INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®
THE RICE INSTITUTE

THE CRYSTAL STRUCTURE OF ARSENOMETHANE

by

John Howard Burns

A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Houston, Texas
May, 1955
ACKNOWLEDGEMENTS

I should like to express my gratitude to Professor Jörg Waser for his patient teaching and for his invaluable guidance during the progress of this research.

In addition I should like to thank Dr. J. S. Rollett of the California Institute of Technology for his advice and assistance in the computation of the least squares refinement. Financial assistance by the Robert A. Welch Foundation is also gratefully acknowledged.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
<td>1</td>
</tr>
<tr>
<td>Introduction</td>
<td>2</td>
</tr>
<tr>
<td>Experimental</td>
<td>4</td>
</tr>
<tr>
<td>Determination of the Structure</td>
<td>7</td>
</tr>
<tr>
<td>Refinement of Parameters</td>
<td>20</td>
</tr>
<tr>
<td>Discussion of the Structure</td>
<td>33</td>
</tr>
<tr>
<td>References</td>
<td>44</td>
</tr>
</tbody>
</table>
SUMMARY

The structure of the yellow form of arsenomethane has been studied by single crystal x-ray techniques at reduced temperature. The crystals are monoclinic and belong to the space group $\text{C}_{2h}^5 - \text{P2}1/\text{n}$, with $a = 8.88\ \text{Å}$, $b = 12.55\ \text{Å}$, $c = 11.61\ \text{Å}$, and $\beta = 101^\circ 46'$. The unit cell contains four molecules. Harker synthesis, Patterson section and Fourier projection methods were used to locate the arsenic atoms. Geometrical considerations were combined with the difference Fourier method to find the carbon atoms. The parameters were refined by application of the least-squares procedure to three dimensional diffraction data.

The molecule consists of a puckered, five-membered ring of arsenic atoms to each of which is attached a methyl group. The As-As bond length varies significantly from $2.42\ \text{Å}$ to $2.45\ \text{Å}$, and the C-As bond length varies from $1.94\ \text{Å}$ to $1.98\ \text{Å}$. The As-As-As bond angle varies from $97^{1/2}_0$ to $105^{1/2}_0$ and the C-As-As bond angle from $94^{1/2}_0$ to $102^{1/2}_0$. 
INTRODUCTION

Arsenomethane exists in two forms at room temperature, a yellow oil and a red solid. The structure and properties of both forms have been studied by Waser and Schomaker (1) who used vapor density measurements and electron diffraction to study the yellow form, and x-ray powder methods to study the red modification. A conclusive structure for the molecule was not obtained, although a possible molecular model consisting of a puckered, five-membered ring of arsenic atoms and an average As-As-As angle of 90° was in agreement with their data.

The unit cell dimensions and space group of the yellow compound in single crystal form have been determined and reported on by the writer (2). These early results may be summarized as follows: The crystals were found to be monoclinic, having unit cell dimensions

\[
\begin{align*}
  a &= 8.88 \text{ Å} \\
  b &= 12.55 \text{ Å} \\
  c &= 11.61 \text{ Å} \\
  \beta &= 101° 46' 
\end{align*}
\]

The space group consistent with the systematic extinctions is \( \text{C}_{2}^{5} \) - P21/n.
Diffraction intensities were measured for three zones, but attempts to determine the detailed structure were unsuccessful.

In this thesis will be discussed a broader approach to the problem, using three-dimensional data. The resulting determination of the complete crystal structure and the dimensions of the arsenomethane molecule will be described.
EXPERIMENTAL

The synthesis of the compound and the details of the low temperature x-ray techniques which were used to study it have been previously described (2). The general procedure involved mounting a capillary containing the oil in position to diffract x-rays, then lowering the temperature of this sample by cooling in a stream of cold air. Because of the tendency of the oil to supercool, special treatment was required to induce crystallization. First, a little liquid nitrogen was poured over the sample causing it to form a glass. Then the temperature was raised, by regulation of the cold air flow, until it was a few degrees below freezing (120°C) at which point the glass undergoes a transition to the crystalline state in a few minutes. The crystallites obtained were melted except for one seed which was then allowed to grow slowly to a single crystal large enough for use. It was oriented by x-ray methods, and finally intensity pictures were taken.

For the recording of three dimensional diffraction data the Weissenberg camera, modified for low temperature, was used with Cu K radiation. The multiple film technique
was employed, and x-ray photographs were made of seven levels of the [001] zone and five levels each of the [100] and [101] zones. Experimental difficulties of crystal growth prevented the recording with the Weissenberg goniometer of diffraction from the [010] zone.

The intensities were measured by visual comparison with a prepared scale. The different values of the integrated spot density of each reflection as found on the three simultaneously exposed films were put on the same scale by using a predetermined film factor, which varied from the equator to higher levels in a way described by Bullen (3). For strong or very weak reflections values from fewer than three films were used, and an average value was found for each reflection. Lorentz-polarization (4) and absorption (5) corrections were applied, and the intensity values of reflections from all levels brought to the same relative scale. This was done by taking the film containing Okl reflections as a basis and comparing the reflections common to this film and the other films to determine the ratio of their scale factors.

The spherical region of reciprocal space accessible by using copper radiation contains 2769 possible reflections not related by symmetry. Of these 432 were
not photographed, 1154 were found to have observable intensity, and 1183 were too weak to be seen on the films.

The density of the frozen compound was measured to be 2.3 g./cm.$^3$, corresponding to twenty (As CH$_3$) groups per unit cell (calculated density, 2.36 g./cm.$^3$). The space group has both two-fold and four-fold positions. With twenty (As CH$_3$) units and an even number of space group positions, the only possibilities for arranging the atoms into molecules are for the unit cell to contain two decamers, four pentamers (or ten dimers in two 4-fold and one 2-fold positions). The pentamer is the obvious choice. Since it is non-centrosymmetric, it must occupy the four-fold positions. The asymmetric unit will thus contain one As$_5$ (CH$_3$)$_5$ molecule.
DETERMINATION OF THE STRUCTURE

The collection of three-dimensional diffraction data made it possible to employ techniques of structure determination not used in the earlier work where only the intensities for three zones were known. The calculation of sections of the three-dimensional Patterson function proved most useful and resulted in the solution of the structure.

The Patterson function is defined as

\[ P(uvw) = \int \int \int \rho(xyz) \rho(x+u, y+v, z+w) \, V \, dx dy dz \]  \hspace{1cm} (1)

and can be represented by the Fourier series

\[ P(u,v,w) = \frac{1}{V} \sum_h \sum_k \sum_{\ell} F(hk\ell)^2 \cos 2\pi(hu + kv + \ell w), \] \hspace{1cm} (2)

where \( \rho(x,y,z) \) is the electron density distribution in the crystal, \( V \) is the volume of the unit cell, and \( F(hk\ell) \) is the structure factor. The structure factor is related to the observed intensity, corrected for Lorentz, polarization, and absorption factors, by the equation:

\[ I = \text{constant} \, |F(hk\ell)|^2. \] \hspace{1cm} (3)
Hence the Fourier coefficients of the Patterson function can be determined experimentally, which is not the case for the electron density itself. The difficulty lies, of course, in the interpretation of $P(u,v,w)$, but in the present instance certain aspects of $P(u,v,w)$ provided the key to the structure.

In practice, the summation of a three-dimensional Fourier series is a long and tedious process by ordinary methods, but it is convenient and sometimes just as useful to make sections through the Patterson function. Harker showed that certain sections can provide direct information about the atomic coordinates (6). While evaluation of sections is still a three-fold summation, one sum was non-trigonometric for the cases considered, and the work was greatly reduced.

The Patterson function has peaks at vector distances from the origin corresponding to all the interatomic vectors in the crystal. Harker showed that the interpretation of the peaks resulting from vectors between the atoms which are related by symmetry is especially simple and informative. The peaks corresponding to these vectors, the so-called Harker peaks, always lie in a plane or along a line, depending on the particular symmetry element relating the atoms. Non-Harker peaks, which do
not result from symmetry related atoms, may also appear in the Harker sections and lines.

In the case of arsénomethane, atoms related by the $2_1$ axis are connected by vectors having a $y$-coordinate of $1/2$. In the Harker section at $y = 1/2$, one would expect to find, among others, peaks at $(2x, 2z)$, where $(x, z)$ are atomic coordinates. Non-Harker peaks would appear if there were also some interatomic vectors having a $y$-coordinate of approximately $1/2$, but not resulting from the $2_1$ operation. The calculation of the Harker section at $y = 1/2$ was carried out, and the resulting vector map appears in Figure 1. The function is represented in the form of a contour map. The five maxima joined by the dashed line are the true Harker peaks and correspond to the five arsenic atoms of one molecule. The heavier peaks are non-Harker and arise because two atoms having the same $y$-coordinate produce an additional peak of twice the weight of the Harker peaks and lying half way between them. Three such peaks may be seen in the figure, indicating that three arsenic atoms have nearly the same $y$-coordinate. The carbon atoms are not expected to show up in this plot because of their relatively small scattering compared to arsenic.
Once the above features of the Harker section had been recognized, the coordinates of the Harker peaks were read and converted to atomic coordinates. In this way tentative $x$ and $z$ parameters were obtained for the five arsenic atoms in the asymmetric unit. The electron density projection, $\rho(x,z)$, could then be obtained by the usual methods.

The electron density in a crystal can be expanded in a Fourier series:

$$\rho(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} F(hk\ell) \exp \left\{ -2\pi i (hx + ky + \ell z) \right\} \quad (4)$$

in which

$$F(hk\ell) = \sum_{j=1}^{N} f_{j} \exp \left\{ 2\pi i (hx_{j} + ky_{j} + \ell z_{j}) \right\} \quad (5)$$

is the structure factor, $f_{j}$ is the atomic scattering factor of the $j$th atom, and $x_{j}, y_{j}, z_{j}$ are the coordinates of the $j$th atom. The summation is taken over all $N$ atoms in the unit cell. In general, the structure factor is a complex quantity and may be written

$$F(hk\ell) = |F(hk\ell)| e^{i\phi} \quad (6)$$

where $\phi$ is the phase angle. For centrosymmetric crystals
such as arsenomethane, $\phi = 0$ or $\pi$ and $F = \pm |F|$. To sum series (4), the observed structure factors are used as the coefficients. However, the sign of each term is not observed and must be found by other means. If the atomic positions, $x_j, y_j, z_j$, are known, the structure factors can be calculated from equation (5), and their signs used with the observed structure factors.

Hence the $x$ and $z$ coordinates of the arsenic atoms found by Harker synthesis made it possible to calculate the $F(h0l)$ values and to make a Fourier projection onto the $x$-$z$ plane. The electron density map obtained by this projection is shown in the upper half of Figure 2. The contours represent levels of equal electron density at equal but arbitrary intervals, and the final positions of the atoms in one molecule are indicated by crosses. Only three of the arsenic atoms were actually resolved in this projection. Their positions correspond closely to the tentative parameters from the Harker section.

By comparison of the $x$ coordinates of all arsenic atoms in the unit cell it was found that there were some interatomic vectors having an $x$-component close to $1/2$. The peaks corresponding to these vectors were easily identified in a Patterson section: $P(1/2, y, z)$, (Figure 3), and their $y$-components found. These
FIGURE 2. FOURIER PROJECTION
FIGURE 3. PATTERSON SECTION
interatomic vectors were used to identify the peaks on
the Harker line which is contained in the same section
at \((\frac{1}{2}, y, \frac{1}{2})\). On this line, peaks occur at \((\frac{1}{2} - 2y)\),
where \(y\) is an atomic coordinate. In this way, the \(y\)
parameters of all five arsenic atoms in the asymmetric
unit were determined. It was then possible to interpret
the remaining maxima in the Patterson section.

This determination of the \(y\)-coordinates provided the
additional information needed for calculation of struc-
ture factors and the making of Fourier projections along
the \(a\) and \(c\) axes. Only the \(x-y\) projection is shown
(Figure 4), because the arsenic atoms are not well
resolved in the other projection. The electron density
contours and crosses marking the refined coordinates are
shown in the top half, and the molecule and its neighbors
are drawn in position in the bottom half of the unit cell.

The net result of the Fourier projections along the
three directions was to obtain fifteen approximate
coordinates for the five arsenic atoms in one molecule.
These five atoms were seen to be bonded in a puckered
ring with an average bond angle of 100°.

Since the scattering of x-rays by the methyl groups
is much less than that of the arsenic atoms, the positions
of the methyl groups could not be readily determined in
FIGURE 4. FOURIER PROJECTION
the presence of the heavier atoms. In a Fourier projection of the electron density it is not possible to clearly distinguish peaks due to the carbon atoms from the ripples in the background due to the effect of the termination of the series. Consequently, the methyl groups were located by the following considerations.

The packing of molecules with methyl groups placed by assumptions explained below was considered first. The average value of the arsenic bonding angle is about 100° (7) as was found for the As-As-As angles in arsenomethane. It was assumed that the C-As-As bond angles have this value and that the C-As distance is 1.98 Å (7). With those requirements each methyl could occupy either of two positions, above the ring or below it. A list was made of all distances between atoms which might interact, considering all locations of the methyl groups just discussed and including the possibility of randomness in the direction of attachment of the corresponding methyl groups in different molecules. The van der Waals radii of the methyl group and of arsenic are both 2.0 Å (7), which allows no non-bonded interaction in the crystal of much less than 4.0 Å. However, the positions of the carbon atoms are based on assumptions only, and small changes in their coordinates will change the interatomic distances.
involved. Since some of them may be increased by parameter changes, the 4.0 Å limit was replaced by the less stringent one of 3.0 Å, and positions leading to interactions below that value were eliminated. Under these conditions, some of the ten possible carbon positions were ruled out; but this did not lead to a unique structure.

The next step in locating the carbon atoms was the use of the difference Fourier method. The contribution to the structure factors due to the arsenic atoms alone was calculated and subtracted from the observed structure factors. The remainders were used as the coefficients in a difference Fourier series, and projections were made along the three principal directions. The electron density maps obtained had, in each case, a larger number of peaks than would correspond to five carbon atoms. Some of these could be attributed to errors in the positions of the arsenic atoms causing them to not be fully subtracted out. Yet to decide which peaks really belonged to carbon atoms, it was necessary to look at the possible locations indicated by the geometrical considerations. It was found that atomic positions could be fitted to the peaks of the three projections reasonably well by making a choice between the geometrically allowed alternatives.
in each case. On the other hand, all peaks in the difference Fourier maps could not be explained by carbon positions or arsenic shifts. One possible explanation might be that there is a randomness in the attachment of some of the methyl groups, but the x-ray pictures show no diffuse streaks or spots to support this. Furthermore, the subsequent least-squares refinement indicates that the majority, if not all, of the molecules have the same configuration.
REFINEMENT OF PARAMETERS

When the correct structure has been established, the calculated and observed structure factors should be in agreement; but they cannot be exactly equal because of random errors of measurement, incomplete correction for absorption, extinction and other effects, and because of the use of certain approximations in the calculated structure factors. For example, the atomic scattering factors used are usually obtained by the use of quantum mechanical approximations and also apply to free atoms rather than to those bonded in a molecule or crystal.

Consequently, the corrected structure is described by finding a set of parameters which brings about the best overall agreement between observed and calculated structure factors. To determine these parameters systematically the method of least squares was first proposed by Hughes (8).

This method was used to refine the structure of arsenomethane. The number of parameters needed for the description of the structure was set at forty by the following assumptions. The calculated structure factors depend on thirty parameters locating the five arsenic and five carbon atoms in the asymmetric unit, and one parameter per atom describing its temperature factor, assumed to be isotropic.
The atomic scattering factors used for arsenic were an average of the values given by Pauling and Sherman (9) with those of Thomas and Fermi (5), diminished by a value of 1.74 to correct for anomalous dispersion (James (10)). For carbon the scattering factors calculated by McWeeny (11) were used. The hydrogen atoms were left out of the structure factor calculations because their coordinates were not known and because their relative contribution to the scattering is small.

The most probable parameters according to the theory of least squares (c.f. Whittaker and Robinson (12)) are those which minimize the quantity

\[ R = \sum_{hkl} w \left| F_O - F_c \right|^2, \]  

where the weight, w, of each term is inversely proportional to the probable error in \( F_O \). For convenience the weight was chosen differently in the application of the method as will be described later.

The trigonometric form of the equations relating the structure factors to the parameters is not convenient for the minimization of R; but if a reasonably good approximation to the structure exists, the equations can be reduced to a linear form. Let \( F_c^0 \) be the structure factor calculated from a set of trial parameters, \( x_j^0 \), including both coordinates and temperature factors, and let \( F_c \) be
the value calculated from the parameters, \( x_j \), being sought. If the corresponding parameters in either set differ by a small amount \( \delta x_j \), the \( F_c \) may be expanded in a Taylor series:

\[
F_c (hk\ell) = F_c^0 (hk\ell) + \sum_j \left( \frac{\partial F_c}{\partial x_j} \right) \delta x_j + \ldots \tag{8}
\]
in which the derivatives are evaluated at \( x_j = x_j^0 \). By retaining only the linear terms of this expansion and substituting into the expression to be minimized, the following equation is obtained:

\[
R = \sum_{hkl} w \left| F_0 - F_c - \sum_j \left( \frac{\partial F_c}{\partial x_j} \right) \delta x_j \right|^2. \tag{9}
\]

This can also be written as

\[
R = \sum_{hkl} w \left[ (F_0 - F_c)^2 + \sum_i \sum_j \frac{\partial F_c}{\partial x_i} \frac{\partial F_c}{\partial x_j} \delta x_i \delta x_j - 2(F_0 - F_c) \sum_j \frac{\partial F_c}{\partial x_j} \delta x_j \right]. \tag{10}
\]

If \( R \) is to be at a minimum, its derivatives with respect to the parameter shifts, \( \delta x_j \), must vanish. This results in the so-called normal equations:

\[
\frac{\partial R}{\partial (\delta x_j)} = \sum_{hkl} \left[ \sum_j w \left( \frac{\partial F_c}{\partial x_j} \delta x_j \right) + w \left( F_0 - F_c \right) \frac{\partial F_c}{\partial x_n} \right] = 0, \tag{11}
\]

one such equation existing for each value of \( n \). The number of these normal equations is the same as the number of parameter shifts to be determined, so the equations can be solved simultaneously for the \( \delta x_j \) values.
To refine a crystal structure by this method the parameter changes are obtained from a solution of the normal equations, and the $F_0^0$ values are recalculated for the new parameters. A new system of normal equations is set up and this process iterated until the parameters no longer change significantly on recycling.

In the refinement of arsenomethane the atomic coordinates from the Fourier projections were used as initial values for thirty parameters, and the initial values of the ten parameters, $Q_1$, describing the temperature factors $(\exp (-Q_1 \sin^2 \theta))$ were set equal to an average of 2.8. This was obtained from a logarithmic plot versus $\sin^2 \theta$ of the ratio of the observed to calculated structure factors for three zones.

Since all reasonable systems of weighting lead to coordinates differing by small amounts compared to the standard deviation of the results (13), the exact weighting factor required by the least squares theory was not used. Instead, a weighting scheme was employed (c.f. reference 8) which assumes that the percentage error in $F_0^2$ is a constant for $F_0$ greater than $4F_{\text{min}}$, and that the absolute error is constant for $F_0$ less than or equal to $4F_{\text{min}}$. A list of weights according to this system follows.
For \(|F_o| > 4F_{\text{min.}}\), \(\sqrt{w} = 1/|F_o|\);
for \(0 < |F_o| < 4F_{\text{min.}}\), \(\sqrt{w} = 1/4 F_{\text{min.}}\);
for \(F_o = 0\), \(F_c > F_{\text{min.}}\), \(\sqrt{w} = 1/4 F_{\text{min.}}\); and
for \(F_o = 0\), \(F_c < F_{\text{min.}}\), \(\sqrt{w} = 0\).

\(F_{\text{min.}}\) is the smallest observable structure factor, for which an average value of 2.0 was used for the entire range of \(s\), although it actually varies with \(s\).

Because the least squares treatment was applied to the refinement of forty parameters using over a thousand observations, the normal equations had to be obtained and solved by high speed computer. For this purpose the digital computer of the Electro Data Corporation of Pasadena, California was employed and the refinement process carried through three cycles.

Even with the use of the computer, certain approximations were necessary in practice. There are forty normal equations and the matrix of their coefficients contains 820 independent elements. Forty of these are diagonal and 780 non-diagonal. Each coefficient is a summation of the form

\[
\sum_{hkl} w \frac{\partial F}{\partial x_1} \frac{\partial F}{\partial x_j},
\]  

(12)

where \(x_1\) and \(x_j\) correspond to parameters \(x, y, z,\) and \(Q\). In the actual computation only the diagonal coefficients were
calculated except for cross terms involving the x and z coordinates of a particular atom. Some of the other off-diagonal coefficients will be shown to be negligible, and the remainder of the coefficients will be discussed. The four classes of matrix elements to be considered below are: diagonal elements, elements involving the same type of parameter for two atoms, elements involving different parameters of the same atom, and the case of different coordinates of different atoms.

The structure factor for arsennomethane may be written as:

\[ F_c = \sum_{i} f_i [\cos 2\pi(hx_i + lz_i) \cos 2\pi ky_i] \exp(-Q_1 \sin^2 \theta), h+k+l = \text{even} \]

\[ -\sum_{i} f_i [\sin 2\pi(hx_i + lz_i) \sin 2\piky_i] \exp(-Q_1 \sin^2 \theta), h+k+l = \text{odd}. \]

In the following discussion only the expression for \(h+k+l = \text{even}\) will be considered since the conclusions obtained are completely general.

Consider first the diagonal elements involving the atomic coordinate x, for which expression (12) has the form:

\[ \sum_{hkl} 16w f_i^2 \exp(-2Q_1 \sin^2 \theta) \pi^2 h^2 \cos^2(2\pi ky_i) \sin^2[2\pi(hx_i + lz_i)]. \]  

Similar expressions are obtained for coordinates y and z. All terms are positive so the sum is large, moreover it is much larger for arsenic coordinates than for carbon coordinates because of the dependence on the atomic
scattering factor. The other diagonal elements involve the temperature factor parameter and are written as

\[ \sum_{hkl} 16w f_i^2 \sin^4 \theta \exp \left[ -2Q_i \sin^2 \theta \right] \cos^2 2\pi(hx_i + \ell z_i) \]
\[ \cos^2 (2\pi ky_i). \]

(14)

This sum also contains only positive terms making it large, and again the coefficients corresponding to arsenic atoms will be larger than those for the carbons, due to the \( f_i^2 \) term.

The first type of off-diagonal element to be considered is where \( x_i, x_j \) of expression (12) are the coordinates along the same axis, for different atoms of the same kind. The sum then has the form:

\[ \sum_{hkl} w f_i f_j \exp \left[ -(Q_i + Q_j) \sin^2 \theta \right] \pi^2 a^2 \]
\[ \left[ \cos 2\pi(ky_i + ky_j) + \cos 2\pi(ky_i - ky_j) \right] \]
\[ \left[ \cos 2\pi(hx_i + \ell z_i - hx_j - \ell z_j) - \cos 2\pi(hx_i + \ell z_i + hx_j + \ell z_j) \right] \]

(15)

when the axis is taken to be \( a \), but \( b \) and \( c \) yield similar expressions. This coefficient is large when atoms overlap, as in a projection, because the cosines whose arguments are coordinate differences will be nearly +1 for all \( hkl \); and the cosines whose arguments are coordinate sums will be nearly +1 at the same time because the center of symmetry allows \( x_i \) to be replaced by \(-x_i \). There may also be
overlapping in three dimensional analysis if the reflections observed do not extend to high enough values of \( \sin \theta/\lambda \) or because of unsymmetrical sampling of reciprocal space. However, there was no overlap in the structure being considered, so the cosines may be expected to be negative as often as positive making the total sum small compared to the diagonal terms for corresponding coordinates.

The non-diagonal elements involving an atomic coordinate \((x_1, y_1, z_1)\) and the parameter \(Q_1\) of the same atom may be illustrated by the evaluation of (12) with \(x_1\) and \(Q_1\) as the parameters, giving

\[
\sum_{hkl} \frac{w_1 f_1^2 \sin^2 \theta \exp(-2Q_1 \sin^2 \theta) \pi h \cos^2 \theta \kappa y_1 \sin \left[4\pi \right. (hx_1 + \ell z_1)]}
\]

(17)

Since there are as many values of \(+|h|\) as of \(-|h|\), enough cancellation is expected to make the sum relatively small, the pertinent comparison being between the square of this sum and the product of the corresponding diagonal elements.

This justifies neglecting these terms insofar as the arsenic coordinates and temperature parameters are concerned. However, while the off-diagonal elements for the carbons will be small compared to the diagonal elements for the arsenics, the relative sizes of the off-diagonal elements for arsenic compared to the carbon diagonal coefficients is not known.
When the element containing the $Q$ values of two atoms is considered, a summation identical to (15) is obtained except that the factor $\pi^2h^2$ is replaced by $\sin^{4}\phi$. Hence the same arguments about overlapping atoms apply, and the coefficients involving $Q_{A_5}$ should be small compared to the diagonal coefficients in $Q_{A_5}$, and likewise for the $Q_C$.

Another type of off-diagonal element is where $x_i$, $x_j$ represent two different coordinates of the same atom. For example, if the derivatives in (12) are evaluated for the $x$ and $y$ coordinates of the $i$th atom, (12) becomes:

$$
\sum_{hki} w_i e^{2\pi^2(\sin^{2}\phi)(\pi^2hk \sin 4\pi x_i \sin 4\pi(hx_i + kz_j))}.
$$

Again, analogous expressions are obtained for other pairs of coordinates of the same atom. If the two axes considered, $x$ and $y$ in this example, are perpendicular, there are as many terms involving $+|h|$, $+|k|$ as there are involving $-|h|$, $+|k|$, and they will tend to cancel each other. For the $x,z$ non-diagonal elements this orthogonality does not exist in the monoclinic system, and the coefficient (12) has to be retained when $\phi$ is significantly different from 90°.

A final case is when the derivatives of (12) are taken with respect to different coordinates of different atoms of the same kind; expressions similar to those above are obtained. Consequently, the same arguments used above can
be advanced to show that these elements will be small for the coordinates of carbon atoms compared to the diagonal terms of both arsenic and carbon coordinates, and that the elements involving the arsenic coordinates will be small compared to the diagonal terms of arsenic.

Up to here the non-diagonal elements for arsenic and carbon coordinates and the non-diagonal elements for the temperature factor have all been considered separately. Nothing has been said about the elements which contain products of derivatives with respect to parameters of different kinds of atoms. These elements will all be small compared to the diagonal coefficients for the arsenic parameters, but it is not known how they compare to the various other terms.

Nevertheless, to save computer time and to reduce the coding problem, only the diagonal coefficients and the $x,z$ cross terms mentioned were used in the least squares refinement. If the problem is solved by using only these terms, then the procedure is justified; but the question may still be asked as to whether the method really does converge in the end.

The actual refinement of the temperature factor was carried out as follows. After the first cycle, the original values of $Q$ were inserted again because the shifts in atomic coordinates resulting from this cycle were
relatively large. For the third cycle the Q-shifts indicated by the second run were taken into account by using a new average Q for the arsenics (2.650) and another for the carbons (3.650). The final values obtained for Q are listed in Table I.

Table I

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>Arsenic</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.511</td>
<td>3.729</td>
</tr>
<tr>
<td>2</td>
<td>2.556</td>
<td>3.673</td>
</tr>
<tr>
<td>3</td>
<td>2.617</td>
<td>3.740</td>
</tr>
<tr>
<td>4</td>
<td>2.712</td>
<td>3.723</td>
</tr>
<tr>
<td>5</td>
<td>2.722</td>
<td>3.695</td>
</tr>
</tbody>
</table>

Table II shows the starting atomic coordinates, those obtained from two least squares cycles, and the final values. By comparison of the last two sets of parameters it is seen that the arsenic atoms did not shift significantly, but the carbon atoms did move by a few thousandths of a unit cell edge and may require further refinement to produce complete convergence.

The second set of parameters in the table are in error by a small amount because three F₀ values erring by approximately a factor of three were used. Had this error been found prior to the final cycle, a more rapid convergence might have been achieved.

The rate and degree of convergence may be seen from a comparison of the following quantities for the three cycles:
\[ R = \frac{\sum |F_0 - F_c|}{\sum |F_0|} \]
\[ \sum w |F_0 - F_q|^2. \]

The standard deviations in parameters obtained by least squares treatment may be estimated by use of equations derived in treatises on the principles of least squares (c.f. reference 12). Cruickshank has put these into convenient form (14). The standard deviation of an observation with unit weight is given by

\[ \sigma^2 = \sum_{hkl} w (F_0 - F_c)^2 /m-s \] (14)

where \( m \) is the number of observations and \( s \) the number of parameters determined from them. For a parameter \( x_r \) the standard deviation is obtained from

\[ \sigma^2 (x_r) = \sigma^2 B_{rr} / D \] (15)

where \( B_{rr} \) is the \( r \)th principal minor of \( D \), a determinant of the form

\[
D = \begin{vmatrix}
b_{11} & b_{12} & \cdots & b_{1m} \\
b_{12} & \cdots & \cdots & \cdots \\
\vdots & \cdots & \cdots & \cdots \\
b_{1m} & \cdots & \cdots & b_{mm}
\end{vmatrix}
\]

with

\[ b_{ij} = \sum_{hkl} w \frac{\partial F_c}{\partial x_i} \frac{\partial F_c}{\partial x_j}. \] (17)
The standard deviations of the parameters are listed in Table II.

Table II

<table>
<thead>
<tr>
<th>Arsenic</th>
<th>Fourier parameters</th>
<th>Parameters after two cycles</th>
<th>Final parameters</th>
<th>$\sigma$</th>
<th>$\sigma(A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>.330</td>
<td>.32644</td>
<td>.32633</td>
<td>.00043</td>
<td>.00382</td>
</tr>
<tr>
<td>y</td>
<td>.202</td>
<td>.20109</td>
<td>.20125</td>
<td>.00029</td>
<td>.00364</td>
</tr>
<tr>
<td>z</td>
<td>.216</td>
<td>.21531</td>
<td>.21534</td>
<td>.00034</td>
<td>.00395</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>.493</td>
<td>.49641</td>
<td>.49621</td>
<td>.00043</td>
<td>.00382</td>
</tr>
<tr>
<td>y</td>
<td>.218</td>
<td>.21636</td>
<td>.21627</td>
<td>.00029</td>
<td>.00364</td>
</tr>
<tr>
<td>z</td>
<td>.411</td>
<td>.40919</td>
<td>.40932</td>
<td>.00034</td>
<td>.00395</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>.742</td>
<td>.74387</td>
<td>.74397</td>
<td>.00043</td>
<td>.00382</td>
</tr>
<tr>
<td>y</td>
<td>.198</td>
<td>.19747</td>
<td>.19759</td>
<td>.00030</td>
<td>.00377</td>
</tr>
<tr>
<td>z</td>
<td>.348</td>
<td>.35345</td>
<td>.35349</td>
<td>.00034</td>
<td>.00395</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>.689</td>
<td>.69305</td>
<td>.69286</td>
<td>.00044</td>
<td>.00391</td>
</tr>
<tr>
<td>y</td>
<td>.101</td>
<td>.10010</td>
<td>.10024</td>
<td>.00030</td>
<td>.00377</td>
</tr>
<tr>
<td>z</td>
<td>.172</td>
<td>.16773</td>
<td>.16777</td>
<td>.00034</td>
<td>.00395</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>.432</td>
<td>.42892</td>
<td>.42870</td>
<td>.00043</td>
<td>.00382</td>
</tr>
<tr>
<td>y</td>
<td>.042</td>
<td>.04213</td>
<td>.04192</td>
<td>.00030</td>
<td>.00377</td>
</tr>
<tr>
<td>z</td>
<td>.142</td>
<td>.14141</td>
<td>.14135</td>
<td>.00034</td>
<td>.00395</td>
</tr>
</tbody>
</table>

Carbon

| 1       |                   |                             |                 |         |             |
| x       | .148              | .15023                      | .15125          | .0047   | .0417       |
| y       | .148              | .13662                      | .13460          | .0030   | .0377       |
| z       | .242              | .26157                      | .25961          | .0034   | .0395       |
| 2       |                   |                             |                 |         |             |
| x       | .525              | .49816                      | .49552          | .0045   | .0400       |
| y       | .378              | .37149                      | .37042          | .0030   | .0377       |
| z       | .442              | .41292                      | .40874          | .0034   | .0395       |
| 3       |                   |                             |                 |         |             |
| x       | .812              | .82496                      | .82002          | .0047   | .0417       |
| y       | .065              | .07139                      | .07282          | .0030   | .0377       |
| z       | .445              | .45486                      | .45444          | .0035   | .0406       |
| 4       |                   |                             |                 |         |             |
| x       | .633              | .65082                      | .65190          | .0046   | .0408       |
| y       | .233              | .22766                      | .22577          | .0030   | .0377       |
| z       | .070              | .06832                      | .06859          | .0034   | .0395       |
| 5       |                   |                             |                 |         |             |
| x       | .440              | .44908                      | .45365          | .0045   | .0400       |
| y       | .935              | .94110                      | .94420          | .0030   | .0377       |
| z       | .258              | .27394                      | .27775          | .0036   | .0418       |
DISCUSSION OF THE STRUCTURE

The bond lengths and angles in the \( \text{As}_5(\text{CH}_3)_5 \) molecule were calculated from the final parameters and are shown in Table III and in Figure 6.

<table>
<thead>
<tr>
<th>Bond</th>
<th>As-As</th>
<th>Bond</th>
<th>C-As</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>2.450 ( \text{\AA} )</td>
<td>1</td>
<td>1.96 ( \text{\AA} )</td>
</tr>
<tr>
<td>2-3</td>
<td>2.429 ( \text{\AA} )</td>
<td>2</td>
<td>1.94 ( \text{\AA} )</td>
</tr>
<tr>
<td>3-4</td>
<td>2.440 ( \text{\AA} )</td>
<td>3</td>
<td>1.99 ( \text{\AA} )</td>
</tr>
<tr>
<td>4-5</td>
<td>2.417 ( \text{\AA} )</td>
<td>4</td>
<td>1.94 ( \text{\AA} )</td>
</tr>
<tr>
<td>5-1</td>
<td>2.425 ( \text{\AA} )</td>
<td>5</td>
<td>1.98 ( \text{\AA} )</td>
</tr>
<tr>
<td>( \sigma ) = 0.005 ( \text{\AA} )</td>
<td>( \sigma ) = 0.06 ( \text{\AA} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The arsenic atoms form a puckered, five-membered ring, and to each atom is attached a methyl group. Figure 5 shows the molecule. The plane of the drawing passes through the two arsenic atoms at the right (atoms 3 and 4 of Figure 6) and the midpoint of a line connecting the arsenic at the top of the figure with the one at the bottom. The distances of the other arsenic and carbon atoms from this plane are given in the figure. Four arsenic atoms are almost coplanar, two lying in the figure plane and two at \( \pm 0.186 \text{\AA} \) from it; but the fifth atom lies 1.253 \( \text{\AA} \) distant from the plane. The ring of As atoms
has very approximately mirror symmetry, the mirror plane being perpendicular to the drawing. In fact, if the two atoms to the right are held fixed, twisting the ring by approximately 6° brings the two atoms close to the drawing plane into that plane and the fifth atom into a position so that the symmetry is quite closely m.

The methyl groups, beginning at the top of the figure and proceeding clockwise occupy alternately positions above and below the ring until the fifth methyl, which necessarily breaks the alternation sequence. It assumes a position more in the plane of the ring than above or below it due to the fact that it is attached to the arsenic atom lying farthest out of the figure plane and because the bonding angle of arsenic is near to 100°.

Figure 6 shows all the bond angles in the molecule. The As-As-As angles are larger on the average than the C-As-As angles (the latter values are known with less accuracy because of the uncertainty in the carbon positions as will be discussed later). The average value of the As-As-As angles is about 102°, and that of the C-As-As angles is 96½°, exclusive of the one value of 102½°. The As-As-As angles appear to fall into three classes: two values near 105½°, two of approximately 100° and one at 97½°.
FIGURE 6. BOND ANGLES
Once the bond lengths and angles have been calculated and it is seen that the values vary from one bond to another, the question arises as to whether this variation corresponds to a real difference in the molecule or is caused by errors in the experimental determination. The use of statistical significance tests based on proper estimates of the standard deviation of the results to answer this question has been suggested by Cruickshank (15), and the necessary statistical procedures have been formulated for use in structure determinations by Cruickshank and Robertson (16). Their results are employed directly in the following discussion.

For molecular parameters such as bond lengths and angles the variance, $\sigma^2$, can be found from those of the atomic parameters.

For the variance in a bond length, $L$, between atoms a and b:

$$\sigma^2(L) = \sigma^2(a) + \sigma^2(b), \tag{18}$$

where $\sigma^2(a)$ and $\sigma^2(b)$ are the variances of atomic parameters in the direction of the bond. By use of equation (18) and the standard deviations of the atomic coordinates given in the previous section, the standard deviations of the bond lengths were calculated and are listed in Table III.

The variance in the angle $\phi$ formed at atom B between two bonds AB and BC is given approximately by
\[ \sigma^2(\phi) = \frac{\sigma^2(A)}{(AB)^2} + \sigma^2(B) \left[ \frac{1}{(AB)^2} - \frac{2 \cos \phi}{(AB)(BC)} + \frac{1}{(BC)^2} \right] \]

\[ + \frac{\sigma^2(C)}{(BC)^2} \]  

(19)

in which \( \sigma^2(A) \) and \( \sigma^2(C) \) are the variances of the atomic coordinates of atoms A and C in the plane of ABC and in directions at right angles to AB and BC respectively, and \( \sigma^2(B) \) is the variance in the coordinates of B in the direction towards the center of a circle passing through A, B, and C. In practice, the atomic variances appeared to be isotropic for the structure described here and the variances and standard deviations of the angles were calculated. The As-As-As angles have a standard deviation of about 20' and the C-As-As angles of about 2°.

It is possible by use of statistical significance tests to compare two experimentally determined bond lengths and to say whether or not they are significantly different. If a normal distribution is assumed for the experimental errors, the probability that the difference in bond lengths observed occurs when the bonds are actually equal can be calculated. If this probability is small, it is said that the bonds are significantly different. Certain arbitrary limits for this probability must be set up if a judgment is to be made. The following significance levels are commonly used in statistical practice (eg. Kendall (17)).
If $P$ is the probability that a certain difference can be found experimentally for two equal bond lengths, the significance levels are:

- $P > .05$ not significant
- $.05 > P \geq .01$ possibly significant
- $.01 > P \geq .001$ significant
- $.001 > P$ highly significant.

For the present structure the bond length differences fall in the following classes determined by the above significance levels.

<table>
<thead>
<tr>
<th></th>
<th>As-As</th>
<th>As-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not significant</td>
<td>$\delta l &lt; .015\AA$</td>
<td>$\delta l &lt; .11\AA$</td>
</tr>
<tr>
<td>Possibly significant</td>
<td>$.020\AA &gt; \delta l \geq .015\AA$</td>
<td>$.15\AA &gt; \delta l \geq .11\AA$</td>
</tr>
<tr>
<td>Significant</td>
<td>$.025\AA &gt; \delta l \geq .020\AA$</td>
<td>$.19\AA &gt; \delta l \geq .15\AA$</td>
</tr>
<tr>
<td>Highly significant</td>
<td>$\delta l \geq .025\AA$</td>
<td>$\delta l \geq .19\AA$</td>
</tr>
</tbody>
</table>

The As-As bond lengths are found to fall into two groups whose averages differ significantly from each other. Bonds 1-2 and 3-4 comprise one group, and bonds 2-3, 4-5, and 5-1 form the other group. The extremes of the two groups do overlap in that bonds 2-3 and 3-4 are not significantly different from each other, and bonds 3-4 and 5-1 differ only by a possibly significant amount. Since the carbon parameters are not so well known as those for arsenic, none of the As-C bonds can be said to differ significantly.

The same significance tests were applied to the bond angles. The three classes of As-As-As bond angles mentioned
previously differ by highly significant amounts, but none of the differences in the C-As-As bond angles are significant except for the one large angle of 102° 29'. It differs from five of the other C-As-As angles with varying levels of significance and is not significantly different from the other four C-As-As angles.

The significant differences in the As-As-As angles are to be expected because even in a free molecule, assuming it has equal bond lengths, the angles cannot be all equal unless the pentagon is planar with 108° angles. This value is too far from the usual bonding angle of arsenic (e.g. crystalline arsenic, reference 7) which is 97° and as a consequence the ring is puckered. At least one bond angle is strained but more likely the strain is distributed over all angles. Indeed the electron diffraction results(1) indicate that the free molecule continually changes from one configuration to another, so that there must be many arrangements having similar energy which the molecule can assume. The precise values of the bond lengths and angles are doubtlessly imposed upon the molecule by packing requirements and represent a balance between energy gained through efficient packing and energy lost by deformation of the molecule necessary to gain packing efficiency. It is of interest to note that distribution of the strain through the five-ring is not only achieved by variation
in bond angles but by small variations in the bond lengths as well.

Finally, the packing of the molecules in the crystal was considered by building a model, from which all non-bonded interactions could be ascertained; and their interaction distances were calculated. The values and the distribution of the contacts among the atoms are found in Table IV. The arsenic atoms in one molecule all have approximately the same number of contacts with other atoms within the range considered. This is not true of the carbon atoms, although they have more interactions than the arsenic atoms. The packing seems to be efficient as there are numerous contacts between atoms and no large holes in the structure can be found.

The final structure was examined with a hope of finding a mechanism by which the transformation from yellow to red arsenomethane occurs. It is thought that perhaps some As-As bonds are broken and new ones formed to give a different structure. One feature of the structure tending to support this idea is that different molecules have some of their arsenic atoms in close contact. Atom 4 of one molecule and atom 5 of the symmetry-related molecule are at 3.95Å from each other, while atom 5 of one molecule is 3.90Å distant from the symmetry-related atom of the same number. The next nearest interaction between two arsenic
Table IV
Non-bonded Interactions

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>With As at:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.90Å</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>3.95</td>
<td>x  x</td>
<td>x</td>
</tr>
<tr>
<td>4.00</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>4.05</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.10</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.15</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.20</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.25</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.30</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.35</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.40</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.45</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>4.50</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

| With C at: |     |    |   |   |   |   |   |   |   |   |
| 3.65   | x  |    |   |   |   |   |   |   |   |   |
| 3.90   | x  x| x  |   |   |   |   |   |   |   |   |
| 3.95   | x  x| x  | xx | x  |   |   |   |   |   |   |
| 4.00   | x  x| x  | xx | x  |   |   |   |   |   |   |
| 4.05   | x  x| x  | xx | x  | xx |   |   |   |   |   |
| 4.10   | x  x| x  | xx | x  | xx | x  |   |   |   |   |
| 4.15   | x  x| x  | xx | x  | xx | x  | x  |   |   |   |
| 4.20   | x  |    | x  |   |   |   |   |   |   |   |
| 4.25   | x  |    | x  |   |   |   |   |   |   |   |
| 4.30   | x  |    |   |   |   |   |   |   |   |   |
| 4.35   | x  |    |   |   |   |   |   |   |   |   |
| 4.40   | x  |    |   |   |   |   |   |   |   |   |
| 4.45   | x  |    |   |   |   |   |   |   |   |   |
| 4.50   | x  |    |   |   |   |   |   |   |   |   |

Total | 5   | 4  | 3 | 4 | 5 | 9 | 11 | 6 | 9 | 5 |

Atoms of different molecules is at 4.2 Å, the distance from As₁ to As₂, and the other As-As interactions are larger. Since two molecules each have two adjacent atoms in close contact with each other, it is possible that the 4-5 bond in each molecule breaks and two new bonds are formed.
between atoms 4 and 5 of different molecules. One dis-
advantage to this mechanism is that the arsenic atoms
concerned are not in favorable positions for the forma-
tion of As-As bonds of the type mentioned while keeping
their normal bond angles. Other possibilities such as
the formation of a bond between two number 5 arsenic
atoms, the number 4 atoms being bonded to two different
molecules, may be found with suitable angles for bonding;
but the As-As interactions other than between the number
5 atoms are not nearly as close as those discussed.
REFERENCES