lanthanides from Dowex-50 resin columns indicate a discontinuity (with atomic number) between gadolinium and terbium with eluting agents such as ammonium lactate.[5] This, of course, could be a result of complex-ion formation rather than sorption on the resin.

There is one objection in the method used here for the evaluation of ΔS°. In deriving equation 9, one of the implied assumptions was that a reference state was chosen in which all M(III) ions would have the same thermodynamic activity, *i.e.*, a resin phase which is essentially all in the hydrogen form. This means that the resin phase activity coefficients are identical for different M(III) ions. The resin phase may be thought of as a concentrated ionic solution having an ionic strength of approximately 2.5. (The hydrogen form resin has a capacity of 5 equivalents per 1000 g. of dry resin, and water absorption increases the volume by a factor of two.) It could hardly be expected that the M(III) ions would all have the same activity coefficients. It is possible to make a crude guess as to how much difference there would be in the activity coefficients. The activity coefficients of aqueous $NdCl_3$ and YCl_3 at an ionic strength of 2.4 are 0.289 and 0.309.[32] Assuming that this ratio is the same as the ratio of resin phase activity coefficients, and that the activity coefficient of neodymium is the same as those of americium and promethium and that of yttrium is the same as those of thulium and lutetium, a difference in ΔF°_{298} of 0.043 kcal. could be expected. This amounts to an error of 2% in the relative value of ΔF°, which would also appear in ΔS° but not in ΔH°.

It is fortuitous that the $\Delta S^{\circ\prime}$'s of americium, promethium, thulium and lutetium are the same within experimental error at 25°. At 0° the difference in $\Delta S^{\circ\prime}$'s of americium and promethium from those of thulium and lutetium amounts to 1 e.u. This is a consequence of the apparently different ΔC_p's. While these data are not extensive enough or precise enough to say that this is a real effect, it is certainly a strong indication, especially since the ΔC_p's of both americium and promethium are approximately 55 while both lutetium and thulium are approximately 44. This might be interpreted as evidence that a different amount of coördinated water is lost on sorption of the heavy lanthanides with respect to the amount lost by the light lanthanides.

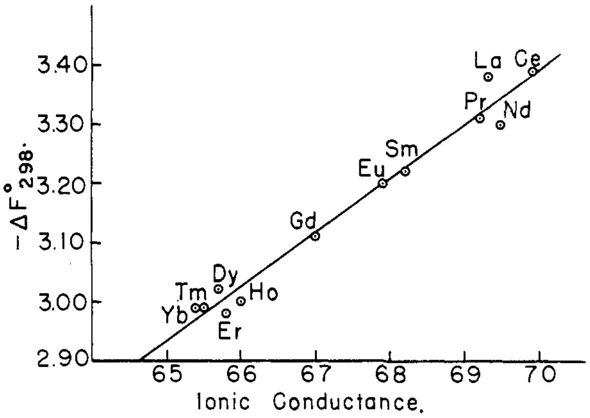

Fig. 2.—Free energy of formation of metal resinate *vs.* ionic conductance at infinite dilution for some lanthanides.

Acknowledgments.—The authors are indebted to Drs. B. B. Cunningham, R. E. Connick and B. G. Harvey for helpful discussions and suggestions. The continued interest of Dr. Glenn T. Seaborg is gratefully acknowledged. Many of the radiometric assays were made by Mrs. Roberta Garrett.

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(32) C. M. Mason, THIS JOURNAL, **63**, 220 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Crystal Structure of Arsenomethane

BY JOHN H. BURNS AND JÜRG WASER

RECEIVED MAY 7, 1956

The yellow form of arsenomethane crystallizes with a monoclinic unit cell of dimensions a = 8.89 Å., b = 12.54 Å., c = 11.55 A., and β = 101°46′. The space group is $C^5_{2h} - P2_1/n$. The arsenic atoms of one molecule are joined in a puckered, five-membered ring; to each arsenic atom is bonded one methyl group. The As–As bond distances vary from 2.42 to 2.44 Å. with an average of 2.428 Å.; the average value of the As–C bond length is 1.95 Å. The As–As–As bond angles have values from 97$^1/_2$° to 105$^1/_2$°, while the average of the C–As–As bond angles is about 97°.

Arsenomethane exists in two forms at room temperature: a yellow oil (m.p. 12°) and a red solid. Both forms were investigated by Waser and Schomaker[1] who used vapor density measurements and electron diffraction of the vapor to study the oil and X-ray powder pictures to investigate the solid. A conclusive structure for the molecule was not obtained, although a puckered five-membered ring of As atoms with an As–As–As bond angle of about 90° appeared to explain their data for the yellow form in a natural way.

In this paper will be described a low temperature, single crystal, X-ray diffraction study of the yellow modification by which its crystal structure was determined.

Experimental Procedure

The yellow form of arsenomethane was obtained by reducing sodium methyl arsonate with hypophosphorous acid. Single crystals were grown and maintained in Pyrex capillaries by cooling with a stream of cold air. Both precession and Weissenberg cameras were employed, the latter being modified in a fashion similar to that described by Collin and Lipscomb[2] to accommodate the cooling apparatus.

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(1) J. Waser and V. Schomaker, THIS JOURNAL, **67**, 2014 (1945).

(2) R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 10 (1951).

The unit cell was found to be monoclinic and the systematic absences indicated the probable space group $C^5_{2h} - P2_1/n$. The monoclinic angle was measured on $h0l$ precession photographs while the lengths of the axes were determined on Weissenberg pictures calibrated for film shrinkage by superimposed diamond powder lines. The best values for a, b and c were obtained by extrapolation of the axial spacings along each of the three directions as suggested by Nelson and Riley.[3] The lattice constants are as follows: $a = 8.89$ Å., $b = 12.54$ Å., $c = 11.55$ Å.; $\beta = 101°46'$.

The Weissenberg instrument was employed to record intensities of seven levels of (001) and five levels each of (100) and (101) using Cu K radiation. The intensities were estimated by comparison with a prepared scale. The different values of the intensity of each reflection as found on 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 the way described by Bullen.[4] An average value for each reflection was found, Lorentz-polarization[5] and absorption[6] factors were applied, and data from various levels were brought to the same relative scale. Of the 2769 reflections accessible with Cu K radiation and not related by symmetry, 432 were not photographed, and of the others 1154 were of observable intensity.

The density of the frozen compound was measured to be 2.3 g./cm.^{3}, corresponding to twenty $AsCH_3$ groups per unit cell (calcd. density of 2.36 g./cm.^{3}). Since the space group has fourfold general positions it seemed reasonable to expect four five-membered rings of $AsCH_3$ groups per unit cell. This was found to be the case as will be described.

Determination of Structure.—Since the methods of inequalities and Patterson projections applied to two zones did not yield a trial structure two sections of the three-dimensional Patterson function were computed. The section at $y = {}^1/_2$ (Fig. 1) contains, among others, Harker maxima at $(2x, 2z)$, where (x, z) are atomic coördinates. Once the Harker peaks were recognized, it was possible to see that the As form a five-membered ring (dotted line) and to measure tentative x and z coördinates. (Three obvious non-Harker peaks of about twice the height of the Harker peaks and lying halfway between them, indicate that the three As involved have about the same y coördinates.) With these tentative coördinates phases were calculated and an $h0l$ Fourier projection made (Fig. 2).

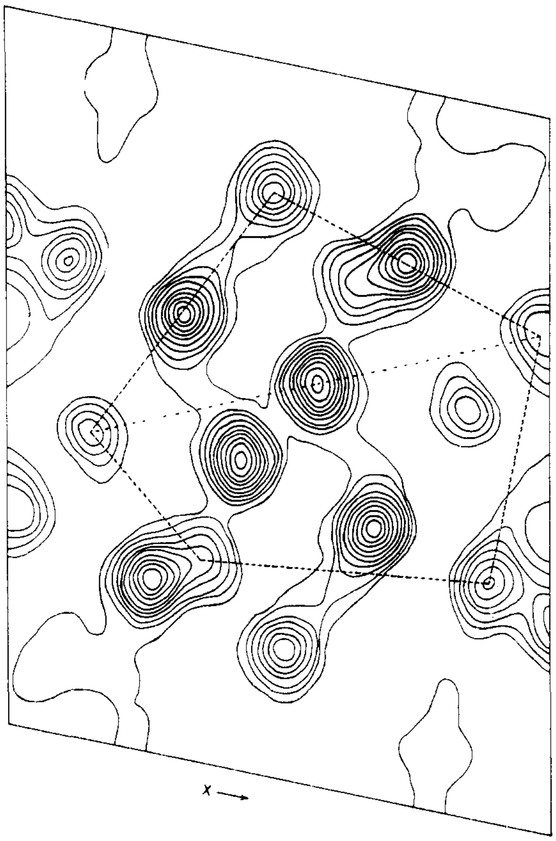

Fig. 1.—Harker section $P(x, {}^1/_2, z)$.

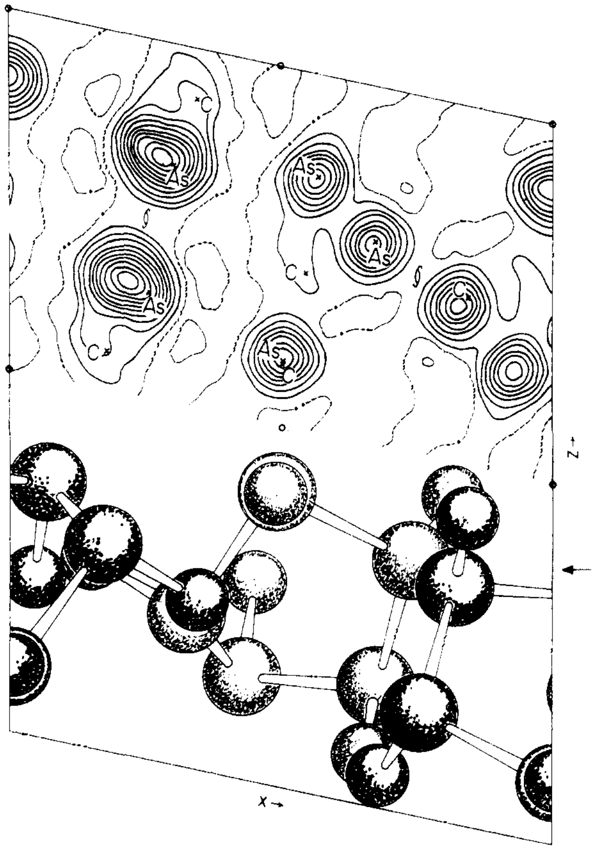

Fig. 2.—Fourier projection $\rho(x,z)$. Crosses indicate final atomic positions. Lowest contour line at -1.37 e/Å.^{2}, all other contours at intervals of 4.75e/Å.^{2}.

Comparison of the x-coördinates of all As in the unit cell indicated the existence of interatomic vectors with an x component close to ${}^1/_2$. Indeed, a Patterson section $P({}^1/_2, y, z)$ (including the Harker line $({}^1/_2, y, {}^1/_2)$) yielded approximate y-coördinates for all five independent As. Fourier projections were made along c (Fig. 3) and a (poorly resolved), and improved values for all As coördinates were obtained.

The methyl peaks in the projections are relatively small and are consequently obscured by diffraction ripples associated with the much larger As peaks and due to the finite termination of the Fourier series. Trial parameters for the methyl groups were obtained by difference Fourier projections combined with consideration of the packing of molecules. The contribution of the As atoms was

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[3] J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. London*, **57**, 160 (1945).

[4] G. J. Bullen, *Acta Cryst.*, **6**, 825 (1953).

[5] C. S. Lu, *Rev. Sci. Instr.*, **14**, 331 (1943).

[6] "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Borntraeger, Berlin, 1935.

subtracted from the observed structure factors and difference Fourier projections made along axial directions. Among the maxima appearing were some due to methyl groups and others indicative of errors in the As positions causing these atoms to be incompletely subtracted out. To decide which peaks corresponded to methyl groups, it was necessary to consider the geometrically allowed alternatives based on the following assumptions. The average value for the arsenic bonding angle is about 100°[7] and the C–As–As angles were given this value while the C–As distance was taken as 1.98 Å.[7] The van der Waals radii of the methyl group and of As are each 2.0 Å.[7] allowing no intermolecular interaction of much less than 4.0 Å. Because of uncertainties in the model chosen this limit was replaced by the less stringent one of 3.0 Å. It was possible to fit the resulting geometrically possible locations to peaks of the difference Fourier projections, although not all such peaks could be explained by C positions or obvious As shifts. Nevertheless, the subsequent convergence of the refinement process and the reasonable values of all final individual atomic temperature factors indicate strongly that a proper choice of all trial coördinates was made.

Refinement of Parameters.—The parameters were refined by the method of least squares, first applied to crystal structure determination by Hughes.[8] Besides three spatial coördinates an additional parameter was used for each atom to describe its temperature factor, assumed to be isotropic. This brings the total number of parameters to forty. 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[10] diminished by 1.74 to correct for anomalous dispersion.[11] For carbon, the scattering factors of McWeeny[12] were used. The hydrogen atoms were omitted from the structure factor calculations because their relative contribution to the scattering is small.

The atomic coördinates from the Fourier projections were used as initial values for the thirty spatial parameters, and the initial values of the ten parameters Q_i, contained in the temperature factors $\exp(-Q_i \sin^2\vartheta)$ were set equal to an average value of 2.8. This number was obtained from plots *versus* $\sin^2\vartheta$ of the logarithm of the ratio of the observed to calculated structure factors for the three zones.

The observational equations were weighted by the following scheme which is similar to one proposed by Hughes[8]

When $|F_o| > 4F_{\min}$ $w = 1/F_o^2$

When $F_{\min} < |F_o| < 4F_{\min}$ $w = 1/(4F_{\min})^2$

When $F_o = 0$; $|F_c| > F_{\min}$ $w = 1/(4F_{\min})^2$ and F_o is replaced by $F_{\min}$

When $F_o = 0$; $|F_c| < F_{\min}$ $w = 0$

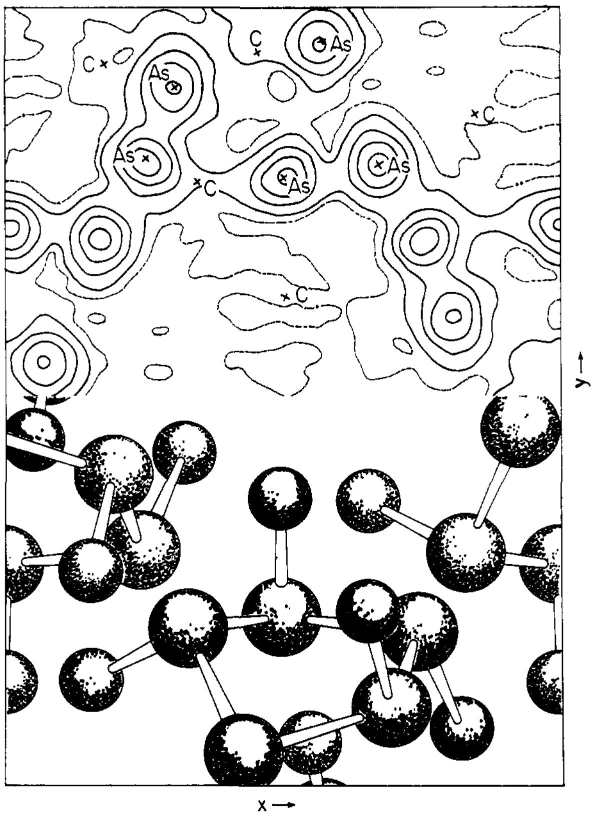

Fig. 3.—Fourier projection $\rho(x,y)$. Crosses indicate final atomic positions. Lowest contour line at $-1.24e/\text{Å}^2$, dashed lines at intervals of $4.39e/\text{Å}^2$, full lines at $8.78e/\text{Å}^2$.

Here F_o and F_c are the observed and computed structure factors for a given reflection and w is the weight of the corresponding equation, while $F_{\min}$ is the magnitude of the smallest observed structure factor. An average value of 8.0 was used for $F_{\min}$, although it actually varies with ϑ.

For the setting up and solving of the normal equations, a digital computer (Datatron, built by the ElectroData Corporation of Pasadena, California) was employed, with Lavine and Rollett's program.[13] With the exception of the cross terms involving the x and z coördinates of the same atom, only the diagonal terms of the matrix of the coefficients of the normal equations are computed. Other elements of the matrix can be shown to be negligible when three-dimensional data are used.

The refinement was carried through four stages. While individual changes in the temperature factors of all atoms were computed routinely, only the averaged changes for all As atoms, and separately for all C atoms, were used for the computation of structure factors and their derivatives. During the refinements the value of the parameter $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|$ decreased from 0.181 for the original parameters to 0.123 while $(\Sigma\, w(|F_o| - |F_c|)^2)/4$ decreased from 46.6 to 19.9. (The final values quoted were actually computed with the parameters resulting from the third cycle which, however, are almost identical with those of the fourth cycle. The temperature parameters used were $Q_{As} = 2.64$, $Q_C = 3.62$.) A table listing all ob-

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[7] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell Univ. Press, Ithaca, N. Y., 1940.

[8] E. W. Hughes, THIS JOURNAL, **63**, 1737 (1941).

[9] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

[10] See ref. 5.

[11] R. W. James, "The Optical Principles of the Diffraction of X-Rays," 2nd Ed., G. Bell and Sons, London, 1954.

[12] R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

[13] L. R. Lavine and J. S. Rollett, *ibid.*, **9**, 269 (1956).

served and computed structure factors has been deposited with the American Documentation Institute.[14]

Table I lists the parameter of all space group independent atoms. Their standard deviations were evaluated by the usual method (see, for example, Cruickshank[15]). The standard deviations of the various parameters are listed along with the parameters in Table I.

Table I

Positional and Temperature Parameters of Space Group Independent Atoms

Atom		Final parameters	σ	Atom		Final parameters	σ
As 1	x	0.3263	0.00039	C 1	x	0.152	0.0042
	y	.2012	.00026		y	.133	.0028
	z	.2154	.00029		z	.265	.0030
	Q	2.576	.0045		Q	2.9	.21
As 2	x	0.4962	.00039	C 2	x	0.496	.0040
	y	.2162	.00026		y	.370	.0029
	z	.4094	.00030		z	.409	.0030
	Q	2.618	.0045		Q	3.5	.21
As 3	x	0.7440	.00039	C 3	x	0.819	.0042
	y	.1977	.00027		y	.073	.0028
	z	.3534	.00030		z	.454	.0031
	Q	2.673	.0044		Q	4.2	.20
As 4	x	0.6928	.00039	C 4	x	0.652	.0042
	y	.1003	.00026		y	.226	.0027
	z	.1677	.00029		z	.069	.0030
	Q	2.773	.0044		Q	4.0	.21
As 5	x	0.4287	.00039	C 5	x	0.454	.0040
	y	.0419	.00027		y	.944	.0028
	z	.1414	.00029		z	.278	.0031
	Q	2.775	.0045		Q	3.4	.21
Av.	Q_{As}	2.683		Av.	Q_C	3.6	

The corresponding bond length and bond angle values for the arsenomethane are listed in Tables II and III. (The contributions to the standard deviations caused by the uncertainty of the unit cell dimensions are negligible.)

Table II

Bond Lengths

	As–As, Å.	σ, Å.		C–As, Å.	σ, Å.
1–2	2.441	0.005	1	1.95	0.05
2–3	2.431	.005	2	1.92	.05
3–4	2.429	.005	3	1.98	.05
4–5	2.419	.005	4	1.93	.05
5–1	2.422	.005	5	1.97	.05
Av.	2.428		Av.	1.95	

Table III

Bond Angles

			C–As–As, degree	σ, degree				As–As–As, degree	σ, degree
1	1	2	98.2	1.8	5	1	2	100.42	0.30
2	2	3	95.6	1.8	1	2	3	99.97	.27
3	3	4	95.8	1.8	2	3	4	105.62	.30
4	4	5	96.4	1.8	3	4	5	105.40	.32
5	5	1	102.8	1.9	4	5	1	97.52	.27
1	1	5	96.9	1.8		Av.		101.79	
2	2	1	94.4	1.7					
3	3	2	97.6	1.8					
4	4	3	95.3	1.8					
5	5	4	98.0	1.8					
	Av.		96.9						

The question arises whether the differences of the determined bond lengths and bond angles correspond to real variations in the actual molecule, or whether the experimental accuracy is insufficient to support claim of reality for the variations. Such questions have been treated statistically by Cruickshank and others[16]; below are listed probabilities P that certain differences δL or $\delta\varphi$ between two experimentally determined distances or angles are caused by experimental errors rather than being real.

P	δL_{As-As}, Å.	δL_{As-C}, Å.	$\delta\varphi_{As-As-As}$, degree	$\delta\varphi_{C-As-As}$, degree
0.05	0.014	0.098	0.83	3.58
.01	.018	.129	1.08	4.70
.001	.023	.165	1.40	6.00

It is clear that at least part of all observed variations are real.

Discussion

The arsenomethane molecule consists of a puckered, five-membered ring of As atoms to each of which is attached a methyl group (Fig. 4). The ring of As atoms has very approximately mirror symmetry, the pseudo mirror plane being approximately perpendicular to the drawing (dashed line). In fact, if As_3 and As_4 were held fixed, a twist of the ring by about 6° would bring As_2 and As_5 into the plane and As quite closely to a position required by symmetry m. A twist of slightly more than 6° in the opposite sense would bring the As five-ring close to symmetry 2, the twofold axis passing through As_3 and midway between As_1 and As_5. The configuration of the As five-ring is thus about mid-way between one of symmetry m and one of symmetry 2.

The variations in the As–As–As angles are closely related to the fact that the only pentagon with all its sides and angles equal is planar with 108° angles and that unsymmetrical distortions are necessary to bring the magnitudes of the angles into the neighborhood of about 100° characteristic for As.[7] One case of such distortions will be described in some detail, that of an equilateral (non-planar) pentagon of As-atoms which has a mirror plane through As_1. Let φ_i be the As–As–As angle at As_i. Choice of a value for $\varphi_3 = \varphi_4$ determines φ_1 by the equation $\sin(\varphi_1/2) = (^1/_2) - \cos\varphi_3$ while $\varphi_2 = \varphi_5$ is left free to assume values in a wide range. Typical pairs for φ_3 and φ_1 are $\varphi_3 = 95°, 100°, 105°$; $\varphi_1 = 71.92°, 84.70°, 98.73°$.

Because of the independence of φ_2 and of φ_5 $(= \varphi_2)$ from the other angles one may be tempted to assume that the average of their observed values,

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(14) Document number 4980, ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting \$2.50 for photoprints, or \$1.75 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(15) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 154 (1949).

(16) See for example D. W. J. Cruickshank and A. P. Robertson, *ibid.*, **6**, 698 (1953).

98.79°, represents the magnitude of the unstrained value of the As–As–As angle. However, the As five-ring does not really have symmetry m, the other three As–As–As angles are observed to be larger than 98.79°, and the unstrained angle should thus be larger also. It may be expected to be close to the average of all five As–As–As angles, 101.79°.

A detailed analysis of distortions of pentagons of symmetry 2 is more complex and leads to the same conclusion. Again the magnitudes of the angles fall into at least two groups which coalesce at 108°.

It appears probable that continuous redistribution over the five angles of the angular strain affects the total amount of such strain very little. This is in accord with the electron diffraction radial distribution curve for the molecule in the vapor phase which indicates that the As five-ring continually changes from one configuration to another.[1]

The average value of the As–As distances is 2.428 Å., close to twice the radius assigned to As by Pauling[7] (2.42 Å.) while the average value of the As–C distances, 1.95 Å., is somewhat smaller than the sum of the covalent radii[7] (1.98 Å.). The observed temperature factors correspond to root mean square displacements of 0.28 Å. for As and of 0.33 Å. for C.

An idea of the order of magnitude of strain energies involved in the ring distortion was obtained by assuming a Hooke-law potential for angular as well as linear distortions, estimating the bond stretching constant to be of the order of 2×10^5 dyne/cm. (Badger's rule[17] yields 1.5×10^5 dyne/cm.) and the bending constant $k/L^2 \approx 0.3 \times 10^5$ dyne/cm. (As Cl_3).[18] This entails about 40 cal./mole for As–As and 2000 cal./mole for As–As–As strain. Assuming the observed variations of the C–As distances and the C–As–As angles to be real and using the same force constants as before, the C–As strain is estimated to be 400 cal./mole, the C–As–As strain 2000 cal./mole. These values are orders of magnitudes only and energies related to rotation about the As–As bond and other interactions between non-bonded atoms may be of importance also.

The closest intermolecular approaches are listed in Table IV. The packing appears to be efficient and no large holes in the structure can be found.

TABLE IV

FREQUENCY OF INTERMOLECULAR DISTANCES

Distance (Å.)	As–As	Frequency As–C	C–C
3.65	..	..	1
3.90	1	..	3
3.95	2	2	4
4.00	..	2	2
4.05	..	..	4
4.10	..	2	6
4.15	1	2	2
4.20	..	1	..
4.25	1	2	2
4.30	2	1	..

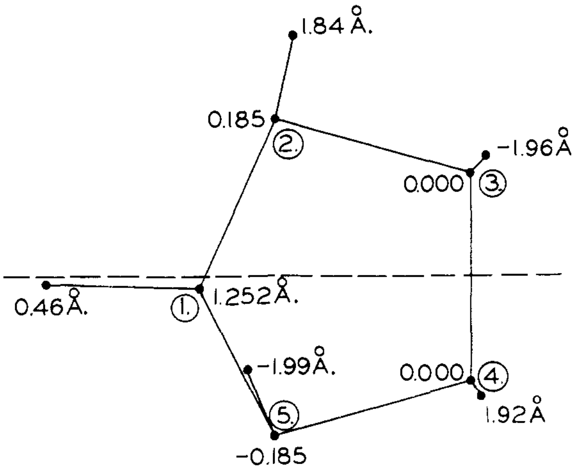

Fig. 4.—Metrical diagram of arsenomethane molecule. The dashed line is midway between As_3 and As_4 and perpendicular to a line connecting them.

Crystals of the yellow modification slowly transform into the dark red solid modification which is microcrystalline and insoluble in the common solvents tried. It can be changed back to the yellow oil by heating to about 200°.[1] A survey of the atomic arrangement in the crystal suggests the following possible mechanism for the solid–solid transformation of yellow form to red form. If the bond between As_3 and As_4 of a given molecule is broken then As_3 may form a bond with an atom As_4' of a molecule related to the first one by a screw axis; this frees atom As_3' of the second molecule to form a bond with atom As_4'' of the next molecule along the screw axis and so on. Similarly, atom As_4 of the molecule considered first is free to form a bond with atom As_3''' of the next molecule along the screw axis in the other direction, and so on. A whole string of molecules related by a screw axis is replaced by this process by a long chain molecule along the same axis. The orientation of the methyl groups and As atoms attached to As_3 and As_4 is favorable to the formation of new bonds (see arrow in Fig. 2 which points to two As atoms of the type discussed). The As atoms forming new bonds have to decrease their mutual distance from 5.1 to 2.4 Å. This is compatible with the *micro*crystallinity of the red form.

Other new bonds which might form in the solid state involve atoms As_4 and As_5 of molecules related by an inversion center, atoms which are in van der Waals contact ($As_4 \ldots As_5' = As_5 \ldots As_4' = 3.95$ Å., $As_5 \ldots As_5' = 3.90$ Å.). If bonds As_4–As_5 and As_4'–As_5' are replaced by bonds As_4–As_5' and As_5–As_4', two As five-rings are transformed into an As ten-ring. The disposition of the methyl groups and As atoms attached to As_4 and As_5 is, however, not very favorable to this interchange of bonds and it is expected that it occurs rarely if at all. It is not unlikely, however, that between two such molecules related by an inversion center, which will be called "unprimed" and "primed," a bond As_5–As_5' may be formed occasionally, bonds

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(17) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

(18) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

As_4–As_5 and As_4'–As_5' being broken. Atom As_4 would then have to be bonded to an atom As_3'' of a molecule related to the unprimed molecule by a screw axis, as described earlier, and similarly As_4' to an atom As_3'''. The unprimed and primed molecules thus would be at the end and beginning of chain segments which are tied together by an As_5–As_5' bond. It is not likely that such interruptions of the chains described earlier occur with the regularity required by the periodicity of a crystal and the formation of bonds As_5–As_5' is thus presumed rare.

While the molecular structure of the yellow form of arsenomethane is that of a puckered substituted five-ring as described in the foregoing, a crystal structure investigation of the related substance arsenobenzene[19] has shown it to consist of hexameric molecules, $As_6(C_6H_5)_6$, the As atoms forming a puckered six-ring of symmetry $\bar{3}$ m and each carrying a phenyl group. No explanation for this difference between the two compounds has been found.

Acknowledgments.—We wish to thank Dr. John S. Rollett for his liberal help in the refinement of the atomic parameters by the Datatron high speed digital computer, and the Robert A. Welch foundation of Houston, Texas, for a grant making the use of this machine possible.

[19] K. Hedberg, E. W. Hughes and J. Waser, reported at the San Francisco, Calif., Meeting of the American Chemical Society, March, 1949.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Solubility of Water in Aromatic Halides[1]

BY JAMES WING[2] AND W. H. JOHNSTON

RECEIVED JUNE 11, 1956

The solubilities of water in benzene, toluene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene and *o*-dichlorobenzene were measured by an isotopic dilution technique using tritiated water as the tracer and counting as acetylene. Hildebrand's solubility formula was applied to the experimental results and values of the solubility parameter δ_2 were obtained. The high values of δ_2 in the case of the halides were explained in terms of the polarity effect on solubility.

Although numerous measurements have been reported for the solubility of water in organic liquids, the solvents were in most cases nonpolar.[3–11] In 1948 Taylor, *et al.*, determined the solubilities of water in various hydrocarbons using tritium hydroxide as a tracer.[3,4] In the present paper a series of measurements are reported for the solubilities of water in various polar organic liquids using tritium as a tracer. A new method was developed for counting tritiated water involving a simple one-step conversion to acetylene.[12]

The sensitivity of modern radiochemical methods have a natural application to the measurement of small solubilities.[13] In the case of water in benzene, the value obtained in the present work is compared with those reported by six previous investigators.

Hildebrand's solubility formula[14] was applied to the experimental solubilities of water in benzene, toluene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene and *o*-dichlorobenzene. The high values of δ_2 indicate a polarity effect on solubility.

Experimental

Reagents.—Tritiated water with an activity of approximately 1 mc. per ml. was supplied by Tracerlab, Inc. The organic solvents, chemical grade, were redistilled in a column of 50 theoretical plates. The iodobenzene was purified by the Esso Research and Engineering Company by means of distillation in an 80-plate column with stainless steel Helipak packing. Following purification, this solvent appeared slightly pink due to the presence of a trace of free iodine. The iodine was removed by extraction with 0.1 *F* sodium sulfite solution; the iodobenzene phase was rinsed with water, dried with calcium hydride overnight and filtered.

Solubility Measurements.—In each measurement a small amount of tritiated water was equilibrated with 20 ml. of organic liquid using a Teflon stirrer in a 100-ml. flask in a Sargent constant temperature bath maintained to ±0.02°. At the end of two hours, the mixture was poured into a testtube immersed in the bath and the organic phase separated from water by gravitation. The efficiency of this separation was reasonably established by the excellent reproducibility of the measurements. The determination of THO in the organic phase was done by isotopic dilution with a large excess of H_2O. A 5.0-ml. aliquot of the equilibrated solvent was removed and mixed with 5.00 ml. of distilled water for two hours at the same temperature. After the two phases were again separated, aliquots of the water phase were withdrawn and analyzed for tritium content.

Measurement of Tritium Activity.—The tritium activities in the tritiated water samples were determined by the acetylene method previously described by the authors.[12] The essential procedure was to pass the tritiated water as a gas through a previously evacuated calcium carbide column, introduce the product acetylene into an evacuated Geiger counter, accurately measure the pressure, add argon gas and count with an ordinary scaler. As previously reported, the fractionation in this reaction was 0.53, *i.e.*, the specific activity of the acetylene was 53% of the specific activity of the original water sample.[12] In studying this fractionation it

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