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CRYSTAL STRUCTURE OF THE CARBON TETRABROMIDE p-XYLENE COMPLEX

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November 16, 1961

Crystal Structure of the Carbon Tetrabromide p-Xylene Complex*

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According to an x-ray diffraction study, crystals of the compound of carbon tetrabromide with p-xylene are orthorhombic, space group Cmc₂m, with $a = 8.48 \pm 0.03$, $b = 8.89 \pm 0.03$, and $c = 17.46 \pm 0.05$ A.

With four molecules per cell, the density is calculated as 2.209 g cm^{-3} .

Each aromatic ring has a bromine atom on each face at a distance of 3.34 A from the center of the ring. Half of the bromine atoms are involved in this interaction which is described as the doner-acceptor type. The structure consists of zig-zag strings of alternate carbon tetrabromide and xylene molecules. Bond distances and angles within these molecules are normal.

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INTRODUCTION

Several compounds of halogenated methanes with benzene and various methyl benzenes have been reported.¹⁻³ Kapustinskii and Drakin² attributed this compound formation to interactions of the π -electrons of benzene with halogen atoms, but no direct structural information has been available. We have determined the crystal structure of the p-xylene carbon tetrabromide compound with results which are consistent with such π -electron interactions. This compound was chosen for study because the relatively high melting point (53°C) permitted work by conventional techniques at room temperature.

EXPERIMENTAL

Crystals of $\text{CBr}_4 \cdot \text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ were prepared by mixing a slight excess of 99.85% pure p-xylene with Eastman carbon tetrabromide. The mixture was warmed and then allowed to cool. The desired compound grew as thin, flat, square platelets. The crystals, which have a high vapor pressure, were preserved by being kept in contact with the mother liquor. A platelet was cut into small rectangular needles which were sealed in small glass capillaries for x-ray examination. After several attempts, one crystal was aligned about a [110] axis. Rotation and Weissenberg photographs (layers zero through five) were recorded by multiple-film techniques. Upon analysis of the data it was decided that they were inaccurate because of absorption. The irregular shape of the crystal made it difficult to correct for this absorption effect.

To overcome this problem, one of the large platelet crystals was melted, and the liquid was sealed in a capillary, 0.3 mm in diameter. It crystallized immediately as a powder. The capillary was mounted on a Weissenberg goniometer head and placed on the stage of a polarizing microscope. A stream of warm air was passed over the capillary to melt the material at one end.

The temperature of the air stream was gradually reduced, and after several attempts a satisfactory single cylindrical crystal was grown. The b axis of the crystal was within a few degrees of being parallel to the capillary axis. This crystal was mounted on the Weissenberg camera and lined up on the b axis by means of oscillation photographs. A rotation pattern, multiple-film Weissenberg exposures for layers zero through five, and a zero-layer single-film quartz-calibrated Weissenberg photograph were taken using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Unit cell dimensions were derived from the quartz-calibrated zero-layer Weissenberg photographs with rotation about the [110] and [010] directions.

Intensities were estimated visually by comparison with a standard film. For the first crystal, 481 independent reflections were observed and 157 others were recorded as too weak to be observed. For the second crystal 298 independent reflections were measured and 195 were recorded as too weak to be measured. In each case the usual corrections for Lorentz, polarization and velocity effects were made. In addition, the data from the second crystal were corrected for absorption by the method of Bond,⁴ assuming a perfect cylinder with $\mu_r = 2.28$.

UNIT CELL AND SPACE GROUP

The first set of pictures (about the [110] orthorhombic axis) at first glance appeared to show monoclinic symmetry, with unit cell dimensions of $a = 6.145$, $b = 17.465$, $c = 6.145 \text{ \AA}$ and $\beta = 92^\circ 48'$. However, closer inspection of the pictures showed that the a and c axes of the primitive monoclinic cell were the face diagonals of a C-centered orthorhombic cell with dimensions:

$$a = 8.48 \pm 0.03 \text{ \AA}$$

$$b = 8.89 \pm 0.03$$

$$c = 17.46 \pm 0.05$$

By using these cell dimensions and the molecular volumes of liquid p-xylene and solid carbon tetrabromide it is calculated that there are 3.6 molecules per unit cell. This indicates that there are four molecules per unit cell, since the volume of the solid compound would tend to be smaller than that of the separate constituents. The calculated density for four molecules per cell is 2.209 g cm^{-3} .

The systematic absences (hkl absent if $h+k$ is odd, $h0l$ absent if l is odd) correspond to the probable space groups $Cmcm$ (D_{2h}^{17}), $Cmc2_1$ (C_{2v}^{12}), and $C2cm$ (C_{2v}^{16}). The higher symmetry group, $Cmcm$, is chosen on the basis that it leads to a structure in good agreement with the data.

DETERMINATION OF THE STRUCTURE

All structure factor calculations were made with the atomic scattering factors of Thomas and Umeda⁵ for bromine, of Hoerni and Ibers⁶ for carbon, and the Internationale Tabellen⁷ for hydrogen. Intensity corrections and least-squares refinements were done with the IBM-650 computer with the INCOR and LS-II programs.⁸ Fourier calculations were made with the IBM-701 computer and a program written by Jones and Dodge.⁹

The structure was found by first assuming space group $Cmcm$. The unit cell contains four molecules of CBr_4 . In space group $Cmcm$, the only positions available for four molecules are at centers of symmetry or at intersections of two mirror planes. Since carbon tetrabromide is tetrahedral, it cannot be at a center of symmetry. Thus this carbon atom,

designated as C_3 , is placed in positions:

$$4 (c): \pm(0, y, 1/4) + C.$$

The bromine atoms can then only be placed on the mirror planes in the two sets of positions:

$$Br_1 \text{ in } 8 (f): \pm(0, y, z; 0, y, \frac{1}{2} - z) + C.$$

$$Br_2 \text{ in } 8 (g): \pm(x, y, \frac{1}{4}; -x, y, \frac{1}{4}) + C.$$

A three dimensional Patterson synthesis based on the first set of data showed peaks corresponding to bromine atoms at 0.00, 0.20, 0.16 and 0.19, 0.45, 0.25 and a carbon atom at 0.00, 0.325, 0.25. The signs of the structure factors calculated with only the carbon tetrabromide molecule as a trial structure were attached to the observed structure factors, and a three dimensional electron density synthesis was computed. From this, the p-xylene molecule was determined to be perpendicular to the yz plane with its center at the origin ($2/m$). For this arrangement, the other carbon atoms must be distributed in two more sets of 8(f) (atoms C_5 and C_6) and in one general set,

$$C_4 \text{ in } 16(h): \pm(x, y, z; x, -y, -z; x, y, \frac{1}{2} - z; \\ x, -y, \frac{1}{2} + z) + C.$$

If the symmetry is assumed to be $Cmc2_1$ or $C2cm$, the Patterson function requires that there be at most only a small deviation from the above structure for the bromine atoms. The electron density function shows that the xylene molecule also conforms at least nearly to the higher symmetry. Therefore the lower symmetry groups were not considered further.

Several cycles of least squares refinement were run based on the structure determined as described above. The unreliability index

$$R = (\sum ||F_o| - |F_c||) / (\sum |F_o|) \text{ did not fall below } 0.20.$$

Further least squares refinements were made with the second set of data, corrected for absorption. After 15 cycles, R was 0.147. The atomic parameters listed in Table I were obtained.

Since this structure appeared to be correct, but the agreement was not as good as desired, hydrogen atoms were introduced into the calculations. They were located by assuming a C-H bond length of 1.08 Å and normal bond angles. This places them in positions,

H₇ and H₈ in 16(h)

H₉ in 8(f).

The symmetry and bond geometry permit two choices of orientation of the methyl group. This orientation was determined from an electron density difference synthesis ($F_o - F_c$ synthesis). Seven additional least squares cycles were run with hydrogen atoms included but their parameters not allowed to change. At the end, R was 0.135. The final assumed coordinates of hydrogen are listed in Table II. The final parameters and their standard deviations are given in Table III. In Table IV are compared the observed and calculated structure factors.

DISCUSSION

The dimensions of the carbon tetrabromide and xylene molecules are normal, although the high thermal motion and high scattering power of bromine prevent high accuracy in the carbon coordinates. The carbon tetrabromide is tetrahedral within the accuracy of the data. With a correction $3(B_i - B_j) / 16\pi^2 = 0.02$ Å for thermal motion,¹⁰ the average C-Br bond distance is 1.93 ± 0.01 Å,¹¹

in agreement with the value 1.942 ± 0.003 Å determined by electron diffraction.¹² The bond distances 1.40 ± 0.01 and 1.50 ± 0.01 Å determined for p-xylene by electron diffraction¹³ are in better agreement with our results than we could expect. Bond angles in the xylene molecule deviate by up to 4° from the expected 120° values, but these deviations are not experimentally significant.

The most interesting feature of the structure is the packing arrangement of the molecules (Fig. 1). Half of the bromine atoms (Br_1) are each directed toward the center of a benzene ring and are at a distance 3.34 Å from that center. Each benzene ring has such a bromine atom on each side with the result that zig-zag strings of molecules run parallel to the c axis. There is no evidence of bonding from one string to another. This arrangement is suggestive of interaction of the bromine atoms with the π -electrons of the ring, and it is reasonable to classify this as a donor-acceptor complex. Many examples of this general type have been reported.¹⁴ Of those of known crystal structure, the benzene-bromine compound ($\text{C}_6\text{H}_6 \cdot \text{Br}_2$) is most analogous to our crystal.¹⁵ In both compounds, each aromatic ring has a bromine atom on each side. The line joining these two neighbors is very nearly perpendicular to the plane of the ring and passes through its center. The distances from bromine atoms to the centers of the rings are practically the same, 3.36 Å in the benzene compound and 3.34 Å in the xylene compound.

The greater stability of crystals of the p-xylene complex relative to those of o-xylene and m-xylene can be used to separate these isomers.³ It seems unlikely that the positions of the methyl groups can have much effect on the donor-acceptor interaction, and therefore the difference in stability probably is to be attributed to the nonexistence of as good a packing arrangement of the less symmetrical isomers in the crystal.

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Table I. Atomic parameters obtained by using only carbon and bromine atoms:

Atom	\underline{x}	\underline{y}	\underline{z}	$\underline{B}, \text{A}^2$
Br ₁	0	0.2040	0.1607	7.2
Br ₂	0.1841	0.4497	1/4	7.4
C ₃	0	0.332	1/4	6.4
C ₄	0.139	0.931	0.020	5.0
C ₅	0	0.864	0.048	4.6
C ₆	0	0.733	0.091	6.2

Table II. Parameters assumed for hydrogen in final calculation.

Atom	\underline{x}	\underline{y}	\underline{z}	$\underline{B}, \text{A}^2$
H ₇	0.248	0.880	0.041	5.9
H ₈	0.106	0.667	0.077	5.9
H ₉	0	0.759	0.147	5.9

Table III. Final atomic parameters and standard deviations.

Atom	\underline{x}	\underline{y}	\underline{z}	$\underline{B}, \text{A}^2$	σ_x	σ_y	σ_z
Br ₁	0	0.2034	0.1608	7.6	-	0.0005	0.0002
Br ₂	0.1840	0.4506	1/4	7.6	0.0005	0.0005	-
C ₃	0	0.331	1/4	5.3	-	0.006	-
C ₄	0.139	0.932	0.0193	5.7	0.003	0.003	0.001
C ₅	0	0.872	0.0497	5.2	-	0.004	0.001
C ₆	0	0.732	0.0970	7.4	-	0.005	0.002

H=0			H=2			H=4			H=6		
2	59	-84	5	139	-158	8	14*	-2	12	7	11
3	81	-82	6	43	54	9	14*	-4	13	14	16
4	22	-15	7	103	103	10	14*	2	14	8*	-2
5	25	22	8	13*	-17	11	30	-31	15	7*	2
6	12*	2	9	33	-31	12	13*	14	16	6*	-2
7	12*	-8	10	14*	8	13	12*	2			
8	48	26	11	17	-12	14	12	2			
9	86	97	12	14*	11	15	11*	5	0	12*	-2
10	33	-24	13	13*	-7	16	9*	-7	1	14	-3
11	64	-81	14	16	7	17	14	-13	2	11*	2
12	23	37	15	20	25	18	6*	2	3	21	19
13	50	62	16	12	-13	19	5*	2	4	11*	-12
14	9	-7	17	20	-23				5	23	-24
15	12*	-2	18	9*	3				6	10	9
16	12*	-4	19	8*	8	0	32	23	7	24	22
17	11*	4	20	6*	-2	1	56	60	8	9*	-3
18	9*	-2				2	22	-19	9	9*	-5
19	9*	-2				3	24	-19	10	8*	3
20	6*	2				4	14*	-5			
			0	13*	26	5	13*	-4			
			1	48	49	6	13*	3	0	6*	2
			2	13*	-13	7	13*	2	1	6	6
			3	13*	13	8	16	6	2	6*	-2
			4	44	-28	9	18	24	3	4*	-2
			5	60	-75	10	9	-5	4	3*	-2
			6	28	25	11	20	-23			
			7	29	31						

H=2			H=4			H=6			H=8			H=10		
0	22	19	0	13*	26	4	14*	-5	0	6*	2	0	6*	2
1	10*	12	1	48	49	5	13*	-4	1	6	6	1	6	6
2	11*	5	2	13*	-13	6	13*	3	2	6*	-2	2	6*	-2
3	90	95	3	13*	13	7	13*	2	3	4*	-2	3	4*	-2
4	67	-64	4	44	-28	8	16	6	4	3*	-2	4	3*	-2
			5	60	-75	9	18	24						
			6	28	25	10	9	-5						
			7	29	31	11	20	-23						

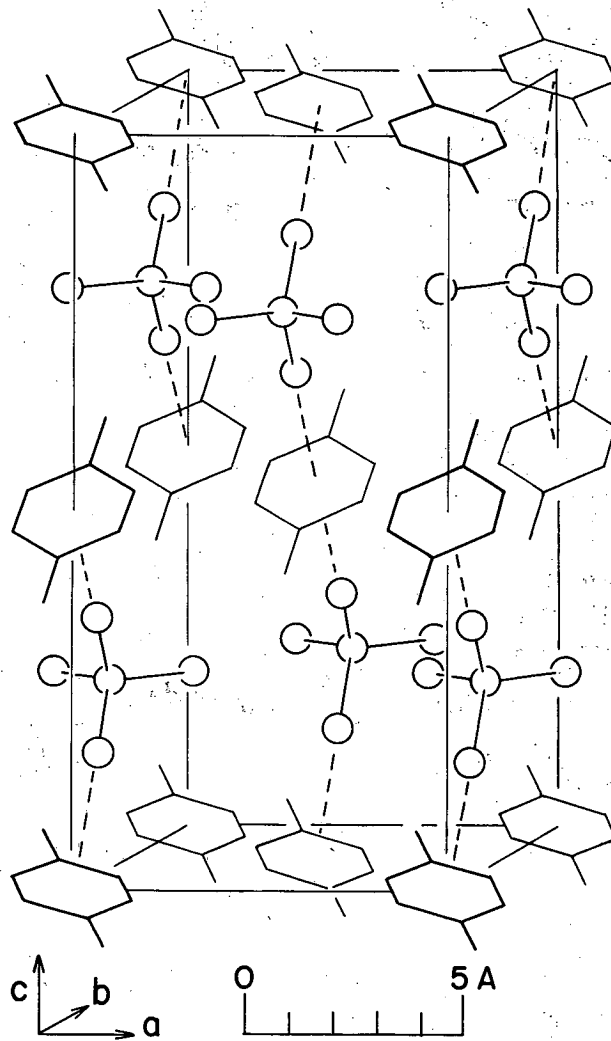
H=1			H=3			H=5			H=7			H=9		
0	50	72	0	74	74	0	42	38	2	20*	-14	0	13*	6
1	30	-40	1	77	70	1	49	-40	3	19*	-5	1	11*	4
2	40	-57	2	34	-29	2	23	-18	4	19	-15	2	11*	-4
3	30	36	3	85	-76	3	37	33	5	19*	8	3	11*	-5
4	61	-66	4	33	-35	4	16	-25	6	22	16	4	11*	-5
5	25	-23	5	57	57	5	37	-32	7	18*	-5	5	11*	4
6	79	79	6	52	67	6	30	39	8	17*	-4	6	9*	7
7	29	15	7	58	-72	7	25	16	9			7	9*	-5
8	20	-15	8	22*	-5	8	21*	-5	10			8	6*	-2
9	32	-18	9	16	28	9	30	-25						
10	29	-33	10	27	-23	10	10	-13						
11	23	25	11	27	-33	11	14	15						
12	33	29	12	30	24	12	13	14						
13	21*	-2	13	31	19	13	17*	-10						
14	20*	3	14	18*	2	14	15*	2						
15	19*	12	15	17	-16									
16	17*	-13	16	16*	-11									
17	15*	2				0	20*	13						
18	13*	8				1	20*	6						

Table V. Interatomic distances and standard deviations.

Atoms ^a	Distance ^b	Atoms	Distance
Br ₁ - 1 Br ₁	3.11 ± 0.01 Å	C ₄ - 1 Br ₁	3.66 ± 0.03 Å
2 Br ₂	3.12 ± 0.01	1 Br ₁	3.57 ± 0.03
1 C ₃	1.93 ± 0.02	1 C ₄	1.40 ± 0.04
2 C ₄	3.66 ± 0.03	1 C ₅	1.39 ± 0.03
2 C ₄	3.57 ± 0.03	C ₅ - 1 Br ₁	3.55 ± 0.04
1 C ₅	3.55 ± 0.04	1 Br ₁	3.73 ± 0.03
1 C ₅	3.73 ± 0.03	2 C ₄	1.39 ± 0.03
Br ₂ - 2 Br ₁	3.12 ± 0.01	1 C ₆	1.50 ± 0.05
1 Br ₂	3.10 ± 0.01	C ₆ - 1 C ₅	1.50 ± 0.05
1 C ₃	1.88 ± 0.02		
C ₃ - 2 Br ₁	1.93 ± 0.02		
2 Br ₂	1.88 ± 0.02		

^a C₃ is in CBr₄. Each xylene molecule contains four atoms C₄ and two atoms C₅, with each C₅ bonded to methyl, C₆.

^b Not corrected for thermal motion.



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Fig. 1. Crystal structure of carbon tetrabromide p-xylene.

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