excess allyl bromide and solvent removed from the filtrate by distillation in vacuum, the residue taken up in ether, and 4 volumes of petroleum ether added. This left a crystalline residue of 7 g. of unchanged 5-isopropyl-2-methylthiobarbituric acid. The petroleum ether solution on concentrating to one-third of its volume and standing in the ice-box gave a white crystalline precipitate which on crystallization from dioxane and recrystallization from isopropyl alcohol amounted to 10.5 g.; yield 43%.

**5,5-Ethylisopropyl-2-methylthiobarbituric Acid.**—This was prepared in the same manner as the above.

*Anal.*[7] Combined alkylimide and S-alkyl determination[5]: 3.956 mg. of substance distilled to 140°; 5.75 cc. of 0.02 *N* $Na_2S_2O_3$. Found: $S(CH_3)$, 7.28; calcd. $S(CH_3)$, 6.94. 5.112 mg. of substance twice distilled to 360°: 7.83 cc. of 0.02 *N* $Na_2S_2O_3$. Found: $S(CH_3)$, 7.67.

## Summary

1. 5-Alkyl-2-alkylthiobarbituric acids have been prepared by the alkylation of 5-alkyl-2-thiobarbituric acid.

2. 5,5-Dialkyl-2-alkylthiobarbituric acids have been prepared by the alkylation of 5-alkyl-2-alkylthiobarbituric acids.

3. The 5-alkyl-2-alkylthio- and the 5,5-dialkyl-2-alkylthiobarbituric acids prepared are shown to have no promise of value as hypnotics.

NUTLEY, NEW JERSEY RECEIVED JANUARY 17, 1938

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[7] Performed by Mr. J. F. Alicino, Chemistry Department, Fordham University.

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[CONTRIBUTION FROM GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 640]

# The Molecular Structures of the Methyl Derivatives of Phosphorus and Arsenic

BY H. D. SPRINGALL[1] AND L. O. BROCKWAY

The electron diffraction investigation of the fluorides and chlorides of silicon, germanium, tin, phosphorus and arsenic,[2] and some fluorine derivatives of carbon, shows bond distances shorter than those calculated by the addition of the corresponding covalent radii.[3] It was suggested that two effects might be responsible for this shortening: (a) an extra ionic character of the bonds which is not present in the compounds from which the table of radii was constructed; and (b) the contribution of some double bond character due to resonance of the molecule among several structures some of which have one or more double bonds. Since structures with double bonds are not possible in the methyl compounds of the elements concerned, a study of these methyl compounds was proposed as a means of distinguishing between the two effects and of testing the covalent radii. Brockway and Jenkins[4] investigated the tetramethyl compounds of silicon, germanium, tin and lead, trimethyl nitrogen, and the dimethyl compounds of sulfur and mercury. This work has now been extended by the investigation of trimethylphosphine and trimethylarsine.

The apparatus for obtaining the photographs and the method of interpreting the results are those described by Brockway.[5] Both compounds were photographed with electrons having wave length 0.0613 Å. and with a camera distance of 10.87 cm.

**Trimethylphosphine.**—This substance was prepared in collaboration with Dr. D. Purdie in Stanford University, by the Grignard reaction ($CH_3MgI$ on $PCl_3$) based on the method of Hibbert,[6] using the stable $[AgIP(CH_3)_3]_4$ complex,[7] for separation and transportation. On heating *in vacuo*, the complex dissociated, and the trimethylphosphine distilling off was condensed at liquid air temperature.

Theoretical intensity curves were calculated for pyramidal models having the phosphorus atom at the apex, and with C–P–C angles of 104, 100 and 96°.

For the 100° model two curves were calculated. One, A, included all interatomic distance terms except the H–H ones. In this the values for the non-bonded C–H distances were calculated by ignoring the free rotation of the methyl groups and treating one "fixed" model in which one of the H atoms of each methyl group is located in that one of the three planes of symmetry of the

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[1] Commonwealth Fund Fellow.

[2] L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934); L. O. Brockway, *ibid.*, **57**, 958 (1935).

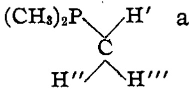
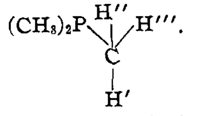
[3] (a) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); (b) N. V. Sidgwick and E. J. Bowen, *Ann. Rep. Chem. Soc.*, **28**, 384 (1931); (c) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[4] L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936).

[5] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

[6] H. Hibbert, *Ber.*, **39**, 161 (1906).

[7] F. G. Mann, A. F. Wells and D. Purdie, *J. Chem. Soc.*, 1828 (1937), and unpublished communications.

molecule, which passes through the carbon atom of that methyl group. (There are two positions in which the given methyl group can satisfy this condition, the characteristic hydrogen atom H′ can be oriented as in (a)  $(\mathrm{CH_3})_2\mathrm{P{-}C(H')(H'')(H''')}$ and as in (b)  $(\mathrm{CH_3})_2\mathrm{P{-}C(H'')(H''')(H')}$. The "a" position was that used in the calculations.) The other, B, neglected both H–H and non-bonded C–H terms. Comparison of these two curves (A) and (B) showed such slight differences that in the 104 and 96° models, (C) and (D), only the simpler curves, corresponding to (B), were calculated.

The P–C distance assumed for all models was 1.87 Å.

The theoretical intensity curve for each assumed model was calculated by use of the formula

$$I = \sum_{ij} Z_i Z_j \frac{\sin sr_{ij}}{sr_{ij}}$$

in which, $r_{ij}$ is the distance between the $i^{\text{th}}$ and $j^{\text{th}}$ atoms; $Z_i$, $Z_j$ their atomic numbers; and $s$ a function of the scattering angle, $\Theta$, and the wave length of the electrons, $\lambda$

$$s = 4\pi \sin \frac{\Theta}{2}\Big/\lambda$$

The summation extends over all the atoms in the molecule.

The curves obtained from the four models are plotted in Fig. 1.

The photographs show the general features of the theoretical curves. The positions of the maxima and minima which were measured are marked on the theoretical curves by vertical lines.

The broad first maximum of the theoretical curves is resolved in the photographs to an apparent double peak. The third observed minimum is displaced in the direction of larger diameters. These first two maxima and the first three minima were not used in attempting to discriminate between the theoretial curves. The maxima were used in the calculation of the radial distribution function.

With the third and fourth observed maxima and the fourth minimum the 100° curves A and B give almost exact correspondence.

The fifth minimum and the fifth maximum are displaced in the direction of larger diameters for all the curves. The 96° curve gives the best agreement for these two characteristics, as it also does with the shallow and ill-defined sixth minimum.

The sixth maximum is displaced toward smaller diameters, very slightly with the 100° model and considerably with the 96° one. In this case alone the 104° model gives the best agreement.

In general, the 100° model gives good agreement over the earlier rings and fair agreement over all rings, the 96° model gives fair agreement over the earlier rings and good agreement with the later ones, and the 104° model gives fair agreement in the inner rings and poor agreement in the outer ones (with the exception of the last).

It would appear that the relatively greater importance of the P–C term over the C–C term causes the theoretical curves to be rather insensitive to changes in the latter term. Thus it is not advisable to decide on the value of the C–P–C angle from this evidence alone.

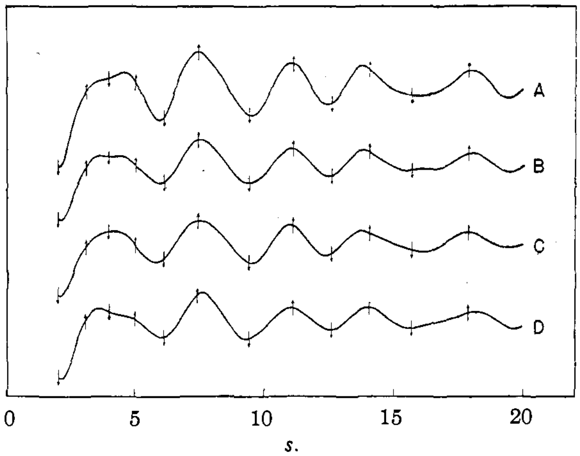


Fig. 1.—Theoretical electron diffraction curves for $P(CH_3)_3$. The observed positions of maxima and minima are marked by vertical lines.

The results are tabulated in the usual fashion in Table I in which the P–C bond length values derived from each of the observed maxima and minima are calculated by the relation

$$(\mathrm{P{-}C})_{\text{obsd.}} = 1.87 \frac{s_{\text{calcd.}}}{s_{\text{obsd.}}}$$

The calculation is carried out only for the series of $s_{\text{calcd.}}$ values derived from the theoretical curve B (C–P–C angle = 100°), since it is apparent that the values from the other curves will differ very little from these values.

The column of $C$ values represents the

TABLE I

| Max. | Min. | $C$ | $s_{\text{obsd.}}$ | $s_{\text{calcd.}}$ P–C 1.87 Å. 100°A | 100°B | 96° | 104° | (P–C)$_{\text{obsd.}}$ |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2.03 | ... | 2.10 | 2.10 | 2.10 | |
| 1 | | 1 | 3.11 | ... | ... | ... | ... | |
| | 2 | | 3.99 | ... | ... | ... | ... | |
| 2 | | 1 | 5.07 | ... | ... | ... | ... | |
| | 3 | | 6.14 | 5.90 | 5.95 | 6.00 | 5.80 | (1.81 Å.) |
| 3 | | 6 | 7.42 | 7.39 | 7.55 | 7.61 | 7.52 | 1.90 |
| | 4 | | 9.46 | 9.50 | 9.42 | 9.25 | 9.55 | 1.86 |
| 4 | | 6 | 11.13 | 11.12 | 11.12 | 11.10 | 11.05 | 1.87 |
| | 5 | | 12.61 | 12.42 | 12.45 | 12.52 | 12.32 | 1.84 |
| 5 | | 4 | 14.06 | 13.75 | 13.84 | 13.99 | 13.70 | 1.84 |
| | 6 | | 15.70 | 16.10 | 15.50 | 15.50 | 16.30 | 1.85 |
| 6 | | 2 | 17.87 | 18.00 | 18.05 | 18.15 | 17.90 | 1.89 |
| | | | | | | | Average | 1.86 |

weighted intensity terms used in the calculation of the radial distribution function.

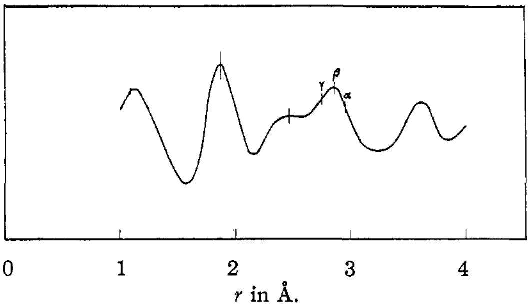


Fig. 2.—Radial distribution function for $P(CH_3)_3$. In each case the maximum corresponding to a given bond distance is marked by a vertical line at the value for this distance, as determined by the method of comparison of actual and theoretical intensity curves. The length of the line corresponds to the contribution of the distance to the intensity of scattering.

The radial distribution function,[8] Fig. 2, was calculated from the six term expression involving the $s$ values corresponding to the six observed maxima, and the estimated intensities of those maxima, by use of the formula

$$D(r) = \sum\nolimits_k I_k \frac{\sin s_k r}{s_k r}$$

The relative intensities, $I_k$, were not used directly but were made the basis for the calculation of the "weighted" intensities, $C$, according to the method suggested by Schomaker. $I$ and $C$ are connected by the relation

$$C_k = I_k s_k^2 e^{-as_k^2}$$

with $a$ so chosen that $C_n = (1/n)C_1$ for a photograph showing $n$ rings.

The curve shows five significant maxima, at 1.12, 1.87, 2.48, 2.85 and 3.63 Å.

Of these indicated distances, the first, 1.12 Å., corresponds to the C–H distance, 1.09 Å. High values of this type are found frequently in radial distribution treatments in regions of small interatomic distances.

The second, third and fourth distances are in the region of highest accuracy and are of great interest to the problem. They correspond, respectively, (a) to the P–C distance, thus the postulated value of 1.87 Å. is confirmed; (b) to the non-bonded P–H distance for which a value of 2.46 Å. is calculated from the models; (c) to the non-bonded C–C distance. The value 2.85 Å. is of importance in settling more accurately the C–P–C angle. The non-bonded C–C distances expected from the various models are for 104°, 2.95 Å.; for 100°, 2.86 Å.; for 96°, 2.78 Å.; ($\alpha$, $\beta$ and $\gamma$, respectively, in Fig. 2). The value indicated for the C–P–C angle by the radial distribution function is, clearly, close to 100°.

The fifth peak corresponds to the mean value of the non-bonded C–H distance. The models indicate that this should lie in the range 2.7 to 3.9 Å.

Final values for the dimensions of the molecule: P–C = 1.87 ± 0.02 Å.; angle C–P–C = 100 ± 4°.

**Trimethylarsine.**—This substance, also, was prepared in collaboration with Dr. D. Purdie, by a method exactly analogous to that used for the phosphine.

Four theoretical intensity curves, analogous to those for trimethylphosphine, were calculated from the pyramidal models having the same angular arrangements as the trimethylphosphine models. The As–C distance 1.98 Å. was assumed for all the models. The curves (A) for the 100° model (only H–H terms neglected) and (B) for the 96° model (H–H and non-bonded C–H neglected) are plotted in Fig. 3.

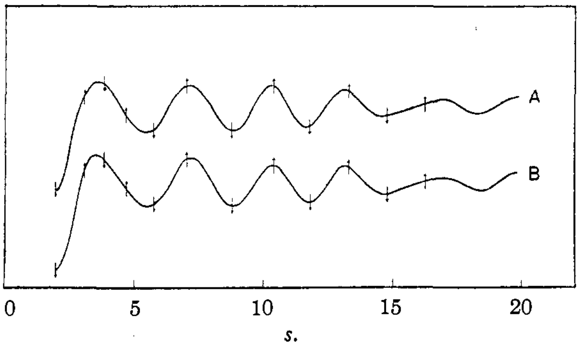


Fig. 3.—Theoretical electron diffraction curves for $As(CH_3)_3$. The observed positions of maxima and minima are marked by vertical lines.

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[8] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

Except in the region of the first theoretical maximum, the photographs show the general features of the theoretical curves, and are everywhere very similar to the trimethylphosphine photographs. The first theoretical maximum is clearly resolved in the photographs into two apparent peaks, just as it is in the trimethylphosphine photographs. In view of this it was expected that the trimethylarsine theoretical curves would show a very broad first maximum, as do the trimethylphosphine curves. The first two peaks were used only in the calculation of the radial distribution function.

Over all the maxima and minima, the correspondence between the observed and calculated $s$ values shows a close similarity to the trimethylphosphine case. Measurements on the sixth ring could be made on only one photograph, and are probably somewhat inaccurate. In the outer, somewhat diffuse, rings the 96° model seems slightly preferable to the 100° one. The final decision is made on the basis of the non-bonded C–C distance obtained from the radial distribution function. The results of the comparison of the theoretical curves with the photographs are given in Table II, in which the $s_{\text{calcd.}}$ values are those for the 96° model.

TABLE II

| Max. | Min. | $C$ | $s_{\text{obsd.}}$ | $s_{\text{calcd.}}$, As–C = 1.98 Å., 96° | (As–C)$_{\text{obsd.}}$, Å. |
|---|---|---|---|---|---|
| | 1 | | ... | ... | |
| 1 | | 1 | 3.11 | ... | |
| | 2 | | 3.93 | ... | |
| 2 | | 1 | 4.76 | ... | |
| | 3 | | 5.82 | 5.55 | (1.89) |
| 3 | | 6 | 7.09 | 7.22 | 2.02 |
| | 4 | | 8.84 | 8.90 | 2.00 |
| 4 | | 6 | 10.49 | 10.39 | 1.96 |
| | 5 | | 11.90 | 11.75 | 1.96 |
| 5 | | 4 | 13.40 | 13.25 | 1.96 |
| | 6 | | 14.91 | 14.72 | 1.96 |
| 6 | | 2 | 16.32 | 17.00 | (2.06) |
| | | | | | Average 1.98 |

The radial distribution curve, Fig. 4, was calculated for the six term expression analogous to that used for the trimethylphosphine.

The curve shows general features closely corresponding to the trimethylphosphine curve, with five significant peaks at 1.20, 1.98, 2.53, 2.93 and 3.83 Å. Of these the first is a high value corresponding to the C–H, 1.09 Å. distance. The next three, in the most accurate range of the curve, correspond, respectively, (a) to the As–C distance (exact agreement with the assumed value), (b) to the non-bonded As–H distance (2.56 Å. from models), (c) to the non-bonded C–C distance. This last distance is that determining the C–As–C angle. The values expected from the various models are, for 104°, 3.08 Å.; for 100°, 3.03 Å.; for 96°, 2.94 Å.; ($\alpha$, $\beta$ and $\gamma$, respectively, in Fig. 4). The close agreement between the last of these values and the observed one indicates that the angle must lie very close to 96°. The fifth corresponds to the mean non-bonded C–H distance for which a range 2.8 to 4.2 Å. is predicted from the models.

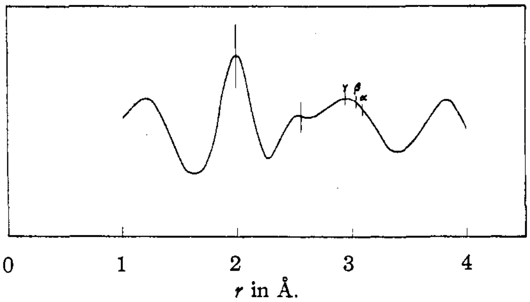

Fig. 4.—Radial distribution function for As(CH$_3$)$_3$. The maxima are marked analogously to those in Fig. 2.

Final values for the dimensions of the molecule: As–C = 1.98 ± 0.02 Å.; angle C–As–C = 96 ± 5°.

## Discussion

The results obtained from these phosphorus and arsenic methyl compounds are an extension of those obtained by Brockway and Jenkins[4] for the methyl compounds of silicon, germanium, tin and sulfur.

The bond distances found for P–C, 1.87 Å., and for As–C, 1.98 Å., are exactly those predicted from the table of covalent radii proposed by Pauling and Huggins,[3c] indicating that with phosphorus and arsenic, also, with respect to factors affecting the interatomic distance, the bond type is the same in the methyl compounds as that in the elements, where the bonds are formed between atoms of the same element. These results strengthen the basis on which the bond shortening found in the chlorides of silicon, germanium, tin, phosphorus and arsenic has been discussed,[2,4,9,10] since it is now established, where

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[9] L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937); *ibid.*, **41**, 747 (1937).

[10] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

before it was only probable, that phosphorus and arsenic fit into the scheme of discussion given for silicon, germanium, and tin, all the elements showing the anticipated additivity of covalent radii when bonded to carbon, but exhibiting a characteristic shortening of radius when bonded to fluorine and chlorine. Brockway and Wall,[2] Brockway and Jenkins,[4] and Brockway[9] discussed this shortening in terms of double bond character pointing out that it is not due to the relative electronegativities or to the existence of dipole moments in the bonds, and eliminating the possibility that it is due to ionic character of the bonds. Gregg, Hampson, G. I. Jenkins, Jones and Sutton,[10] however, from a consideration of (a) series of halides of the same element and (b) series of compounds of the same halogen with different elements, point out that the case may be more complex.

We wish to express our gratitude to Professor L. Pauling for the interest which he has taken in this work, and to Dr. S. Weinbaum for assistance with the calculations.

## Summary

By electron diffraction investigation of the gases, the structures of trimethylphosphine and trimethylarsine have been determined. The molecules are pyramidal with the phosphorus and arsenic atoms at the respective apices.

Trimethylphosphine has a bond angle of 100 ± 4° with the P–C bond = 1.87 ± 0.02 Å.; trimethylarsine has a bond angle of 96 ± 5° with the As–C bond = 1.98 ± 0.02 Å. These distances agree with the sums of the covalent radii given by Pauling and Huggins. From these results a firmer basis is obtained for the discussion of the bond shortening in the corresponding chlorides.

Pasadena, Calif. Received January 25, 1938

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[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 395]

# A Low Temperature Calorimeter. The Heat Capacity and Entropy of Thallium from 14 to 300°K. Low Temperature Studies. No. 3

By J. F. G. Hicks, Jr.[1]

A portion of the low temperature program in progress in this Laboratory has been devoted to the measurement of specific heats. This present paper is the first in this series of investigations.

The heat capacity of thallium has been measured by several previous investigators[2] and of this work the data of Clusius and Vaughen are the most complete. However, their method of measurement was not particularly well adapted to precision work above 150°K., and therefore in this region they report only three points. Although the change in heat capacity with temperature from 150 to 300°K. is small, the heat capacity is large and variations of 2% produce a significant effect upon the entropy at 298°K.

The calculations of Latimer, Schutz and Hicks[3] of the entropy of aqueous thallous ion indicated that the thermochemical data on thallium and its compounds were of unusual self-consistency. However, the entropy of thallous ion depended much upon the entropy of metallic thallium. Since that time a revised value of the entropy of thallous ion[4] derived from more recent heat of solution and e. m. f. data has appeared. The entropy of thallium as redetermined in the present work has been lowered by only 1%, which lowering does not produce a change larger than experimental error in the new value for thallous ion. It was felt, however, that the heat capacity data were of sufficient interest to justify presentation of a complete study over the temperature range 14 to 300°K.

**Material.**—The sample of thallium used in these measurements was obtained from the American Smelting and Refining Company, Denver, Colorado, and was not subjected to further purification. It was cast to fit the calorimeter by melting *in vacuo* in an iron mold and stored under water prior to loading. The ingots consisted of large (of millimeter size) crystals.

Qualitative analysis using standard methods failed to disclose the presence of other elements and photographs of the arc spectrum[5] set the upper limit of impurities (including indium and gallium) at one part in 10,000 of thallium.

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(1) National Research Council Fellow in Chemistry, 1933–1935. Paper II, This Journal, **59**, 1962 (1937).

(2) Clusius and Vaughen, *ibid.*, **52**, 4686 (1930); see this paper for references to earlier work.

(3) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

(4) Brown, Smith and Latimer, This Journal, **59**, 921 (1937).

(5) The author is indebted to Mr. P. A. Cole of the M. I. T. Physics Department for the spectroscopic examination.