The slope for the solubility of barium bromate in glycine solutions is much less than that obtained for barium or calcium iodates. This cannot be explained readily by changes in the value of the distance of closest approach of an ion to a dipolar ion. It may be that in solutions of such high ionic strength, the "salting out" effects[5] are becoming appreciable.

Summary

The solubilities of barium iodate and of calcium iodate have been determined in glycine solutions, alanine solutions and glycine solutions containing potassium chloride.

It has been shown in two cases that the effects of ionic strength and of dipolar ions on the solubility of a salt are independent and additive and that the solubility of barium iodate or calcium iodate in glycine solutions is given by

$$\frac{1}{Z_1Z_2}\log\frac{s}{s_\infty} = 0.505\left(\frac{78.54}{D_d}\right)^{3/2}\frac{\sqrt{\mu}}{1+A\sqrt{\mu}} + 0.207\,M$$

The solubilities of barium iodate and calcium iodate in glycine solutions obey the Kirkwood limiting law up to 0.15 M. Using the slopes of these curves and crystal radii it is possible to calculate from the Kirkwood equation values of the dipole radii of glycine and alanine which are of the correct order of magnitude.

DAVIS, CALIF. RECEIVED AUGUST 5, 1940

[CONTRIBUTION FROM THE GEORGE EASTMAN LABORATORY OF PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

An X-Ray Determination of the Crystal Structure of Tetraphenylarsonium Iodide, $(C_6H_5)_4AsI$

BY ROSE C. L. MOONEY[1]

The halides of tetraphenylarsonium were first prepared and described by Blicke and his associates.[2] Methods for the use of tetraphenylarsonium ion in quantitative analysis were subsequently devised by Willard and Smith.[3] We are indebted to Professor Willard for crystals of the three compounds. A study of these crystals by means of X-rays was undertaken in order to compare the structural arrangement with those of other halides, and particularly to determine the size and configuration of the cation complex, the tetraphenylarsonium ion. The configuration of phenyl groups about an inorganic nucleus has never before been described. The molecular compounds tetraphenyltin, tetraphenyllead, and tetraphenylgermanium have been studied by X-rays, but no positions were determined for the phenyl groups, though it was established that the molecule had the symmetry S_4.[4]

The initial stages of the investigation of the three halides of tetraphenylarsonium gave the following results. The chloride and bromide were shown to be isomorphous, to belong to the orthorhombic system, and to have four molecules in the unit cell. The iodide was found to be tetragonal, and to have only two molecules in the unit cell. It soon appeared that the latter crystal presented more favorable conditions for the precise determination of atomic positions directly from diffraction data than either the chloride or the bromide. The first complete analysis was therefore made for the iodide, and is reported here. Work on the other two crystals is still in progress.

Description of the Crystals.—The iodide of tetraphenylarsonium is quite insoluble; 0.14 g. dissolves in 100 cc. of water at 25°. Our sample was in the form of a fine powder. It was satisfactorily recrystallized for our purposes by slow cooling from hot aqueous solution. Colorless, very brilliant prismatic needles, about 0.02 cm. in cross section, and from 0.5 to nearly 1 cm. long, were thus obtained. The form showed only prism faces in general, with occasional development of terminal pyramidal faces. The disposition of these faces indicated a four-fold alternating axis coincident with the needle axis. The birefringence was found to be small and negative.

Experimental Methods.—The X-ray data consisted of powder, oscillation and equi-inclination Weissenberg photographs, all taken with Cu Kα radiation filtered through nickel. The

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[1] Guggenheim Fellow, 1939–1940.

[2] Blicke and Marzano, THIS JOURNAL, **55**, 3056 (1933); Blicke and Monroe, *ibid.*, **57**, 720 (1935); Blicke and Cataline, *ibid.*, **60**, 423 (1938); Blicke, Willard and Taras, *ibid.*, **61**, 88 (1939).

[3] Willard and Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 186, 269, 305 (1939).

[4] George, *Proc. Roy. Soc.* (London), **113A**, 585 (1927).

oscillation photographs were largely exploratory; the powder photograph measurements were used to get a final accurate value of the cell dimensions; the Weissenberg intensities were used for the structure determination. Each Weissenberg exposure was recorded on two films, superimposed in the camera. It was found that absorption through the first film reduced the intensity of the second by 75%. By careful cross reference between the two films, it was possible to get a dependable evaluation of relative intensities, and particularly to avoid errors in estimation of very intense reflections. Arbitrary numerical values were assigned to observed intensities by visual comparison with a timed-exposure blackening scale. These numerical values were reduced by the polarization and Lorentz factor. The resulting number was recorded as F^2, the "observed intensity," from which F, the "observed amplitude," was derived. No correction was made for absorption in the crystal, since those used were hair-thin needles, practically square in cross section.

Cell Size and Density.—The tetragonal cell of tetraphenylarsonium iodide, measured first from layer line separation on rotation photographs, and recalculated from a powder photograph, has the following dimensions

$$a \text{ (or } b) = 12.194 \text{ Å.}, c = 7.085 \text{ Å.}, c/a = 0.58$$

The specific gravity, measured by flotation, is 1.6. The density, calculated from the cell size and molecular weight, is 0.798 g./cc. per molecule. There must therefore be two molecules in the unit cell, which gives a calculated density of 1.596 g./cc., in excellent agreement with the experimental value.

Space Group.—Inspection of the indices of observed planes shows only one characteristic absence: namely, planes of index hkl are absent unless the sum of the indices is even. The structure is therefore based on the body-centered lattice. Such a lattice, with no additional space group vanishings, is common to a large number of tetragonal space groups. However, the absence of a plane of symmetry in the Weissenberg patterns narrows the choice to the following four:

$$C_{4h}^{6}\text{–I } 4_1/\text{a} \qquad C_{4h}^{5}\text{–I } 4/\text{m} \qquad C_4^5\text{–I } 4 \qquad S^2\text{–I } \bar{4}$$

The geometrical form of the crystal points at once to I $\bar{4}$ as the correct space group. However, an unambiguous choice may be made by the use of X-ray data alone, in the following manner. The first space group may be eliminated at once, for it does not provide the two-fold positions required by iodine and arsenic. In order to choose the correct space group from the remaining three, reference must be made to regularities in observed intensities. Striking regularities are at once noted; planes with h and k even are very strong when l is equal to $4n$, and very weak otherwise. The reverse is true for planes having h and k odd; but if h or k is odd—in which case l is odd—there is no special regularity. It is safe to attribute such regularities to the iodine–arsenic distribution, for it is obvious that reflections from this crystal cannot be extraordinarily strong unless iodine and arsenic are in phase; nor can they be very weak unless the opposite is true. A few calculations are sufficient to show that only one of the arrangements for iodine and arsenic provided by the possible space groups can satisfactorily explain the observed regularities in very strong and very weak planes. It follows that the space group must be S_4^2 – I $\bar{4}$, with one heavy atom in either (c) or (d), the choice depending on the choice of origin.[5]

Structure Determination.—It has been shown that arsenic and iodine are in the special two-fold positions of S_4^2–I $\bar{4}$, both of which are four-fold alternating axes. Let arsenic occupy the positions (a) $000,\frac{1}{2}\frac{1}{2}\frac{1}{2}$; and iodine the positions (d) $0,\frac{1}{2},\frac{3}{4}$; $\frac{1}{2},0,\frac{1}{4}$. The forty-eight carbon atoms, distributed in six sets, must occupy eight-fold general positions of the space group, given by: (g) xyz; $\bar{x}\bar{y}z$; $y\bar{x}\bar{z}$; $\bar{y}x\bar{z}$; and these plus $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Eighteen parameters are therefore required to fix the positions of the carbon atoms. Since the c-dimension is short, and the location of the heavy atoms known, the most direct way of obtaining information as to the distribution of the many carbons seemed to be by means of the method of Fourier series. A projection of the electron density on the c-face was therefore calculated by this method. The function

$$\rho_{(xy)} = \sum_0^{\alpha}\sum_0^{\alpha}\left\{[F(hk0)\cos(2\pi\, hx/a + 2\pi\, ky/b)] + [F(\bar{h}k0)\cos(2\pi\, hx/a - 2\pi\, ky/b)]\right\}$$

was evaluated at intervals of $2\pi x/a = 12°$, and $2\pi y/b = 12°$ in the xy plane. The F values, obtained as described previously, from a Weissenberg photograph of the equatorial layer line,

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[5] "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Erster Band, Gebrüder Borntraeger, Berlin.

were given the known signs of the arsenic–iodine contribution. Because of the high scattering power of arsenic and iodine compared to carbon, the signs were practically certain to be correct, except, perhaps, for very faint reflections whose effect upon the results would in any case be small.

The resulting graph, showing the contours of electron density peaks, is given in Fig. 1. In addition to the large peaks due to arsenic and iodine, at 0,0 and $0,{}^1/_2$, respectively, six small peaks appear in the neighborhood of arsenic, indicating the positions of component carbons of a phenyl group. The coördinates of the peaks, read directly from the graph, give at once twelve of the required eighteen carbon parameters, at least to a first approximation. From the disposition of the peaks, it is clear that the phenyl group is tilted out of the c-plane by a rather large angle. Measurements from arsenic to carbon peaks, and from carbon to carbons, give, fairly closely, distances corresponding to the projection on the c-plane of a hexagonal group extending tetrahedrally from the arsenic, with a bonding distance in the neighborhood of two ångströms. Calculation of the z distances appropriate to this arrangement supplies the final six carbon parameters. The positions of all the atoms—except of course, hydrogen, which cannot be located by these methods—are now approximately known. It remains to test the correctness of the structure, by comparing, plane by plane, its calculated intensities (or amplitudes) with those observed experimentally; and to make such changes in the parameter values as will improve the agreement between the two.

Calculation and Comparison of Theoretical and Observed Amplitudes.—The structure has no center of symmetry. The structure amplitude, F, is of the form: $F^2 = A^2 + B^2$ where

$$A = 4f\{[\cos 2\pi\,(hx + ky) + \cos 2\pi\,(hy - kx)]\cos 2\pi\,lz\}$$
$$B = 4f\{[\cos 2\pi\,(hx + ky) - \cos 2\pi\,(hy - kx)]\sin 2\pi\,lz\}$$

The symbol f is the atomic scattering factor,[6] and x, y and z the parameters of a given set of atoms. For this crystal, the structure amplitude for a given plane will be the sum of eight F's—one for iodine, one for arsenic, and six for carbons. The presence of the heavy atoms might be expected to make the calculated structure amplitudes insensitive to changes in the carbon positions. However, we are not concerned with changes in the positions of single carbons, but of the phenyl group as a whole, whose dimensions, already well known, are again checked by the electron density projection. It happens that the combined carbon contributions, though never large enough to change the sign of the structure amplitude, do make appreciable changes in its magnitude. Further, it may be seen from the structure amplitude expression that planes hkl are not equivalent to planes $\bar{h}kl$ (or khl). For such a pair of planes, the arsenic and iodine, in many cases, make identical contributions, so that the observed intensity differences are due solely to carbon. It was therefore possible to determine quite accurately the orientation of the phenyl groups about carbon, as well as the bonding distance from arsenic to phenyl. Only slight changes in the values obtained directly from the graph (Fig. 1) were necessary to produce exceptionally good agreement between observed and calculated amplitudes throughout the range of observations, which extended to values of sine Θ/λ = 0.48. Furthermore, a change in the bond direc-

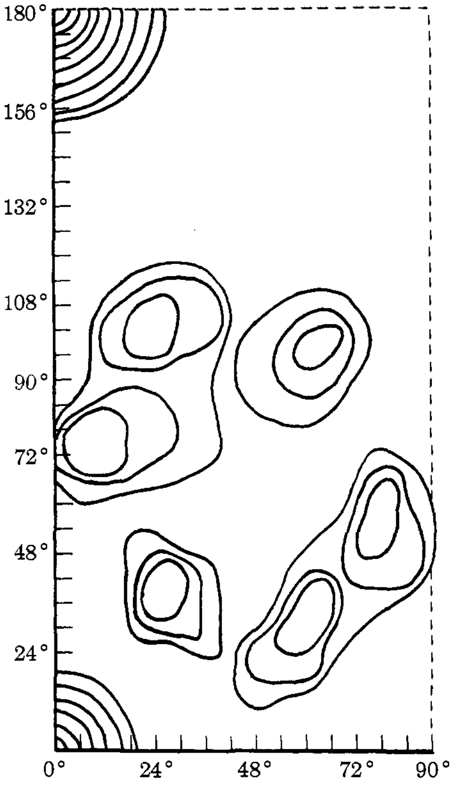

Fig. 1.—Electron density distribution projected on xy plane. The heavy peak at the origin is due to arsenic, the still heavier one at $0, {}^1/_2$ to iodine. The ring of six small peaks indicates the carbon positions.

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(6) Numerical values were obtained from tables given in Tabellen, ref. 4.

tion by ±5° from the tetrahedral angle, or a rotation of the tetrahedron as a whole by a like amount around the z axis, materially impaired the agreement. The correct structure of tetraphenylarsonium iodide is therefore given by the parameters listed in Table I. They are expressed in angular measure, that is, in terms of $2\pi x$, $2\pi y$, and $2\pi z$, where x, y, and z are fractions of a, b, and c cell dimensions, respectively.

Table I

Parameters for $(C_6H_5)_4AsI$ Structure

	$2\pi x$	$2\pi y$	$2\pi z$		$2\pi x$	$2\pi y$	$2\pi z$
Arsenic	0°	0°	0°	Carbon_3	19.2°	101.0°	124.0°
Iodine	0	180	270	Carbon_4	59.0	96.4	142.5
Carbon_1	23.6	39.8	58.5	Carbon_5	78.7	64.9	124.0
Carbon_2	3.0	73.7	77.7	Carbon_6	62.5	36.8	77.7

Table II shows experimental structure amplitudes, and those calculated from the parameters given in Table I. The excellent agreement leaves no doubt as to the correctness of the structure. Due to the fact that no correction was made for temperature, the calculated structure amplitudes become larger than the observed ones for high glancing angles. The relative values remain in agreement; that is to say, calculated values for strongly reflecting planes in any given region of sin Θ/λ remain greater than those for neighboring weak reflections.

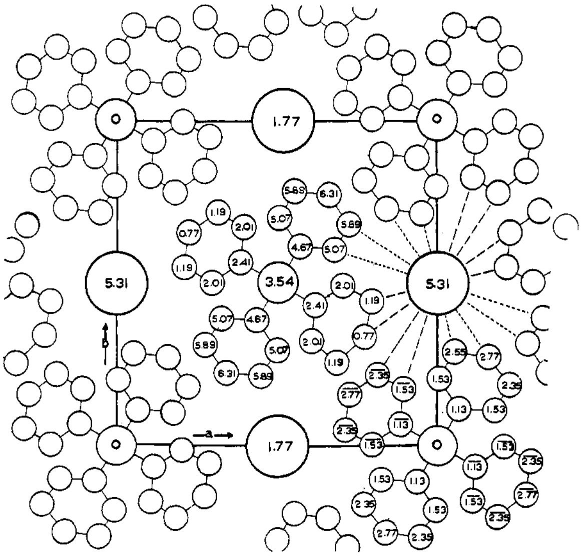

Fig. 2.—Projection of the structure of tetraphenylarsonium iodide on the c-face. The circles, in descending order of size, mark the positions of iodine, arsenic and carbon. The numbers give heights, in ångströms, with reference to the basal plane. The coördination is indicated for one iodine; dashed lines show connection to carbons appearing in the figure; dotted lines to carbons directly above or below these.

Table II

Experimental and Calculated Structure Amplitudes

Indices	sin Θ/λ	$F_{\text{exptl.}}$	$F_{\text{calcd.}}$	Indices	sin Θ/λ	$F_{\text{exptl.}}$	$F_{\text{calcd.}}$
			A. Planes *hk*0, 0*kl*, *h*0*l*				
110	0.056	13	6	260	0.259	54	69
200	.082	59	56	620	.259	39	40
011	.083	80	74	170	.290	0	0
101	.083	55	48	710	.290	23	30
220	.116	60	67	550	.290	7	4
130	.130	16	20	460	.296	57	70
310	.130	45	36	640	.296	46	65
002	.141	48	39	071	.296	34	44
031	.142	78	64	701	.296	30	36
301	.142	55	49	503	.297	29	44
400	.164	64	78	800	.328	31	46
202	.166	26	18	280	.338	20	52
330	.174	21	17	820	.338	36	57
240	.184	54	56	660	.388	34	42
420	.184	69	75	802	.360	0	14
150	.210	15	15	703	.360	16	31
510	.210	20	24	480	.368	41	54
013	.211	37	41	840	.368	33	42
103	.211	37	46	910	.372	6	17
051	.217	46	63	190	.372	0	11
501	.217	37	31	091	.378	26	38
402	.218	18	21	901	.378	29	49
440	.232	50	65	860	.410	41	66
350	.239	19	22	680	.410	16	40
530	.239	5	12	10,00	.411	28	56
600	.247	42	63	10,20	.419	34	57
303	.248	35	38	2,10,0	.419	31	54
			B. Some *hkl* planes				
211	0.117	68	57	242	0.234	15	11
121	.117	38	32	123	.235	36	45
112	.155	71	63	213	.235	23	39
231	.165	53	51	152	.254	60	63
321	.165	44	43	512	.254	47	51
222	.185	12	15	233	.262	39	51
141	.188	50	46	323	.262	28	43
411	.188	55	48	143	.275	28	33
132	.194	45	63	413	.275	28	43
312	.194	50	73	622	.298	11	11
431	.217	34	36	262	.298	18	20
341	.217	42	56	642	.330	0	15
251	.231	46	55	462	.330	8	17
521	.231	40	38	822	.368	0	6
422	.234	18	20	282	.368	8	17

Discussion of the Structure.—Figure 2 is a projection of the structure on the c-face. The arrangement may be visualized as two interpenetrating body-centered lattices, one of iodine ions, the other of tetraphenylarsonium ions, the former being displaced with reference to the origin (arsenic) by a translation of $0,\frac{1}{2},\frac{3}{4}$. Both the arsenics and the iodines lie in fourfold rotary reflection axes. No additional symmetry is required by the space group. The tetraphenylarsonium ion consists of the central arsenic, to which four phenyl groups are connected at strictly tetrahedral angles. The bonding distance from carbon to arsenic is 1.95 Å., which is in agreement with the sum of the arsenic and carbon tetrahedral radii. The planes of the four phenyl groups are disposed so that the complex ion has two reflection planes at right angles to each other and to the basal plane. This symmetry is probably a property of the ion, since it results in very satisfactory "closest approach" distances between neighboring phenyls, that is, 3.4 Å.

The hydrogens can be thought of as lying in the same plane as the phenyl group to which they are bound, and at distances of about an ångström from the binding carbons, in the general positions supplied by the space group. However, since their location cannot be detected by X-ray methods, the iodine coördination distances have been calculated with reference to carbon positions. A given iodine is at closest distance to sixteen carbons, which lie smoothly on a sphere of average radius 4.13 Å. The individual distances vary only between 4.01 and 4.22 Å. The sixteen carbons, in pairs, belong to eight different tetraphenylarsonium groups; that is to say, each iodine is coördinated to eight cations, the connection, in each case, being to the edge of one phenyl group. Conversely, each tetraphenylarsonium group is surrounded by eight iodines, so that each of its phenyl groups is held, by two different carbon pairs, to two different iodines. Thus the stability of the lattice may be explained by the fact that the cations and anions fit neatly together, with uniform and entirely normal distances between them. Table III lists these and other distances calculated from the structure.

TABLE III

DISTANCES IN STRUCTURE

C–C	in ring	1.39 Å.
As–C	tetrahedrally bonded carbon	1.95
I–C	coördination distance	4.13
C–C	closest distance, neighboring phenyls in arsonium group	3.40
C–C	closest distance, neighboring arsonium groups	3.50

It is not easy to find other crystal structures with which to compare this one directly. No other salt of tetraphenylarsonium has as yet been investigated. A great many iodides, of course, are well known, but none having a cation of comparable size, for the tetraphenylarsonium tetrahedron, measured from terminal carbons, has an edge 7.76 Å. in length. Among the iodides having rather large cations, both tetramethylammonium and tetraethylammonium, like the arsonium compound, are tetragonal, and have two molecules in the unit cell. Tetramethylammonium iodide, whose cation tetrahedron side is about 2.5 Å., has a structure which has been described as a distorted CsCl grouping, with the iodines forced out of cubic positions by the large cations. The tetraethylammonium iodide structure is not completely known; but the iodines, like those of tetraphenylarsonium, occupy strictly body-centered positions.

In conclusion, it may be pointed out that this structure determination furnishes a good example of the power of the Fourier method in a favorable case; for despite the presence of the very heavily scattering arsenic and iodine atoms, it has been possible to determine the positions of the carbons directly from diffraction data, with no preliminary assumptions. The results of the work may be briefly summarized as follows. The crystal structure of a new iodide, that of tetraphenylarsonium, has been determined. The tetraphenylarsonium ion, a group which is large compared with the usual ionic cations, and which has not been known long chemically, has been described and measured for the first time.

Summary

The crystal structure of tetraphenylarsonium iodide, $(C_6H_5)_4AsI$, has been completely and accurately determined directly from X-ray diffraction data. The crystal is tetragonal, and has the space group S_4^2–I $\bar{4}$. There are two molecules in the unit cell of dimensions: a = 12.194 Å., c = 7.085 Å. The structure may be described as two interpenetrating body-centered lattices, one of tetraphenylarsonium ions, the other of iodine ions, the latter being shifted with respect to the former by a translation, $0,\frac{1}{2},\frac{3}{4}$. The tetraphenylarsonium ion is a strictly tetrahedral grouping of four phenyl groups to a central arsenic, the binding distance being 1.95 Å. The cation is surrounded, at distances of 4.13 Å., by eight iodine ions, each iodine being nearest to one edge (two connected carbons) of a phenyl group. The iodine coördination sphere consists of sixteen carbons.

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