogen gas at room temperature, both issuing from an evaporation vessel containing liquid nitrogen. The liquid level in the evaporation vessel was auto-

---

* Present address: Faculty of Science, Toho University, Narashino, Chiba 275, Japan.