Part of this work was carried out in Alabama Polytechnic Institute, Auburn, Alabama, under contract No. N7ONR–377, T.O.I. It was first presented as a paper to the meeting of the Crystallographic Society of America in Ann Arbor, Michigan, on 8 April 1949. My heartiest thanks are due to Prof. Ray Pepinsky for his interest and encouragement.

References

Buerger, M. J. (1948*a*). *Acta Cryst.* **1**, 259.
Buerger, M. J. (1948*b*). *Proc. Nat. Acad. Sci., Wash.*, **34**, 277.
Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Zachariasen, W. H. (1945). *Theory of X-ray Diffraction in Crystals*. New York: Wiley.

Acta Cryst. (1950). **3**, 217

The Structure of Tetraphenylmethane*

By H. T. Sumsion† and Dan McLachlan, Jr.

Department of Metallurgy, University of Utah, Salt Lake City, Utah, U.S.A.

(*Received* 27 *September* 1949)

The crystal structure of tetraphenylmethane is reported. The C–C distances in the six-membered rings are 1·39A. and the bond lengths about the central carbon atoms are 1·47A. The crystallographic data are in agreement with previous work by George. The structure is a loose packing of molecules so arranged as to account for the observed planes in the crystal habit.

Introduction

The structure of tetraphenyl methane was undertaken as a part of a program to study spectroscopically and by X-rays a series of compounds wherein two, three and four phenyl groups are attached to the same carbon atom. These compounds are interesting because they frequently have a very low density and also because their bond character is easily altered by the substitution of active groups to form colored compounds such as crystal violet, and malachite green.

Tetraphenylmethane was first studied by George (1926), whose crystallographic findings are in agreement with the present work; but the conclusions pertaining to structure are somewhat at variance, mostly because structure determination was not the main object of his work.

A comparison of the crystallographic data of George and the present authors is shown in Table 1.

Table 1. *Crystallographic data*

Density by flotation (g.cm.$^{-3}$)	Cell dimensions (A.)		Molecules per unit cell	Space group	Authors
	a	c			
1·173	10·86	7·26	1·91	$P\bar{4}2_1c$	George
—	10·87	7·23	1·89	$P\bar{4}2_1c$	Sumsion & McLachlan

Experimental

From a sample of purified tetraphenylmethane a prismatic, needle-like crystal, having dimensions of 0·02 cm. in the two short directions and about 0·25 cm. in the longest direction, was selected and was exposed to filtered cobalt radiation to produce powder, rotation and Weissenberg pictures. Five layer lines were observed on the rotation picture and from this picture data were taken for the adjustment of the Weissenberg camera in taking equi-inclination photographs of each layer. Rotation pictures using copper and also molybdenum radiation were then taken, but no further data were obtained. The intensities were determined by visual methods, using the multiple-film technique (Robertson, 1943*a*). The Lorentz and polarization factors were taken from the tables of Buerger & Klein (1946), while the temperature factors were according to Debye and Waller.

Determination of structure

Since $P\bar{4}$ is a subgroup of $P\bar{4}2_1c$ it is logical to suspect that the tetraphenylmethane molecule might be in this configuration (see Fig. 1). Also, since the $P\bar{4}2_1c$ space group requires eight equivalent points, and the two molecules per unit cell furnish a total of eight phenyl groups but only two central carbon atoms, it was therefore suspected that the central carbon atoms of the molecule are in the special position 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, while the atoms of the phenyl groups are in the eight general positions, with the restriction that they conform to $P\bar{4}$ in sets of four. As a preliminary guess it was assumed that the distances between the central carbon atom and its nearest atoms in the phenyl groups are 1·49 A., while the distances between the carbon atoms in the ring are 1·39 A. These restrictions reduce the structure to a two-parameter problem, the angle (θ) of rotation of the phenyl groups about the tetragonal

---

* Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy by H. T. Sumsion at the University of Utah.

† Now with the Carborundum Company, Niagara Falls, N.Y., U.S.A.

bonds of the central carbon, and the angle (ψ) of rotation of the entire molecule about the z axis, where θ is measured from a vertical plane through z, and ψ is measured horizontally from the xz plane. The possible extreme values of ψ are 0 and 45°. The 45° angle is the position suspected by George. To determine in which of the two extremes the molecule may be most nearly oriented, a Patterson projection (Fig. 2) was made and compared with 'theoretical Patterson projections' (Robertson, 1943*b*; Binnie & Robertson, 1949). The angle near zero for ψ turned out to be most nearly correct and by repeated trials came out to be $7\frac{1}{2}$°, and θ to be 55°.

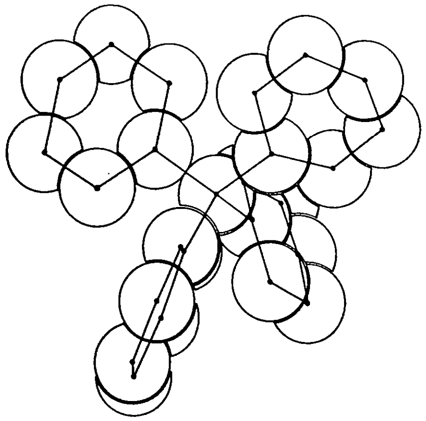
Fig. 1. A single molecule of tetraphenylmethane.

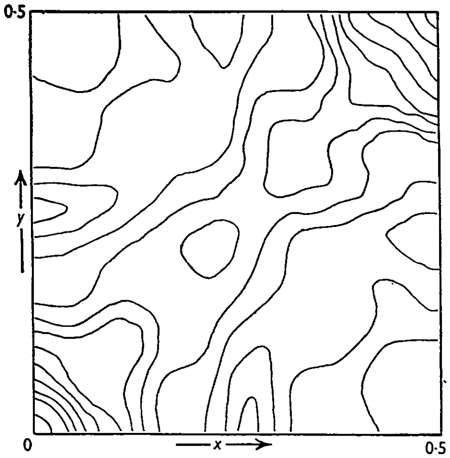

Fig. 2. A Patterson projection of tetraphenylmethane from the X-ray data.

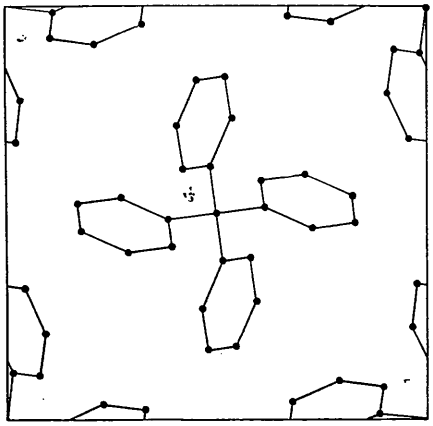
Fig. 3. The final trial structure of tetraphenylmethane used for determining the phases.

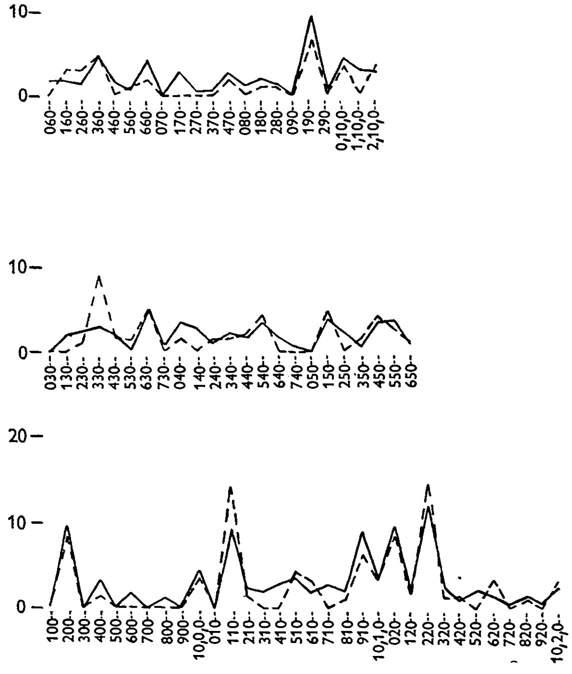

Fig. 4. A comparison of the observed (broken lines) and calculated F_{hk0} values.

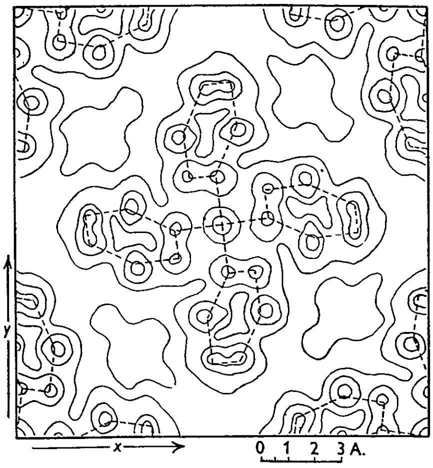

Fig. 5. The Fourier projection of tetraphenylmethane with the trial structure superimposed in broken lines.

Fig. 3 is the projected structure upon which the final signs of the $F_{(hk0)}$ Fourier parameters were determined, while Fig. 4 gives graphically the correlation between observed and calculated values.

Fig. 5 shows a Fourier projection along the z axis, using the strips of Patterson & Tunnell (1942), with the structure shown in Fig. 3 superimposed on it in broken lines. Fig. 6 shows the final structure.

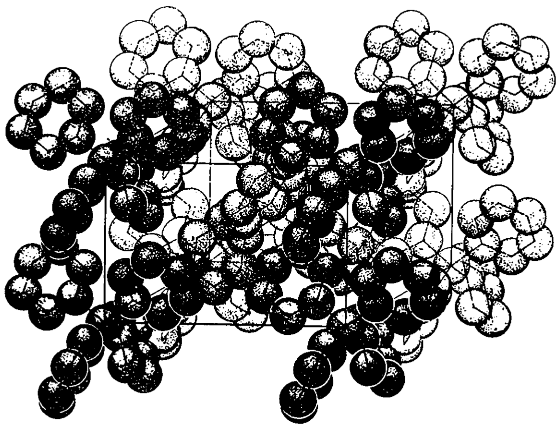

Fig. 6. A three-dimensional model of the tetraphenylmethane structure.

Discussion of the structure

The positions of the atoms are given in Table 2. The atom no. 0 is the central carbon atom and the other atoms are numbered about the six-membered ring.

Fig. 6 was drawn to scale from the data of Tables 1 and 2. Table 2 was used to calculate the interatomic distances, showing that the tetrahedral bonds on the central carbon atom are 1·47 A. while the bonds in the rings are 1·39 A. Fig. 6 indicates the presence of much void space which may account for the low density (1·173 g.cm.$^{-3}$) of this compound, and Fig. 5 indicates that the void space follows planes in the (110) direction in coincidence with the developed planes of the habit of needle crystals.

Table 2. *Atomic coordinates*

Atom number	x	y	z
0	0	0	0
1	0·112	−0·016	0·119
2	0·104	−0·079	0·311
3	0·207	−0·093	0·423
4	0·223	0·034	0·037
5	0·327	0·020	0·149
6	0·319	−0·043	0·341

We are appreciative of a grant from the University of Utah Research Fund for carrying out this project. We are indebted to Dr W. J. Horton for preparation of the crystals and to A. Morrey Bailey for assistance in making certain of the drawings.

References

Binnie, W. P. & Robertson, J. M. (1949). *Acta Cryst.* **2**, 116.

Buerger, J. M. & Klein, G. E. (1946). *J. Appl. Phys.* **17**, 285.

George, H. W. (1926). *Proc. Roy. Soc.* A, **113**, 585.

Patterson, A. L. & Tunnell, G. (1942). *Amer. Min.* **27**, 655.

Robertson, J. M. (1943*a*). *J. Sci. Instrum.* **20**, 169.

Robertson, J. M. (1943*b*). *Nature, Lond.*, **152**, 411.

Acta Cryst. (1950). **3**, 219

Structure and Growth Mechanism of Photolytic Silver in Silver Bromide*

By Chester R. Berry and Robert L. Griffith

Research Laboratories, Eastman Kodak Company, Rochester 4, *N.Y., U.S.A.*

(*Received* 3 *October* 1949)

An investigation has been made by X-ray and electron diffraction of single crystals of pure silver bromide during the process of photolytic decomposition induced by irradiating the crystals with ultraviolet light. The orientation of the silver determined from the X-ray diffraction patterns is quite different from the orientations determined from the electron diffraction patterns. This corresponds to differences in the silver orientations in the body and near the surface of the silver bromide crystals. Two different mechanisms of silver separation in these two regions of the crystals, one based on the motion of cations, and the other on the aggregation of F-centers, appear to account for the silver orientations observed.

Introduction

These investigations were initiated to determine whether there is any preferred orientation of the silver produced by photodecomposition of silver bromide.† Dankov (1939) has suggested that the peculiar photosensitivity of silver bromide may be due to the almost exact correspondence of the length of the face diagonal of the silver unit cell with the cube edge of silver bromide. This would enable the silver to grow on the silver bromide in certain orientations with nearly perfect correspondence of atomic periodicities at the boundary. The two conditions which preserve this correspondence are growth of (100) faces together, one rotated 45° to the other, and growth of (110) faces together, one rotated 90° to the other.

---

* Communication No. 1291 from the Kodak Research Laboratories.

† By microscopic examination, Trivelli & Sheppard (1925) recognized the 'vectorial decomposition' of silver bromide. Photomicrographs shown in their paper appear to agree with present observations.