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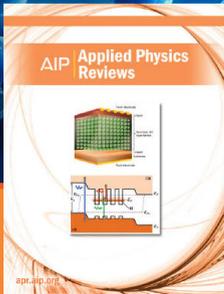
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## Electron Diffraction Study of Lead Tetramethyl†

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(Received November 29, 1957)

A reinvestigation of  $\text{Pb}(\text{CH}_3)_4$  has shown the diffraction pattern to be in agreement with a symmetrical molecular structure and the complex atomic scattering factors of Ibers and Hoerni. The measured interatomic distances are  $\text{Pb}-\text{C}=2.203\pm 0.010$  Å and  $\text{Pb}\cdots\text{H}=2.79\pm 0.05$  Å.

EARLY electron diffraction studies led to reports of unequal bond length and hence of low symmetry for uranium hexafluoride, tungsten hexafluoride, osmium tetroxide, and a number of other molecules, all containing both heavy and light atoms. When the present investigation was begun, these results had just been explained<sup>1</sup> as representing not genuine molecular asymmetry but rather gross error in the atomic electron scattering factors used for the interpretation of the diffraction data. Tests of this explanation for molecules of undoubted symmetry seemed to be in order, and lead tetramethyl was chosen as the first. Meanwhile, Ibers and Hoerni<sup>2</sup> have made new calculations of atomic scattering factors, and for these the new photographs provide an important experimental test.

An early study<sup>3</sup> of lead tetramethyl, based on inadequate photographs on which only three rings were measured, failed to reveal any anomaly.

### EXPERIMENTAL

The sample of lead tetramethyl (99.8%) was supplied by Dr. G. B. Guthrie, Jr., of the Bartlesville Laboratory of the U. S. Bureau of Mines. The photographs were made on Kodak-50 plates in our new apparatus at camera distance 9.627 cm and electron

wavelength 0.0618 Å; they were interpreted visually in the usual way.<sup>4</sup>

### OUTLINE OF THEORY, RESULTS, AND DISCUSSION

The diffraction pattern (visual curve, Fig. 1) is indeed characteristic of a compound having two major interatomic disturbances of about equal weight and a few tenths of an angstrom difference in  $r$ . That is, the envelope of the molecular intensity curve decreases gradually to a minimum and then increases again. The conventional interpretation would accordingly be that there were two pairs of  $\text{Pb}-\text{C}$  bonds of difference length in the  $\text{Pb}(\text{CH}_3)_4$  molecule, but like the early examples just mentioned it would be wrong.

The essential point<sup>1</sup> is that the atomic scattering factor for electrons is not the *real* function conventionally assumed on the basis of the Born approximation—which is exact only in the limit of small  $Z$  and  $\lambda$ —but is instead a *complex* function  $f=|f|\exp(i\eta)$ , where both  $|f|$  and  $\eta$  are functions of  $Z$ ,  $s=\pi q/10=(4\pi/\lambda)\sin\varphi/2$ , and  $\lambda$ . The usual intensity function then becomes

$$sI(s) = k \sum_{ij} f_i f_j^* \frac{\sin r_{ij} s}{r_{ij}} = k \sum_{ij} |f_i| |f_j| \cos(\Delta\eta)_{ij} \frac{\sin r_{ij} s}{r_{ij}},$$

the phase angle  $\eta$  being an increasing function of both  $Z$  and  $s$ . The amplitude of a term reaches zero at a certain point  $s_{ij}^0$ , the cutoff point, and thereafter changes sign,  $s_{ij}^0$  being defined by  $(\Delta\eta)_{ij} = \eta_j - \eta_i = \pi/2$ .

\* Contribution No. 2281 from the Gates and Crellin Laboratories of Chemistry.

† This work was supported by the Office of Naval Research under Contract N6onr-24423.

<sup>1</sup> V. Schomaker and R. Glauber, *Nature* **170**, 290-291 (1952).

<sup>2</sup> J. A. Ibers and J. A. Hoerni, *Acta Cryst.* **7**, 405 (1954).

<sup>3</sup> L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.* **58**, 2036 (1936).

<sup>4</sup> K. Hedberg and A. J. Stosick, *J. Am. Chem. Soc.* **74**, 954 (1952).

## A single "heavy-light" term

$$|f_i||f_j|\cos(\Delta\eta)_{ij} \frac{\sin r_{ij}s}{r_{ij}}$$

of  $sI(s)$  is roughly equivalent to a pair of ordinary terms with coefficients  $\frac{1}{2}|f_i||f_j|$  and distance values  $(r+\Delta r/2)_{ij}$  and  $(r-\Delta r/2)_{ij}$ . The difference  $\Delta r_{ij}$  of the two virtual distances is referred to as the "apparent split"; it is given to a good approximation by

$$\Delta r_{ij} \cdot s_{ij}^0 = \pi.$$

In this investigation, the atomic scattering amplitudes  $|f_i|$  were used for all the atoms just as given by

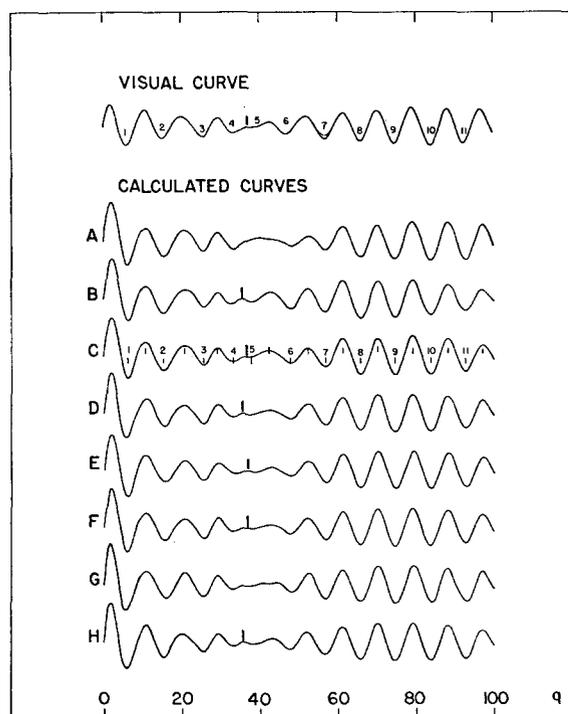


FIG. 1. Electron diffraction curves for  $\text{Pb}(\text{CH}_3)_4$ . The dashed part of the visual curve is a correction made after some of the calculated curves had been examined. The calculated curves are for models with  $\text{Pb}-\text{C}=2.21\text{A}$ ,  $\text{C}-\text{H}=1.09\text{A}$ ,  $a_{\text{C}-\text{H}}=0.00136\text{A}^2$ ,  $a_{\text{Pb}\cdots\text{H}}=0.006\text{A}^2$ , and the following varied parameter values.

| Model          | $\text{Pb}\cdots\text{H}$<br>(A) | $\delta_{\text{PbC}}$<br>(A) | $\delta_{\text{PbH}}$<br>(A) | $a_{\text{C}-\text{C}^0}$<br>(A <sup>2</sup> ) |
|----------------|----------------------------------|------------------------------|------------------------------|--|
| A              | 2.80                             | 0.12                         | 0.15                         | 0.0126   |
| B              | 2.80                             | 0.14 <sup>b</sup>            | 0.15                         | 0.0126   |
| C              | 2.80                             | 0.13                         | 0.15                         | 0.0126   |
| D <sup>a</sup> | 2.80                             | 0.13                         | 0.15                         | 0.0110   |
| E <sup>a</sup> | 2.80                             | 0.13                         | 0.15                         | $\infty$                                       |
| F <sup>a</sup> | 2.80                             | 0.13                         | 0.15                         | 0.0126   |
| G <sup>a</sup> | 2.90                             | 0.13                         | 0.15                         | 0.0126   |
| H <sup>a</sup> | 2.70                             | 0.13                         | 0.15                         | 0.0126   |

<sup>a</sup> C—H terms omitted.

<sup>b</sup> Theoretical value.<sup>2</sup>

<sup>0</sup>  $2a_{ij} = \langle (\Delta r_{ij})^2 \rangle_{\text{Av}} - \langle (\Delta r_{\text{Pb}-\text{C}})^2 \rangle_{\text{Av}}$ .

TABLE I. Quantitative comparison, model C. Summary of final results.

| Ring | Minimum            |                      |     | Maximum            |                      |     |
|------|--------------------|----------------------|-----|--------------------|----------------------|-----|
|      | $q_0^a$            | $q_c/q_{\text{obs}}$ | $w$ | $q_0^a$            | $q_c/q_{\text{obs}}$ | $w$ |
| 1    | 6.08               | 1.020 <sup>a</sup>   | 0   | 11.07              | 0.957 <sup>a</sup>   | 0   |
| 2    | 15.55              | 0.990                | 1   | 19.96              | 1.032 <sup>a</sup>   | 0   |
| 3    | 25.79              | 0.988                | 2   | 29.44              | 0.988                | 5   |
| 4    | 33.21              | 1.000                | 2   | 36.90              | 0.989 <sup>a</sup>   | 0   |
| 5    | 39.92              | 0.952 <sup>a</sup>   | 0   | 43.66              | 0.971                | 1   |
| 6    | 47.64              | 1.003                | 1   | 52.68              | 0.993                | 2   |
| 7    | 57.42              | 0.990                | 5   | 61.66              | 0.993                | 10  |
| 8    | 65.88              | 0.997                | 10  | 70.40              | 0.996                | 10  |
| 9    | 74.81              | 1.000                | 10  | 78.57              | 1.008                | 5   |
| 10   | 83.31 <sup>b</sup> | 1.006                | 5   | 88.09 <sup>b</sup> | 1.001                | 2   |
| 11   | 91.89 <sup>b</sup> | 1.009                | 2   | 97.27 <sup>b</sup> | 0.998                | 1   |

$\langle q_c/q_{\text{obs}} \rangle_{\text{Av}}$ : unweighted, 0.9959; weighted, 0.9970.

Av dev: unweighted, 0.0069; weighted, 0.0049.

Final results and estimated limits of error:

$$\text{Pb}-\text{C} = 2.21 \times 0.9970 = 2.203 \text{ A } (\pm 0.010 \text{ A}).$$

$$\text{Pb}\cdots\text{H} = 2.80 \times 0.9970 = 2.79 \text{ A } (\pm 0.05 \text{ A}).$$

$$\text{C}-\text{H} = 1.09, \text{ assumed. } \angle \text{HCPb} = 109.0^\circ \pm 4.0^\circ.$$

$$q_{\text{PbC}}^0 = 10/\pi s_{\text{PbC}}^0 = 38.5 \pm 1.5.$$

$$q_{\text{PbH}}^0 = 33.3 \pm 3.5.$$

<sup>a</sup> Av. of C. W. and V. S.

<sup>b</sup> V. S. only.

<sup>0</sup> Not included in unweighted average.

Ibers and Hoerni,<sup>2</sup> but the phase angle differences were varied somewhat. The intensity function was approximately modified, as described in Appendix I, for convenience of calculation by our routine punched-card method.<sup>5</sup>

The calculated curves, some of which are shown in Fig. 1, demonstrate the sensitivity of the diffraction pattern to variation of the critical parameters. It turns out that in the region of the  $\text{Pb}-\text{C}$  cutoff point ( $q \sim 38$ ), the pattern is extremely responsive to almost all the parameters. As an outstanding example, maximum 4, indicated by heavy bars in Fig. 1, is a very sharp although rather weak feature. To fit maximum 4 to its observed position and shape, the cutoff points of both  $\text{Pb}-\text{C}$  and  $\text{Pb}\cdots\text{H}$  have to be moved out about 10% from the calculated value<sup>2</sup> (curves A, B, and C), and the temperature factors of  $\text{C}\cdots\text{C}$  and  $\text{Pb}\cdots\text{H}$  have to be critically adjusted (curves C, D, and E). The resulting temperature factors are consistent with the observed vibrational frequencies.<sup>6</sup>

The  $\text{C}-\text{H}$  term, as expected, does not play an important role (curves C and F). Our data do provide a determination of the  $\text{Pb}\cdots\text{H}$  distance (curves G and H). Curve C, based on our best model, is in excellent agreement with the visual curve and measured ring diameters; see Fig. 1 and Table I.

<sup>5</sup> Shaffer, Schomaker, and Pauling, J. Chem. Phys. **14**, 659 (1946).

<sup>6</sup> Young, Koehler, and McKinney, J. Am. Chem. Soc. **69**, 1410 (1947).

The cutoff points determined are in fair agreement with the theoretical values<sup>2</sup>  $q_{\text{Pb-C}}^0 = 35.8$  and  $q_{\text{Pb-H}} = 30.2$ . The Pb—C bond length, 2.203 Å, is in excellent agreement with Pauling's covalent radius for quadrivalent lead, 1.430 Å,<sup>7</sup> which leads to the radius sum 2.200 Å for Pb—C, but is incompatible with the early electron diffraction value,  $2.29 \pm 0.05$  Å.<sup>1</sup>

#### APPENDIX I

A familiar form of the molecular scattering function appropriate for correlation with the visually estimated intensity for  $\text{Pb}(\text{CH}_3)_4$  is

$$sI(s) = \frac{4}{r_{\text{Pb-C}}} \frac{|f_{\text{Pb}}||f_{\text{C}}|}{\sum_i |f_i|^2} \cos \Delta \eta_{\text{Pb-C}} \sin r_{\text{Pb-C}} s$$

$$+ \frac{12}{r_{\text{Pb...H}}} \frac{|f_{\text{Pb}}||f_{\text{H}}|}{\sum_i |f_i|^2} \cos \Delta \eta_{\text{Pb...H}} \exp(-a_{\text{Pb...H}} s^2) \sin r_{\text{Pb...H}} s$$

$$+ \frac{6}{r_{\text{C...C}}} \frac{|f_{\text{C}}|^2}{\sum_i |f_i|^2} \exp(-a_{\text{C...C}} s^2) \sin r_{\text{C...C}} s$$

$$+ \frac{12}{r_{\text{C-H}}} \frac{|f_{\text{C}}||f_{\text{H}}|}{\sum_i |f_i|^2} \cos \Delta \eta_{\text{C-H}} \exp(-a_{\text{C-H}} s^2) \sin r_{\text{C-H}} s.$$

For convenience in punched-card calculation, the function

$$J(s) = sI(s) \frac{\sum |f_i|^2 \cos \delta_{\text{Pb-C}} s}{|f_{\text{Pb}}||f_{\text{C}}| \cos \Delta \eta_{\text{Pb-C}}}$$

$$= \frac{2}{r_{\text{Pb-C}}} \{ \sin(r+\delta)_{\text{Pb-C}} s + \sin(r-\delta)_{\text{Pb-C}} s \}$$

$$+ \frac{6}{r_{\text{Pb-H}}} \phi \exp(-a_{\text{Pb...H}} s^2) \{ \sin(r+\delta)_{\text{Pb...H}} s + \sin(r-\delta)_{\text{Pb...H}} s \}$$

$$+ \frac{6}{r_{\text{C...C}}} \psi \exp(-a_{\text{C...C}} s^2) \sin r_{\text{C...C}} s + \frac{12}{r_{\text{C-H}}} \omega \exp(-a_{\text{C-H}} s^2) \sin r_{\text{C-H}} s,$$

with

$$\phi = (|f_{\text{H}}| \cos \Delta \eta_{\text{PbH}} \cos \delta_{\text{Pb-C}} s) / (|f_{\text{C}}| \cos \Delta \eta_{\text{PbC}} \cos \delta_{\text{Pb...H}} s),$$

$$\psi = (|f_{\text{C}}| \cos \delta_{\text{Pb-C}} s) / (|f_{\text{Pb}}| \cos \Delta \eta_{\text{PbC}}),$$

$$\omega = (|f_{\text{H}}| \cos \Delta \eta_{\text{C-H}} \cos \delta_{\text{PbC}} s) / (|f_{\text{Pb}}| \cos \Delta \eta_{\text{PbC}}),$$

<sup>7</sup> L. Pauling, Proc. Roy. Soc. (London) **A196**, 343 (1949).

and  $\delta_{ij} = \frac{1}{2} \Delta r_{ij}$  was evaluated instead.

For the range of interest,  $\phi$ ,  $\psi$ , and  $\omega$  are approximately constant except for  $q$  less than 15 (in the region for  $q$  less than 15, Gaussian approximations may be used for  $\phi$ ,  $\psi$ , and  $\omega$ ).

The functions  $\phi$ ,  $\psi$ , and  $\omega$  were approximated as constants in this investigation. If the variations of the cutoff points are assumed to be due merely to changes in a scale factor  $\gamma$  in  $\Delta \eta(s) = \Delta \eta_{\text{I and H}}(\gamma s)$ , the constant approximations for  $\phi$ ,  $\psi$ , and  $\omega$  are valid for all the variations of  $s_0$ 's illustrated.