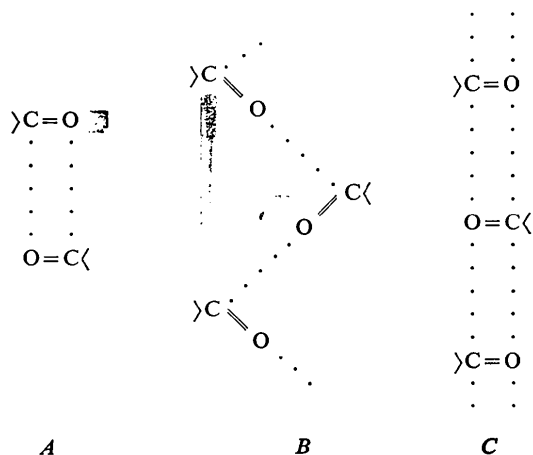


this arrangement (type *A*) the carbonyl groups are anti-parallel with an angle  $O(2) \cdots C(2)=O(2)$  of  $82.6^\circ$ ; it is thus different from the two infinite types commonly found: type *B* (e.g. Gatehouse & Craven, 1971) and type *C* (e.g. Craven & Cusatis, 1969).



Although this interaction is weak it seems to have some importance for the three dimensional packing of the molecules in the crystal structure. In metharbutal, the two other carbonyl groups are not involved in such intermolecular close approaches.

This work was supported in part by Grant No. GU-3184 of the National Science Foundation and in part by Grant No. NS-02763 of the U.S. Public Health Service, National Institutes of Health. The IBM 7090 and 1130 computer programs were modified and adopted by Dr R. Shiono, Department of Crystallog-

raphy, University of Pittsburgh. The author wants to thank Professor B. M. Craven for discussions and Mrs Joan Klinger for technical assistance.

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## The Crystal Structure of 1,2,3,3-Tetrachloro-4,5-dimethylspiro[2.3]hexa-1,4-diene at $-65^\circ\text{C}$

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(Received 31 July 1972; accepted 4 October 1972)

Crystals of 1,2,3,3-tetrachloro-4,5-dimethylspiro[2.3]hexa-1,4-diene ( $\text{C}_8\text{H}_6\text{Cl}_4$ ) are triclinic, space group  $P\bar{1}$ ;  $a = 8.189$  (4),  $b = 8.763$  (5),  $c = 8.334$  (3) Å,  $\alpha = 91.34$  (2),  $\beta = 110.09$  (2),  $\gamma = 106.61$  (2)°,  $Z = 2$ ,  $D_m = 1.48$  g cm $^{-3}$ ,  $D_x = 1.52$  g cm $^{-3}$ . The integrated intensities of 1979 independent reflexions were measured with an automated diffractometer, of which 1607 were used in the refinement. The data were collected at  $-65^\circ\text{C}$  using a refrigerated goniometer. The structure was solved by direct methods and refined by full-matrix least-squares analysis to a final least-square residual of 0.072. The two rings of the molecule are mutually orthogonal and bond lengths are slightly shorter than the values reported for related cyclopropenes and cyclobutenes.

### Introduction

Although the structures of some compounds containing carbon rings in a spiro arrangement have been

studied by crystallographic techniques, all of these have contained relatively large numbers of carbon atoms in the rings. The smallest spiro compound whose structure has been reported to date is spiro[4.4]nonane-1,6-

dione (Altona, de Graaf, Leeuwstein & Romers, 1971). Many of these compounds are gaseous at ambient conditions and some structural studies using microwave and electron diffraction techniques have been reported, including a microwave study of spiro-pentyl chloride by Woerner & Harmony (1966) and an electron diffraction study of spiro-pentane by Donohue, Humphrey & Schomaker (1945).

The synthesis of 1,2,3,3-tetrachloro-4,5-dimethylspiro[2.3]-hexa-1,4-diene,  $C_8H_6Cl_4$ , has recently been reported by Semmelhack & DeFranco (1971) and the present study was undertaken to confirm the identification of the compound and to determine its molecular geometry. This is the first report of a crystallographic study of a spiro compound with less than nine carbon atoms in the rings and the first structural study of a spiro compound containing the maximum possible number of substituents.

### Experimental

Crystals of the compound were supplied by Professor M. F. Semmelhack of Cornell University. Samples were placed in Lindemann glass capillaries under a dry nitrogen atmosphere. They were held rigid by glass wool wedged into the capillary.

It soon became apparent that the samples were degrading too quickly in the X-ray beam at ambient temperature to allow any meaningful investigation of the crystals other than the determination of the Laue group. The melting temperature of the compound is 36–37°C and at room temperature the white crystals appear to have a thin liquid layer on their surface with ill defined crystalline edges. In the X-ray beam the fraction of material in the liquid state increases, allowing the remaining solid material to change its orientation as the crystal is rotated in the X-ray beam. An attempt was therefore made to obtain diffraction data at reduced temperatures.

An Air Products and Chemicals AC-1-101A refrigerated goniometer head was used with a Picker FACS-I automated diffractometer. Some minor modifications were made to the apparatus because of the particular problems arising from the nature of the crystal and in order to make the goniometer head compatible with the FACS-I goniostat and computer software. These modifications were:

(i) in order to restrict the range of  $\varphi$  to 180°, the Friedel equivalent reflexion was collected if  $\varphi$  was calculated to be greater than 180°;

(ii) the goniometer head was fitted with a metal rod which made contact with two rods attached to the  $\chi$  circle if  $\varphi$  exceeded the allowed range and a collision was then registered;

(iii) the leads to the goniometer were wrapped in tin foil earthed to the  $\chi$  circle. Contact with the incident collimator then registered a collision;

(iv) a transparent plexiglass shroud was used in place of the standard beryllium shroud which fits over the

sample. This produced significant additional background scattering only at  $2\theta$  values less than 10°;

(v) after the crystal was centred in the beam, the entire base of the goniometer head, including the arcs and translation beds were covered with Duco cement. This provided improved rigidity to the crystal support and the cement was easily removed after data collection had been terminated.

Several samples were examined at  $-65 \pm 3^\circ\text{C}$  and at this temperature the compound was stable in the X-ray beam for an indefinite period of time. It was discovered by examination of the diffraction space of each sample, that all of the samples were composed of at least two crystals. A sample of approximate dimensions  $0.5 \times 0.5 \times 0.5$  mm, containing two crystals, one of which made up *ca.* 77% of the total volume, was chosen for data collection. The main body of the data were collected from the larger crystal, but the integrated intensity of some reflexions from the smaller crystal were also collected in an attempt to determine the degree of overlap of reflexions from the two crystals.

The lattice constants and the orientation of the larger crystals were determined by a least-squares fit to the centred position of eleven reflexions (with  $2\theta$  values between 35 and 51° where the  $K\alpha_1$  and  $K\alpha_2$  peaks were well resolved). The lattice constants are given below with estimated standard deviations from the least-squares analysis. The integrated intensities of the 1979 independent reflexions between the  $2\theta$  values of 2.5 and 50° were measured using Mo  $K\alpha$  radiation, a graphite monochromator, a  $\theta$ - $2\theta$  scan mode and a scan rate of  $2^\circ.\text{min}^{-1}$ . The background on each side was counted for 10 sec.

### Crystal data

$a = 8.189$ (4) Å	$V = 533.3$ Å <sup>3</sup>
$b = 8.763$ (5)	F.W. 243.95
$c = 8.334$ (3)	$Z = 2$
$\alpha = 91.34$ (2)°	$D_m = 1.48$ g cm <sup>-3</sup>
$\beta = 110.09$ (2)	(floatation at 22°C)
$\gamma = 106.61$ (2)	$D_x = 1.52$ g cm <sup>-3</sup>
$\mu(\text{Mo } K\alpha) = 10.45$ cm <sup>-1</sup>	(at $-65^\circ\text{C}$ )
$\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å	$F(000) = 244$
Space group $P\bar{1}$	$T = -65^\circ \pm 3^\circ\text{C}$ .

### Structure determination and refinement

The data were corrected for Lorentz and polarization effects but no absorption or extinction corrections were made. The scattering factors for the carbon and chlorine atoms were calculated from the series coefficients given by Cromer & Mann (1968). Those for the hydrogen atoms were interpolated from the values given by Stewart, Davidson & Simpson (1965). A Wilson statistical calculation was used to determine a scale constant and an overall temperature factor of  $3.8$  Å<sup>2</sup>. The average values of  $|E|$  and  $|E^2 - 1|$  were 0.807 and 0.953 respectively, indicating the centro-

symmetric space group  $P\bar{1}$ . The 358 reflexions with  $|E| > 1.4$  were used with the logical symbolic addition method programs of Germain & Woolfson (1968) to obtain eight tentative solutions to the structure. The solution with the highest figure of merit revealed the positions of the four chlorine atoms. An electron-density map, calculated after one cycle of full-matrix least-squares refinement, revealed the positions of the six ring-carbon atoms. The two methyl carbon atoms were found after one more cycle of least-squares and Fourier calculations. The least-squares calculations

were carried out with the full-matrix program *ORFLS* (Busing, Martin & Levy, 1962) and the program *FORDAP* (Zalkin, 1965) was used for all Fourier calculations. The least-squares residual  $R_w$ , given by  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ , was lowered to 0.14 using unit weights in the refinement, with individual isotropic temperature factors. Variation of anisotropic temperature factors lowered  $R_w$  to 0.085. The six hydrogen atoms were located from a difference Fourier map and  $R_w$  was lowered to 0.083.

The orientation of the smaller crystal contained in

Table 1. *Observed and calculated structure factors* ( $\times 10$ )

The reflexions marked with an asterisk were excluded from the refinement because of their lower reliability. The reflexions marked with an '#' were excluded from the refinement because of their overlap with reflexions from the twin.

h	k	l	$F_o$	$F_c$
1	0	0	1000	1000
2	0	0	1000	1000
3	0	0	1000	1000
4	0	0	1000	1000
5	0	0	1000	1000
6	0	0	1000	1000
7	0	0	1000	1000
8	0	0	1000	1000
9	0	0	1000	1000
10	0	0	1000	1000
11	0	0	1000	1000
12	0	0	1000	1000
13	0	0	1000	1000
14	0	0	1000	1000
15	0	0	1000	1000
16	0	0	1000	1000
17	0	0	1000	1000
18	0	0	1000	1000
19	0	0	1000	1000
20	0	0	1000	1000
21	0	0	1000	1000
22	0	0	1000	1000
23	0	0	1000	1000
24	0	0	1000	1000
25	0	0	1000	1000
26	0	0	1000	1000
27	0	0	1000	1000
28	0	0	1000	1000
29	0	0	1000	1000
30	0	0	1000	1000
31	0	0	1000	1000
32	0	0	1000	1000
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38	0	0	1000	1000
39	0	0	1000	1000
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267	0	0	1000	1000
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269	0	0	1000	1000
270	0	0	1000	1000
271	0	0	1000	1000
272	0	0	1000	1000
273	0	0	1000	1000</

the sample was such that the reflexions from both crystals in the reciprocal lattice planes, defined by the equation  $h+k+l=0$ , overlapped completely, indicating that the two crystals are related as rotation twins about the axis [111] (Cahn, 1954). The structure factors calculated from the refined structural parameters also showed that the ratio  $F_o/F_c$  for the reflexions for which  $h+k+l=0$  was *ca.* 1.2. Other planes parallel to the former, (*i.e.* planes for which  $h+k+l=N$ ) did not give any indication of systematic overlap from the two twins. Therefore, the reflexions for which  $h+k+l=0$  were deleted from those used in the least-squares refinement. The final cycles of least-squares were carried out with the remaining 1607 reflexions for which  $F_o/\sigma > 1.8$ , and with the weights,  $w$ , given by

$$w^{-1/2} = 0.26115 + 0.02473|F_o| + 0.000697|F_o|^2 + 0.000046|F_o|^3.$$

The weighting scheme is based on the assumption that the average value of  $||F_o| - |F_c||$  in a range of  $|F_o|$  gives a better approximation to  $\sigma$ , or  $w^{-1/2}$ , than counting statistics because of the probable presence of systematic errors in the data which may have a greater contribution to the real error in  $|F_o|$  than the counting statistics. The final value of  $R_w$  and the conventional  $R$  value were 0.072 and 0.060 respectively. The observed and calculated structure factors are given in Table 1. The final positional and thermal parameters are given in Table 2 with estimated standard errors.

A TLS rigid-motion analysis was applied to the thermal parameters of the carbon and chlorine atoms following the procedure of Schomaker & Trueblood (1968). All of the atoms in the molecule could be de-

Table 2. *Structural parameters*(a) Positional coordinates ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	6514 (4)	7529 (3)	2813 (4)
C(2)	7648 (4)	6758 (4)	3594 (4)
C(3)	8817 (4)	7281 (3)	2546 (4)
C(4)	6788 (4)	8429 (4)	-224 (4)
C(5)	7776 (5)	9710 (4)	872 (4)
C(6)	7458 (4)	8178 (4)	1614 (4)
C(7)	5689 (7)	7590 (7)	-1986 (6)
C(8)	8657 (7)	11463 (4)	1313 (6)
Cl(1)	4605 (1)	7743 (1)	3042 (1)
Cl(2)	7848 (1)	5567 (1)	5175 (1)
Cl(3)	8929 (2)	5721 (1)	1238 (1)
Cl(4)	11071 (1)	8570 (1)	3736 (1)

Positional coordinates ( $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
H(7,1)	602 (11)	662 (9)	-215 (9)	11 (2)
H(7,2)	416 (10)	696 (7)	-219 (7)	9 (1)
H(7,3)	550 (8)	810 (6)	-268 (7)	6 (1)
H(8,1)	989 (11)	1161 (8)	192 (9)	9 (2)
H(8,2)	821 (7)	1181 (5)	232 (2)	6 (1)
H(8,3)	838 (6)	1202 (5)	22 (5)	5 (1)

(b) Thermal parameters ( $\times 10^3$ )

The temperature factor expression is

$$\exp[-2\pi^2(h^2a^*2U_{11} + \dots + 2hka^*b^*U_{12} + \dots)].$$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	31 (1)	41 (2)	39 (2)	6 (1)	14 (1)	3 (1)
C(2)	34 (1)	39 (2)	34 (1)	5 (1)	11 (1)	5 (1)
C(3)	38 (2)	39 (2)	44 (2)	10 (1)	16 (1)	5 (1)
C(4)	41 (2)	46 (2)	36 (2)	8 (1)	14 (1)	6 (1)
C(5)	39 (2)	41 (2)	38 (2)	12 (1)	13 (1)	10 (1)
C(6)	29 (1)	38 (1)	39 (2)	8 (1)	11 (1)	5 (1)
C(7)	65 (3)	74 (3)	40 (2)	4 (2)	7 (2)	-5 (2)
C(8)	64 (3)	40 (2)	59 (2)	7 (2)	16 (2)	8 (2)
Cl(1)	39 (1)	88 (1)	62 (1)	27 (1)	28 (1)	24 (1)
Cl(2)	53 (1)	49 (1)	40 (1)	9 (1)	12 (1)	14 (1)
Cl(3)	84 (1)	49 (1)	65 (1)	31 (1)	41 (1)	10 (1)
Cl(4)	28 (1)	64 (1)	69 (1)	10 (1)	15 (1)	12 (1)

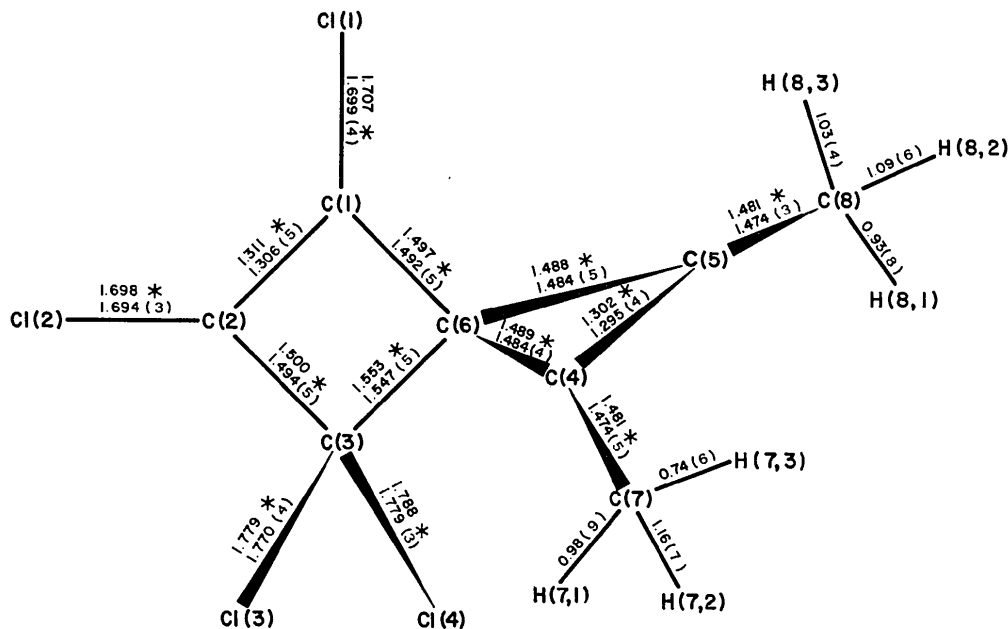


Fig. 1. Bond lengths and atom numbering sequence. The numbers in parentheses are estimated standard deviations. The bond lengths corrected for rigid-body thermal motion are marked with an asterisk.

scribed as forming a rigid body with a r.m.s. discrepancy between the observed  $U_{ij}$  and those calculated from the rigid-body parameters of  $0.0028 \text{ \AA}^2$ . The results of the rigid-motion analysis are shown in Table 3. The translation tensor,  $\mathbf{T}$ , is nearly isotropic, but the libration tensor,  $\mathbf{L}$ , shows a major axis with a r.m.s. rotation of  $5.1^\circ$ . The direction of this axis corresponds approximately to a line through C(2) and C(6). Corrections to the bond lengths were made using the program written by Robert Blessing (Johnson, 1970), and are those given in Fig. 1 marked by an asterisk. The uncorrected bond lengths are also shown with estimated standard deviations in brackets. The bond angles are given in Fig. 2. The errors in the bond angles not involving a hydrogen bond are *ca.*  $0.3^\circ$  based on the estimated standard deviations in Table 2. The errors in the bond angles which include a hydrogen bond are *ca.*  $5^\circ$ . The real errors in the bond lengths and bond angles may be as large as three times these values because only diagonal matrix elements were used to calculate them. Also, although the weighting scheme presumably gives the most probable values of the least-squares parameters, it cannot completely account for the contribution of systematic errors in the data to the estimated standard deviations of the least-squares parameters. Fig. 3 shows a stereogram of the molecule.

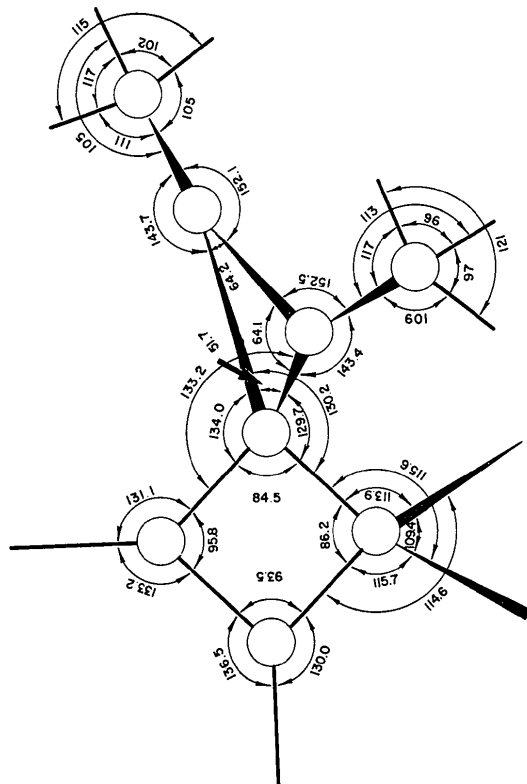


Fig. 2. Bond angles.

Table 3. Rigid-body thermal parameters

Reference axes are  $\mathbf{a}$ ,  $\mathbf{c}^*\lambda\mathbf{a}$  and  $\mathbf{c}^*$ .

$\mathbf{L}(\circ^2)$	8.5 (0.8)	0.8 (0.9)	-0.9 (0.9)	
		15.7 (0.9)	-8.0 (0.8)	
			19.5 (0.9)	
Principal axes of $\mathbf{L}$				
	R.m.s. amplitude	Direction cosines ( $\times 10^3$ )		
$L_1$	$5.1^\circ$	71	613	-786
$L_2$	3.1	82	779	621
$L_3$	2.9	993	28	113
Principal axes of reduced $\mathbf{T}$				
	R.m.s. amplitude	Direction cosines ( $\times 10^3$ )		
$T_1$	0.20 $\text{\AA}$	73	-670	735
$T_2$	0.17	-297	-729	-676
$T_3$	0.17	948	-45	-161
Displacement of libration axes from (0,0,0) ( $\text{\AA}$ )				
Axis $L_1$ along axes $L_2$ and $L_3$		6.600		4.041
Axis $L_2$ along axes $L_1$ and $L_3$		2.737		3.775
Axis $L_3$ along axes $L_1$ and $L_2$		2.631		6.479
Effective screw translations ( $\text{\AA}$ )				
	Parallel to $L_1$		0.019	
	Parallel to $L_2$		-0.017	
	Parallel to $L_3$		-0.014	
R.m.s. $\Delta U_{ij}$			0.0028 $\text{\AA}^2$	
$\sigma(U_{ij})$			0.0033 $\text{\AA}^2$	

## Discussion

Comparison of the detailed molecular geometry of this compound with the geometry of spiro-pentane and spiro-pentyl chloride is not particularly fruitful because of the presence of the double bonds in 1,2,3,3-tetrachloro-4,5-dimethylspiro[2.3]-hexa-1,4-diene. However, as is expected, the rings are nearly orthogonal to each other, which was observed to be the case in the previous studies.

Much of the interest in spiro compounds has centred on the question of the possible existence of aromaticity in the rings. Table 4 compares the bond length of the four membered ring with the bond lengths of related cyclobutene rings. It would appear that the bond lengths of spiro-diene are slightly shorter than those of the equivalent bond lengths for four membered rings. Chang, Porter & Bauer (1970) have noted that the presence of halogen substituents appears to shorten the bonds adjacent to the double bond. The spiro arrangement of the rings appears to shorten all of the bonds in the four membered ring. The lengths of the double bond and the single bonds in cyclopropane as determined by electron diffraction, are 1.304 (3) and 1.519 (12)  $\text{\AA}$  respectively (Chiang, 1970). The equivalent single bonds of spiro-diene appear shortened but the double bond is not significantly shortened. However, the length of this bond may be influenced by the bonding at the spiro carbon atom, C(6). The angle subtended by C(4) and C(5) at C(6) is strained, and it may not be energetically advantageous to force this angle to smaller values.

Table 4. Comparison of bond lengths with related cyclobutenes

Compound	Experimental method	Average of			References
		[C(1)-C(2)]	[C(1)-C(6)], [C(2)-C(3)]	[C(3)-C(6)]	
Cyclobutene	Microwave	1.342 (4) Å	1.517 (3) Å	1.566 (3) Å	Bak, Led, Nygaard, Rastrup-Andersen & Sørensen (1969)
<i>cis</i> -3,4-Dichloro-cyclobutene	Electron diffraction	1.349 (6)	1.505 (4)	1.583 (13)	Bastiansen & Derissen (1966)
Perfluorocyclobutene	Electron diffraction	1.342 (6)	1.508 (3)	1.595	Chang, Porter & Bauer (1970)
1,2,3,3-Tetrachloro-4,5-dimethylspiro-[2.3]-hexa-1,4-diene*	X-ray diffraction	1.311 (5)	1.498 (5)	1.553 (5)	

\* The values corrected for rigid-body thermal motion are given here with the errors calculated for the uncorrected bond lengths.

Table 5. Molecular planes

(a) Equations of planes  $Ax + By + Cz = D$ . Coordinates refer to the directions of the  $a$ ,  $c^*a$  and  $c^*$  axes.

Plane	A	B	C	D
Cyclobutene	-0.3363	-0.6611	-0.6708	-6.2084
Cyclopropene	0.9205	-0.3806	-0.0884	2.7732
Cl(3)-C(3)-Cl(4)	0.2273	0.6307	-0.7419	2.6240

(b) Dihedral angles

Plane	Angle (°)
Cyclobutene/cyclopropene	89.9
Cyclobutene/Cl(3)-C(3)-Cl(4)	89.8
Cyclopropene/Cl(3)-C(3)-Cl(4)	88.0

(c) Distances to planes (Å). Atoms defining the plane are marked with an asterisk.

	Planes		
	Cyclobutene	Cyclopropene	Cl(3)-C(3)-Cl(4)
C(1)	0.003*	0.959	0.109
C(2)	-0.003*	0.049	
C(3)	0.003*	-1.084	0.000*
C(4)	-0.675	0.000*	
C(5)	0.619	0.000*	
C(6)	-0.003*	0.000*	
C(7)		0.010	
C(8)		0.020	
Cl(1)	0.012		0.200
Cl(2)	-0.031	0.029	
Cl(3)	-1.418		0.000*
Cl(4)	1.478		0.000*

In our comparison of the bond lengths determined here with those of isolated cyclopropane and cyclobutene rings it must be noted that bond lengths determined by microwave or electron diffraction techniques may be affected by different systematic errors than those determined by X-ray diffraction. Nevertheless, because of the magnitude of the differences in bond lengths discussed previously, we would conclude that the molecular geometry, together with the rigid-body character of the molecule suggest the existence of some degree of aromaticity in spiro-connected rings.

The equations of the planes of the molecule and the dihedral angles between them are given in Table 5. The three planes formed by the two rings, and Cl(3), C(3) and Cl(4) form a nearly orthogonal set. The atom C(5) is slightly closer to the plane of the cyclobutene ring than the atom C(4), indicating a slight distortion of the molecule from mirror symmetry. This distortion and also the difference in the angles C(6)-C(3)-Cl(3) and C(6)-C(3)-Cl(4) are presumably driven by the molecular packing. The only intermolecular contacts in the structure which are shorter than the sum of van der Waals radii are a 3.400 Å contact between Cl(4) and the atom Cl(1) on an adjacent molecule and a 3.545 Å contact between the atom Cl(3) and the equivalent atom on an adjacent molecule.

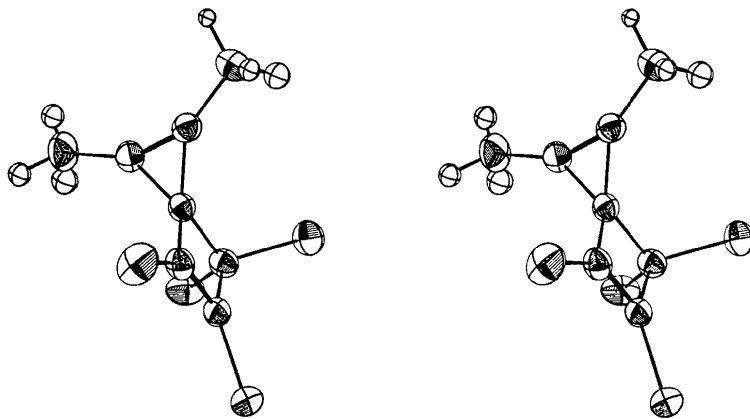


Fig. 3. Stereogram of the molecule. The ellipsoids of the non-hydrogen atoms are scaled to include 40% probability.

The authors thank Professor Semmelhack for the samples and the National Research Council of Canada for support in the form of operating grants.

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## Use of Constraints on Thermal Motion in Structure Refinement of Molecules with Librating Side Groups

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(Received 19 June 1972; accepted 10 October 1972)

Explicit formulae are derived which express, for molecules consisting of a rigid core to which side groups that are free to librate around a single bond are attached, the second and third cumulants of the scattering density function as functions of molecular translation and libration parameters. These formulae and their derivatives with respect to the molecular motion parameters have been incorporated into a least-squares refinement program which determines directly the values of the position and thermal-motion parameters which give the best fit to the observed data.

### Introduction

It was originally pointed out by Cruickshank (1956), that molecular librations cause a systematic displacement of the maxima of scattering density away from the actual equilibrium positions of atoms in the molecule. Cruickshank (1961) also pointed out that in the case of anisotropic librations the nature of these displacements can be very complex. More recently, Schomaker & Trueblood (1968) analyzed the motions of rigid molecules in terms of translations, librations, and screw motions. These are represented by three tensors, designated **T**, **L**, and **S**, whose values may be determined by a least-squares fit to the anisotropic thermal parameters resulting from a conventional crystal structure refinement. Johnson (1970a) extended this analysis to segmented rigid bodies, in which portions of molecules are relatively rigid but are connected together by single bonds, allowing two or more segments to rotate

with respect to one another about the direction of the bond.

Willis & Pawley (1970), Pawley & Willis (1970), and Pawley (1970) have discussed various aspects of the problem of relating the structure factor formula directly to molecular motion parameters, and thereby constraining the thermal parameters in a refinement to fit a physical model. Johnson (1969, 1970b) has described a procedure, applicable to centrosymmetric rigid molecules, for relating the second and third cumulant coefficients in the structure-factor formula to the molecular motion parameters.

This paper extends Johnson's treatment to molecules consisting of a rigid core and one or more attached side groups which are free to librate around a single bond. The resulting formulae have been incorporated into a least-squares program using thermal constraints. No *a priori* assumptions are made about the configuration of the molecule, but thermal parameters are con-