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The Crystal and Molecular Structure of 1,2,3,4-Tetrachlorobutadiene

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The crystal and molecular structure of a crystalline isomer of 1,2,3,4-tetrachlorobutadiene (m.p. 51°C) was determined by the heavy-atom method. The crystals are monoclinic with the space group $P2_1/n$. The lattice constants are $a=3.872$, $b=9.087$, $c=10.061$ Å and $\beta=101.2^\circ$, and two molecules are contained in the unit cell. The structure was refined by the least-squares method, to give the final R value of 0.11 for the 355 observed reflexions. The molecule is planar and the carbon skeleton takes *trans* configuration. The Cl atoms are attached in the *cis*, *cis* positions. The bond lengths are in good agreement with those observed in the other butadiene derivatives. The bond angle C–C–Cl (122°) also agrees with that of chloroprene.

Introduction

1,2,3,4-Tetrachlorobutadiene, $C_4H_2Cl_4$, is one of the starting materials for the synthesis of an organic semiconductor, 1,2,3,4-tetracyanobutadiene (Miura & Haga, 1969). It is obtained in either oily form (b.p. 173°C) or crystalline form (m.p. 51°C) through dehydrochlorination of 1,2,2,3,3,4-hexachlorobutane with potassium hydroxide. The crystalline tetrachlorobutadiene shows only one nuclear magnetic resonance peak at $\tau=2.88$ ppm, which agrees with neither of the two peaks of the oily tetrachlorobutadiene ($\tau=2.23$, and 3.51 ppm). Although this fact indicates that the crystal is either the *cis*, *cis*-tetrachloro- or the *trans*, *trans*-tetrachloro form, it is difficult to say which is the case. Miura & Haga inferred that it may be the *cis*, *cis* form, in view of the fact that the 1,2,3,4-tetrachlorobutadiene from hydrolysis of hexachlorotellurophene has a melting point of 51°C (Mack, 1965). The present author attempted an X-ray structural analysis of the crystalline 1,2,3,4-tetrachlorobutadiene, in order to confirm their conclusion.

Experimental

The crystals were grown from a methanolic solution by slow evaporation. They were colourless transparent

needles about 5 mm in length and 0.5 mm in thickness. Because the crystal is so volatile that it sublimes completely in air within an hour, the crystals with dimensions of 0.1 × 0.1 × 0.3 mm were sealed in Lindemann glass capillaries for the X-ray work. One crystal specimen was consumed per one layer, as they are unstable to X-rays and decompose after two days irradiation. The Cu $K\alpha$ radiation was used throughout the experiment. The cell constants were obtained from equatorial Weissenberg photographs about the a and b axes, on which powder diffraction lines of copper were superposed for the calibration purpose.

Crystal data

$C_4H_2Cl_4$, M.W. 191.86, Monoclinic, $a=3.872 \pm 0.005$, $b=9.087 \pm 0.002$, $c=10.061 \pm 0.004$ Å, $\beta=101.22 \pm 0.08^\circ$, $U=347.2$ Å³, $D_m=1.817$ g.cm⁻³, $Z=2$, $D_x=1.835$ g.cm⁻³, $F(000)=188$. Linear absorption coefficient for Cu $K\alpha$ radiation $\mu=146$ cm⁻¹, Absent reflexions, $0k0$ for k =odd, $h0l$ for $h+l$ =odd, Space group $P2_1/n$.

Intensity data were collected for the layers $0kl-2kl$ about the a axis and $h0l-h2l$ about the b axis, by the multiple film equi-inclination method. The intensities were estimated visually by comparison with a standard scale. Non-zero independent reflexions 355 in total,

were collected. The usual Lorentz polarization and spot shape corrections were applied, but no absorption and extinction corrections were made. The structure factors were put on the same scale by the least-squares method and reduced to the approximately absolute values by Wilson's method.

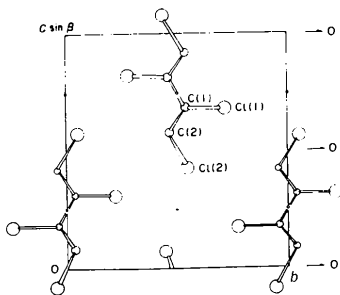


Fig. 1. A projection of the structure along the *a* axis.

Structure determination

The general position of the space group $P2_1/n$ is fourfold and there are only two molecules in the unit cell; therefore, the centre of gravity of the molecule must lie on twofold special positions, and the molecules are required to have a centre of symmetry. A three-dimensional sharpened Patterson function was calculated, from which the positions of the two independent chlorine atoms were easily deduced. The phases of the structure factors were calculated from the coordinates of the two chlorine atoms. From the three-dimensional electron density map calculated, the coordinates of the two carbon atoms were obtained. The positional parameters and isotropic temperature factors were refined by four cycles of the diagonal least-squares. The *R* value was 0.14 at this stage. The positional parameters and anisotropic temperature factors were then refined by four cycles of the block-diagonal least-squares. A

Table 1. The final atomic parameters and their standard deviations

(All quantities $\times 10^4$)

The anisotropic temperature factors are of the form:

$$\exp \{ -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl) \}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C(1)	7532 (32)	5373 (11)	6842 (10)	1073 (145)	93 (14)	110 (12)	1 (55)	-38 (57)	37 (19)
C(2)	8275 (34)	4639 (12)	5781 (10)	933 (129)	140 (17)	52 (10)	-2 (60)	148 (50)	-6 (20)
Cl(1)	6383 (10)	7222 (3)	6797 (3)	1683 (47)	116 (4)	128 (4)	111 (18)	268 (18)	13 (6)
Cl(2)	8364 (10)	5509 (4)	4276 (3)	1407 (43)	182 (5)	98 (3)	-70 (19)	231 (17)	14 (6)

Table 2. Observed and calculated structure factors

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	
H ₁ K= 0	0	-12	6	8	0	24	24	5	6	5	-4	3	2	-8	8	7	9	8	9	-9	3	3	2	6	5		
	2	2	3	-11	9	8	1	30	33	6	5	6	-3	2	3	-5	14	18	H ₁ K= 2	5	-8	3	3	10	9		
	4	19	23	-10	6	5	2	44	51	8	4	3	-2	9	13	-4	2	2	-9	6	5	-7	6	6	5	7	6
	6	6	4	-9	5	4	3	14	14	9	3	4	-1	12	16	-3	11	13	-8	6	6	-5	3	1	6	6	5
	8	28	34	-8	17	18	4	5	5	H ₁ K= 3	2	0	18	20	-7	11	13	-7	6	5	-3	16	16	8	2	3	
H ₁ K= 1	0	-7	14	13	5	4	2	1	9	11	1	13	12	-1	3	3	-6	13	11	-2	6	6	-6	K= 1	8		
	-11	7	6	-6	22	22	6	32	36	H ₁ K= 0	3	2	10	10	0	11	14	-5	4	3	-1	5	5	-6	5	5	
	-7	35	34	-5	20	20	7	11	10	1	18	16	3	5	4	1	2	3	-4	13	15	0	4	5	-3	6	5
	-5	17	11	-4	22	22	8	5	5	2	55	54	4	5	4	3	13	14	-3	6	7	1	23	15	-2	9	8
	-3	57	58	-3	34	34	9	8	7	3	12	0	5	5	2	4	5	5	-2	5	7	2	2	2	-1	7	6
	-1	10	21	-2	3	1	11	3	3	4	10	8	7	5	4	5	8	7	-1	9	10	5	6	5	0	6	6
	1	58	60	-1	6	7	H ₁ K= 1	2	5	3	2	8	5	4	6	5	4	0	3	2	6	2	1	2	10	11	
	2	5	0	0	63	75	-12	3	3	6	16	13	9	3	2	7	6	5	1	6	5	H ₁ K= 0	7	3	4	3	
	3	11	13	1	36	45	-10	5	4	7	5	4	H ₁ K= 0	4	8	3	3	2	9	8	1	12	12	5	4	3	
	5	36	41	2	24	25	-9	17	16	8	4	3	0	51	52	9	2	2	3	6	5	2	12	12	H ₁ K= 2	8	
	6	4	0	3	24	24	-8	9	8	9	4	4	1	14	14	H ₁ K= 3	4	4	11	11	3	11	11	-7	4	4	
	7	5	5	4	3	2	-6	8	7	10	11	13	-7	13	12	0	6	7	5	6	5	4	10	10	-6	3	4
	9	4	3	5	13	11	-4	33	32	11	3	3	3	17	17	H ₁ K= 0	5	6	4	3	5	12	11	-5	6	7	
H ₁ K= 2	0	6	9	7	-2	16	16	H ₁ K= 1	3	4	7	7	1	25	24	H ₁ K= 0	6	7	7	7	-4	4	3				
	-10	14	12	8	18	15	-1	52	57	-12	3	4	5	15	15	2	6	5	0	16	15	8	3	3	-3	2	3
	-9	16	15	9	10	9	0	3	3	-7	5	3	6	7	6	3	3	1	1	21	21	H ₁ K= 1	7	1	3	3	
	-6	8	9	H ₁ K= 2	1	1	2	0	-6	19	17	7	13	12	4	19	41	2	4	3	-8	8	9	2	4	3	
	-4	7	6	-9	6	5	2	2	2	-5	36	33	8	13	13	5	8	7	3	20	10	-5	7	7	3	4	5
	-2	23	28	-7	20	19	3	19	16	-4	18	15	H ₁ K= 1	4	7	11	11	5	9	7	-3	5	4	4	2	2	
	0	37	36	-6	15	16	4	28	25	-3	4	5	-10	10	11	8	7	9	7	7	-2	15	11	5	4	3	
	2	18	14	-5	8	8	6	8	6	-2	17	19	-9	6	5	9	4	4	8	6	5	0	20	10	H ₁ K= 3	8	
	4	5	4	-4	16	19	7	17	14	-1	8	10	-8	12	11	10	2	3	9	5	8	1	4	5	0	7	3
	6	8	6	-3	10	15	8	4	3	0	14	17	-7	16	15	H ₁ K= 1	5	6	3	7	6	H ₁ K= 0	9				
	8	6	8	-2	3	4	11	4	5	1	4	4	-6	7	7	-11	6	7	-8	7	7	4	5	4	1	11	10
	10	2	2	-1	15	16	H ₁ K= 2	2	2	16	14	-4	11	10	-8	9	8	-7	5	5	6	4	4	3	4	3	
H ₁ K= 3	0	0	0	0	10	9	-9	4	3	3	33	32	-3	16	15	-7	12	11	-6	12	10	8	4	5	4	4	5
	1	10	12	1	24	25	-8	4	4	4	9	5	-2	31	31	-6	9	7	-5	5	4	H ₁ K= 2	7	7	3	4	
H ₁ K= 0	1	2	20	16	-7	7	6	5	4	3	-1	19	20	-3	27	25	-4	35	30	-8	4	4	-6	K= 1	9		
	1	20	12	3	2	1	-6	14	12	6	13	11	0	17	18	-2	19	16	-3	12	10	-7	6	6	-6	8	8
	2	24	28	4	11	9	-5	4	3	7	12	10	1	22	24	-1	10	9	-2	6	5	-5	2	2	-4	5	5
	3	31	36	5	14	14	-4	24	23	8	6	5	2	25	24	0	20	20	-1	5	4	-3	9	11	-3	4	4
	4	58	53	6	6	4	-3	16	16	11	2	3	4	15	14	1	24	29	1	5	5	-2	2	4	-2	8	9
	5	23	24	7	6	5	-2	10	13	H ₁ K= 2	3	5	14	14	2	6	4	2	8	9	-1	3	3				
	6	8	8	8	3	3	-1	4	3	-10	7	6	6	6	6	3	3	3	3	4	3	0	4	4			
	7	9	7	9	3	3	0	5	4	-9	7	6	7	8	6	4	8	9	4	21	24	1	3	4			
	8	8	8	10	1	1	1	15	15	-8	14	12	10	5	6	5	9	9	5	7	7	5	3	6			
	9	3	3	H ₁ K= 3	1	2	7	6	-7	8	7	H ₁ K= 2	4	6	8	8	6	4	3	H ₁ K= 0	8						
	11	4	5	1	6	7	3	6	4	-6	4	4	-10	6	5	7	5	5	8	4	5	0	7	7			
H ₁ K= 1	1	H ₁ K= 0	2	4	13	12	-5	3	2	-9	5	4	8	4	4	H ₁ K= 2	6	1	4	2							

weighting scheme, $w = (F_{\max}/F_o)^2$ if $|F_o| \geq 4F_{\min}$ and $w = 1$ otherwise, was employed, where $F_{\min} = 1.60$ and $F_{\max} = 4F_{\min}$. The atomic scattering factors for carbon and chlorine were taken from *International Tables for X-ray Crystallography* (1962).

The final atomic parameters are listed in Table 1 with standard deviations in parentheses, where (x, y, z) , $(\bar{x}, \frac{1}{2} + y, \bar{z})$, $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, \bar{y}, \frac{1}{2} - z)$ were taken as the coordinates of the equivalent points for $P2_1/n$. Hydrogen atoms could not be located on the difference map. A comparison of the observed and calculated structure factors is given in Table 2.

Results and discussion

A projection of the structure along the a axis is presented in Fig. 1. The molecule is *cis, cis*-1,2,3,4-tetrachlorobutadiene, which agrees with the conclusion of Miura & Haga (1969). The molecule is planar and the carbon skeleton has *trans* configuration. Interatomic distances and bond angles are shown in Fig. 2. The C(1)–C(2) distance (1.336 Å) and C(2)–C(2') distance (1.492 Å) are in good agreement with those found for similar molecules. Almenningen, Bastiansen & Traetteberg (1958) reported the structure of 1,3-butadiene by the electron diffraction method. They obtained 1.483 ± 0.01 Å for the C–C bond and 1.337 ± 0.005 Å for the C=C bond. Schomaker & Pauling (1939) investigated the structure of 1,3-butadiene by the electron diffraction method and obtained 1.35 ± 0.02 Å for the C=C bond and 1.46 ± 0.03 Å for the C–C bond. As for the substituted 1,3-butadiene, Akishin, Vilkov & Tatevskii (1958) obtained 1.36 Å for the C=C bond and 1.46 ± 0.04 Å for the C–C bond of chloroprene by the electron diffraction method, assuming the planar *trans* carbon skeleton. Karle & Dragonette (1965) determined the crystal structure of *cis, cis*-1,2,3,4-tetraphenylbutadiene and observed a *trans* carbon skeleton, where the length of the C–C bond and the C=C bond were 1.493 ± 0.010 Å and 1.357 ± 0.010 Å, respectively.

The bond angle of C=C–C (121.67°) obtained in this study is in good agreement with that of chloroprene (122°) [\angle C=C(Cl)–C] (Akishin, Vilkov & Tatevskii, 1958), and those of 1,3-butadiene ($124 \pm 2^\circ$) (Schomaker & Pauling, 1939), (122.4°) (Almenningen, Bastiansen & Traettenberg, 1958). The angle C=C–Cl (121.98°) obtained in this study is in good agreement with that of chloroprene (122°) (Akishin, Vilkov & Tatevskii, 1958). The distance between Cl(1)···Cl(2) in a molecule is 3.292 Å. This is shorter than twice the van der Waals radius of the chlorine atom (1.80 Å). The molecule is planar, and the equation of the best plane is given by

$$0.9362x + 0.1642y + 0.1222z = 4.3902,$$

where x, y, z are the coordinates in Å referred to the crystal axes. In Table 3 are shown the displacements of atoms from the best plane. The molecular planes,

which are related to each other by the twofold screw axis, make an angle of 19° .

Table 3. Deviations of atoms from the molecular plane

	Distance to the plane
C(1)	–0.013 Å
C(2)	0.015
Cl(1)	0.006
Cl(2)	–0.007

The packing of the molecules is entirely due to the van der Waals force and a molecule is in contact with the adjacent ones with van der Waals radii. The intermolecular distances are shown in Fig. 3.

The thermal ellipsoids calculated from the anisotropic temperature factors listed in Table 1 are shown in Fig. 4. The motion appears to consist chiefly of a rigid body libration about the centre of gravity.

Computation

All the calculations were carried out using an IBM 360/75 computer at the Mitsubishi Computer Centre

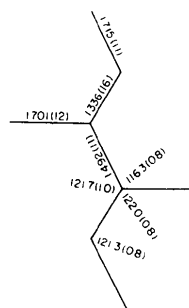


Fig. 2. Interatomic distances and bond angles, with their standard deviations in parentheses.

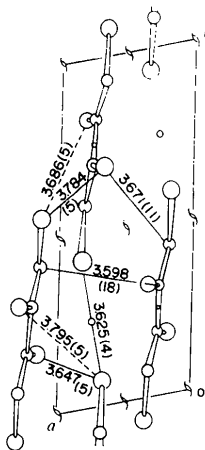


Fig. 3. Intermolecular distances less than 3.8 Å, with their standard deviations in parentheses.

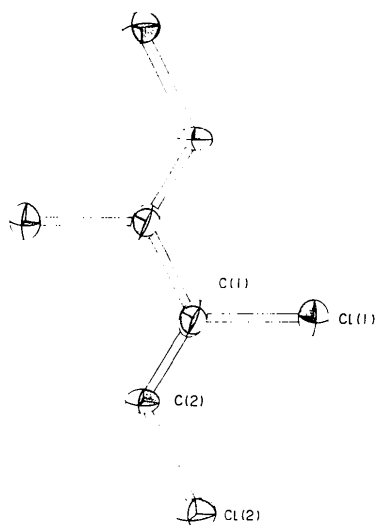


Fig. 4. The ellipsoids of thermal motion with a probability of 50%.

and a MELCOM 9100 computer in our laboratory. Calculations of $|F_o|$, F_c , Fourier syntheses, diagonal least-squares, block-diagonal least-squares, bond lengths

and angles and best plane were carried out by *RDTR-3*, *RSSF-4*, *RSDL-3*, *HBL-IV*, *RSDA-4* and *RSBP-3* of the UNICS computer program system, respectively (*Crystallographic Society of Japan*, 1967). Thermal ellipsoids were plotted by the *ORTEP* program written by Johnson (1965).

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The Crystal and Molecular Structure of Trimethyltin Nitrate Monohydrate

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The crystal and molecular structure of the compound $(\text{CH}_3)_3\text{SnNO}_3 \cdot \text{H}_2\text{O}$ has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the monoclinic space group $C2/c$ with four formula units in a cell of dimensions $a=6.687(1)$, $b=11.495(1)$, $c=11.441(1)$ Å and $\beta=104.42(1)^\circ$. Refinement by full-matrix least-squares methods has given a conventional R value of 3.9% for the 463 observed reflexions. The tin atom has a slightly distorted trigonal bipyramidal environment consisting of a planar trimethyltin fragment with a unidentate nitrate group and a water molecule occupying the apical positions in a disordered manner. The Sn–O bonds are 2.22(3) Å (nitrate) and 2.47(2) Å (water). The mean Sn–CH₃ bond length is 2.11(2) Å. Intermolecular hydrogen bonding (O...O contact 2.72(3) Å) is proposed between the water of one molecule and the nitrate group of an adjacent molecule, leading to a one-dimensional polymeric linkage between molecules.

Introduction

Recently $\text{CH}_3\text{Sn}(\text{NO}_3)_3$, the remaining member of the series $(\text{CH}_3)_{4-n}\text{Sn}(\text{NO}_3)_n$ ($n=0, 1, 2, 3, 4$), was prepared and characterized by Ferraro, Potts & Walker (1970). The variation in the chemical and structural features of this series is of obvious interest. The second member of this group, anhydrous trimethyltin nitrate, has been

studied spectroscopically (Clark & O'Brien, 1963; Clark, O'Brien & Pickard, 1965; Yasuda & Okawara, 1965) along with its monohydrate, but the interpretations of their infrared spectra have been contradictory. Mössbauer studies of these two compounds (Cordery-Hayes, Peacock & Vuceli, 1967; Jones & Wood, 1970) have shown the very large quadrupole splittings of 4.14 (5) mm.sec⁻¹ for the anhydrous compound and 4.40 (5) mm.sec⁻¹ for the monohydrate. Thus, the tin nuclei in these compounds have asymmetric electric

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