bon dioxide gas until the solution gives no color with phenolphthalein.[7] Concentration of the aqueous solution at 6 mm. and not over 65° leaves a dry residue which is extracted twice with 300-cc. portions of boiling ethanol, the insoluble portions remaining on the filter. Removal of the alcohol (15 mm. and 50°) and addition of 300 cc. of dry acetone (in which monoacetone-*d*-galactose and the unreacted diacetone-*d*-galactose are soluble) yields the crystalline potassium salt of diacetone-*d*-galacturonic acid. Addition of dry acetone to the concentrated mother liquors gives a second crop of the potassium salt, which is recrystallized by dissolving in a small volume of ethanol and then adding acetone. The yield of the potassium diacetone-*d*-galacturonate is 60–80 g. (49–65%); m. p. 200–205° (dec.); $[\alpha]^{20}\text{D}$ −61.1 (*c*, 2.046; H_2O).

Conversion of Diacetone-*d*-galacturonic Acid Potassium Salt to Diacetone-*d*-galacturonic Acid.[2]—A solution of 60 g. (0.19 mole) of the *carbonate-free* potassium salt ($C_{12}H_{17}O_7K\cdot 0.5H_2O$) in sulfuric acid (376 cc. of 0.5 *N*) is extracted four times with 250-cc. portions of ether. The combined ethereal extractions, dried over anhydrous sodium sulfate, are concentrated to dryness at 15 mm. and 50°. The residue is dissolved in 50 cc. of warm benzene. Crystallization is induced by adding 200 cc. of petroleum ether. The yield of diacetone-*d*-galacturonic acid is 40–45 g. (78–88%); m. p. 157°; $[\alpha]^{20}\text{D}$ −84.0°.

Hydrolysis of Diacetone-*d*-galacturonic Acid to *d*-Galacturonic Acid.[4]—A solution of 40 g. (0.15 mole) of diacetone-*d*-galacturonic acid (m. p. 157°) in water (120 cc.) is heated on a water-bath at 95 to 100° for two hours. After decolorizing with 5 g. of activated carbon the clarified solution should be concentrated ***immediately*** as ***rapidly*** as possible to a mobile sirup (50°, 6 mm.). The sirup is transferred to an evaporating dish and upon vigorous scratching it will set to a solid crystalline cake.[8] The product is collected on a Büchner funnel, washed with ethanol, dry ether, and dried over phosphorus pentoxide at 25° and 12 mm. pressure. The yield of *d*-galacturonic acid is 20–25 g. (65–81%). The product, being a mixture of the α- and β-forms, will show an initial rotation of +60° ⟶ +80° depending on the time involved in concentrating the final solution. Pure α-*d*-galacturonic acid sinters at 110–111° and decomposes at 159–160°. The $[\alpha]^{20}\text{D}$ is +98° initial, final value +50.9° (*c*, 2.1; H_2O).

Summary

An improved method for the synthesis of *d*(+)-galacturonic acid has been described. The yield is 50 g. of *d*(+)-galacturonic acid from 100 g. α-*d*-galactose.

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[7] It is convenient to invert a glass funnel in a jar whose diameter is slightly greater than that of the funnel. The carbon dioxide gas is then introduced into the solution through the stem of the funnel.

[8] If the crystallization is not spontaneous it can be induced by the addition of absolute alcohol.

MADISON, WISCONSIN RECEIVED JUNE 4, 1938

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 644]

The Molecular Structure of Arsenious Oxide, As_4O_6, Phosphorus Trioxide, P_4O_6, Phosphorus Pentoxide, P_4O_{10}, and Hexamethylenetetramine, $(CH_2)_6N_4$, by Electron Diffraction

BY G. C. HAMPSON AND A. J. STOSICK

In a recent paper,[1] which was published while this work was in progress, there were reported the results of an electron diffraction investigation of the structures of phosphorus trioxide, phosphorus pentoxide and arsenious oxide. The values which we have obtained for P_4O_6 and As_4O_6 are in good agreement with those of Maxwell, Hendricks and Deming. On the other hand, the latter authors were unable to deduce a structure for P_4O_{10} and came to the conclusion that the molecule probably has lower symmetry than that of the point group T_d. The reason for their failure probably lies in the fact that the molecule has an abnormally short P–O distance and we were led to our final structure, which gives an excellent fit with the photographs, only after very many models had been shown to be wrong.

The visual method of measurement was used, the results being compared in the usual way with the approximate scattering formula

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

in which r_{ij} is the distance between the *i*th and *j*th atoms, $Z_i Z_j$ their atomic numbers and $s = (4\pi \sin \theta/2)/\lambda$, where θ is the scattering angle and λ the wave length of the electrons. Radial distribution curves[2] were also calculated and interatomic distances deduced from them. When a molecule contains several approximately equal distances, the radial distribution method fails to resolve the closely spaced maxima and very little information can be obtained from the curve. A modification of the method, suggested by Dr. V. Schomaker of these Laboratories, in which the estimated intensities are multiplied by a factor

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[1] Maxwell, Hendricks and Deming, *J. Chem. Phys.*, **5**, 626 (1937).

[2] Pauling and Brockway, THIS JOURNAL, **57**, 2684 (1935).

TABLE I

Max.	Min.	I	c	s_0	s(VII)	s(VIII)	s_{VII}/s_0	s_{VIII}/s_0
	1			1.602	1.41	1.45	(0.881))	(0.905)
1		20	3	2.365	2.33	2.34	.986	.989
	2			3.273	3.19	3.20	.975	.978
2		30	20	4.239	4.25	4.26	1.002	1.005
	3			5.434	5.39	5.37	0.992	0.988
3		6	12	6.240	6.24	6.23	1.000	.998
	4			7.055	6.95	6.94	0.986	.984
4		10	50	8.121	7.95	7.99	.979	.984
	5			9.213	9.20	9.18	.999	.996
5		4	25	10.278	10.42	10.35	1.014	1.007
	6			11.261	11.00	10.90	0.977	0.968
6		4	35	12.353	11.84	11.89	.959	.963
	7			13.292	13.12	13.11	.987	.986
7		4	45	14.218	14.33	14.36	1.007	1.010
	8			15.347	15.37	15.41	1.002	1.004
8		1	12	16.309	16.15	16.18	0.991	0.992
	9			17.298	17.05	17.09	.986	.988
9		2	25	18.212	18.13	18.17	.996	.998
	10			19.246	19.17	19.22	.996	.999
10		2	25	20.224	20.08	20.03	.993	.990
	11							
11		1	10	22.087	21.84	21.89	.990	.991
							Mean .9909	Mean .9909

$s^3e^{-as^2}$, with a chosen such that the exponential factor is equal to one-tenth for the last measured ring, gave a satisfactory resolution of most of the distances, and was invaluable in fixing the model for P_4O_{10}.

As_4O_6, P_4O_6, P_4O_{10}, and $(CH_2)_6N_4$ were measured in Oxford using the apparatus described by de Laszlo;[3] for his assistance in operating the electron diffraction camera we are greatly indebted to Dr. A. H. Gregg. The measurements on As_4O_6, P_4O_6, and P_4O_{10} were then repeated in Pasadena using the apparatus described by Brockway,[4] and the two sets of results were found to agree to within 1%. With the latter apparatus two or three extra outer rings were obtained, but the longer jet-to-camera distance employed in the de Laszlo apparatus enabled some inner fine structure to be resolved which was of great help in the P_4O_{10} investigation.

Experimental

The As_4O_6 used was the C. P. arsenious oxide of commerce which was not further treated.

The P_4O_6 was prepared by the method of Wolf and Schmager,[5] a modification of the older method of Thorpe and Tutton.[6] The trioxide so prepared contains 1 to 2% of free yellow phosphorus even after repeated vacuum distillation. The greater share of this free phosphorus was removed by irradiating the impure oxide for two days with a mercury vapor lamp. This treatment largely converts the yellow form into the much less volatile red form permitting separation by a subsequent distillation *in vacuo*.

The P_4O_{10} used was commercial C. P. phosphorus pentoxide which was sublimed in a stream of oxygen to remove lower oxides. This treatment is necessary since the lower oxides are all more volatile.

The hexamethylenetetramine was a commercial sample purified by vacuum sublimation.

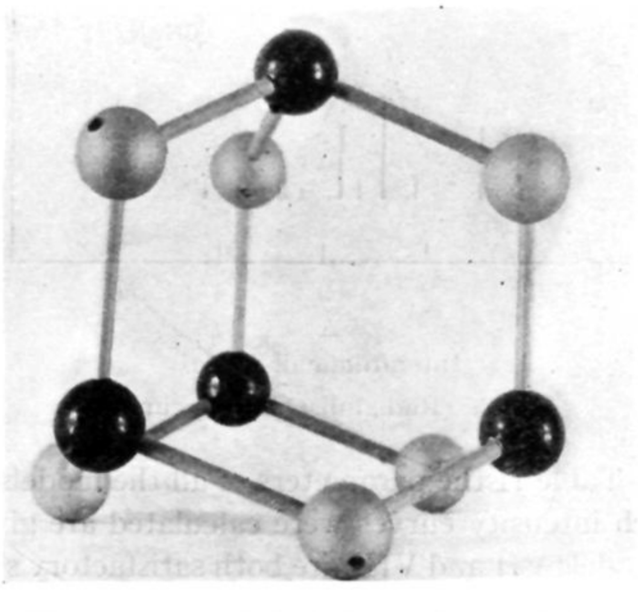

Fig. 1.—Photograph of model of As_4O_6, P_4O_6, or $(CH_2)_6N_4$. The black balls represent As, P, or N; the silver balls represent O or CH_2.

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[3] De Laszlo, *Proc. Roy. Soc.* (London), **A146**, 672 (1934).

[4] Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

[5] Wolf and Schmager, *Ber.*, **62**, 771 (1929).

[6] Thorpe and Tutton, *J. Chem. Soc.*, **57**, 545 (1890).

Arsenious Oxide.—The models tried for As_4O_6 consist of four As atoms at the positions (v,v,v), ($\bar{v},\bar{v}$,v), ($\bar{v}$,v,$\bar{v}$) and (v,$\bar{v},\bar{v}$) and six O atoms at the positions ($\pm$u,0,0), (0,$\pm$u,0) and (0,0,$\pm$u) (Fig. 1).

The photographs of As_4O_6 show thirteen maxima, eleven of which were measurable. The first, second and fourth maxima are strong. Preceding the fifth maximum and following the sixth maximum there are deep minima of about equal depth. The fifth and sixth maxima are of equal intensity. The values of s_0 for the maxima and minima and the estimated intensities of the maxima are given in Table I together with the weighted intensity values, c, used in the modified radial distribution method. The corresponding values of s for models VII and VIII are also given.

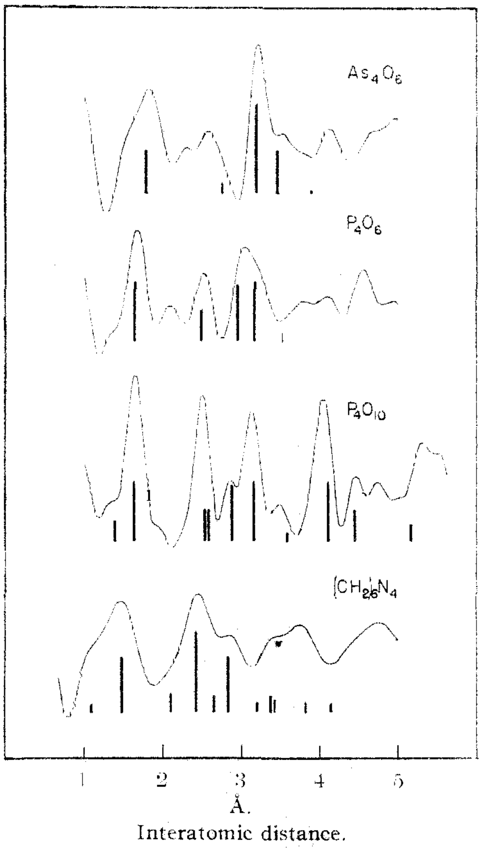

Fig. 2.—Radial distribution curves.

In Table II the parameters of all the models for which intensity curves were calculated are given.

Models VII and VIII are both satisfactory since both are in qualitative agreement with the photographs. Model V is not satisfactory because for it the eighth maximum becomes a shelf, and model VI is not satisfactory because the sixth maximum has become weaker than the fifth.

Table II

Model	u	v	As–As	As–O	O–As–O	As–O–As
I	2.310	1.155	3.26 Å.	2.00 Å.	109°28′	109°28′
II	2.057	1.308	3.70	2.00		
III	1.890	1.160	3.27	1.79		
V	1.890	1.142	3.23	1.78	97°20′	130°14′
VI	2.038	1.142	3.23	1.84	102°34′	121°58′
VII	1.981	1.142	3.23	1.82	100°39′	125°6′
VIII	1.959	1.142	3.23	1.81	99°54′	126°20′

Models VII and VIII lead to the following values of the interatomic distances and valence angles

Model VII	Model VIII
As–As = 3.20 Å.	As–As = 3.20 Å.
As–O = 1.80 Å.	As–O = 1.79 Å.
O–As–O = 100°39′	O–As–O = 99°54′
As–O–As = 125°6′	As–O–As = 126°20′

The radial distribution method applied to the As_4O_6 photographs gives a curve with maxima at 1.82 and 3.21 Å. corresponding to the values given above for the distances in the molecule. The curve for this calculation is given in Fig. 2. In Fig. 3 the theoretical intensity curves for As_4O_6 are

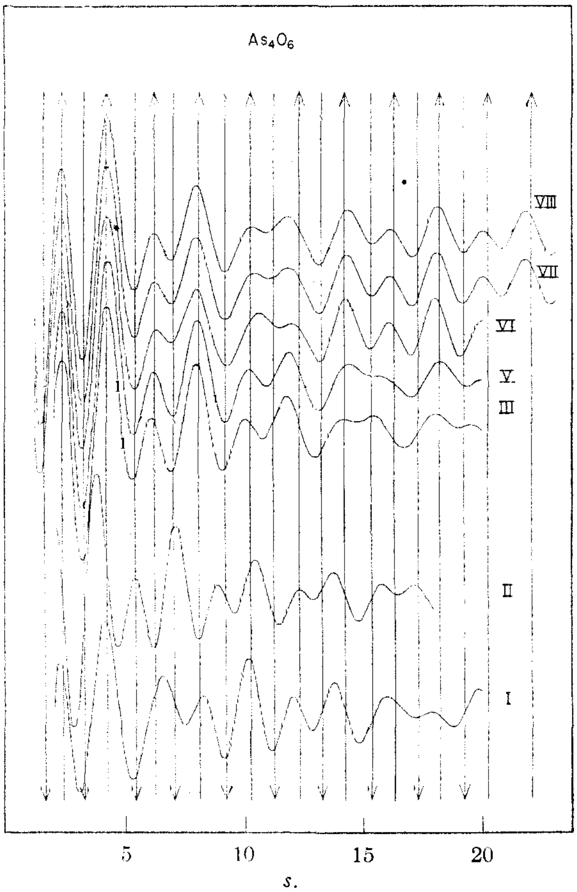

Fig. 3.—Calculated intensity curves for As_4O_6.

TABLE III

Max.	Min.	I	c	s_0	s(VI)	s(VIII)	s_{VI}/s_0	s_{VIII}/s_0
	1			1.803	1.60	1.62	(0.887)	(0.899)
1		12	2	2.659	2.49	2.47	(.936)	(.929)
	2			3.581	3.40	3.39	.949	.947
2		10	8	4.591	4.57	4.56	.995	.993
	3			5.623	5.86	5.91	(1.042)	(1.051)
3		1	2	6.641	6.30	6.30	0.949	0.949
	4			7.542	7.08	7.02	.939	.931
4		5	20	8.514	8.39	8.37	.985	.983
	5			9.634	9.70	9.68	1.007	1.005
5		1	6	10.687	10.72	10.71	1.003	1.002
	6			11.820	11.23	11.19	0.950	0.947
6		2	16	12.863	12.49	12.42	.971	.966
	7			14.319	14.09	14.05	.984	.981
7		2	18	15.548	15.69	15.62	1.009	1.005
	8				16.95	16.84		
8		1			17.70	17.58		
	9				18.52	18.44		
9		2	16	19.90	19.71	19.63	0.990	0.9866
							Mean .9802	Mean .9769

given. As final values of the distances the following are given:

As–As = 3.20 ± 0.03 Å. As–O–As = 126 ± 3°

As–O = 1.80 ± 0.02 Å. O–As–O = 100 ± 1.5°

Maxwell, Hendricks and Deming[1] give As–As = 3.20 ± 0.05 Å. They were unable to fix the oxygen parameter because of the much greater scattering power of the As atoms. Fair agreement was found with the oxygen valence angle As–O–As equal to 120°, 127.5° or 140°.

Phosphorus Trioxide.—The models used for P_4O_6 are of the same type as for As_4O_6. The four P atoms are at positions (v,v,v), $(\bar{\bar{v}},\bar{v},v)$, $(\bar{v},v,\bar{v})$, and $(v,\bar{v},\bar{v})$, and the six O atoms at (±u,0,0), (0,±u,0), and (0,0,±u).

The photographs of P_4O_6 show nine maxima, eight of which are measurable. The first, second and fourth maxima are strong; the second maximum is followed by a weak, almost shelf-like maximum; the sixth and seventh maxima are strong, of nearly equal intensity, separated by a broad and deep minimum; and the minimum following the weak eighth maximum is slightly deeper than that which precedes.

The values of s_0 for the maxima and minima and the estimated intensities of the maxima are given in Table III. Values of the parameters of models for which theoretical intensity curves were calculated are listed in Table IV.

Models VI and VIII were found to be in satisfactory qualitative agreement with the photographs. Model VII is unsatisfactory because the minimum following the eighth maximum has become weaker than that which precedes. Also any model with the value of the parameter u greater than that of model VIII would make this same minimum too deep in comparison with the preceding one.

TABLE IV

Model	u	v	P–P	P–O	O–P–O	P–O–P
IV	1.600	1.064	3.010	1.597	90°11′	140°48′
I	1.664	1.064	3.010	1.620	93°10′	136°31′
V	1.750	1.064	3.010	1.654	96°53′	130°59′
VII	1.780	1.064	3.010	1.666	98°6′	129°6′
VI	1.800	1.064	3.010	1.675	98°50′	127°52′
VIII	1.820	1.064	3.010	1.684	99°41′	126°39′
III	1.900	1.064	3.010	1.721	102°36′	121°53′
II	2.128	1.064	3.010	1.843	109°28′	109°28′

Models VI and VIII lead to the following values of the interatomic distances:

Model VI	Model VIII
P–P = 2.95 Å.	P–P = 2.94 Å.
P–O = 1.64 Å.	P–O = 1.65 Å.
O–P–O = 98°50′	O–P–O = 99°41′
P–O–P = 127°52′	P–O–P = 126°39′

A final choice of model must lie between models VI and VIII, possibly favoring model VI. This leads to the final values of the distances:

P–P = 2.95 ± 0.03 Å.

P–O = 1.65 ± 0.02 Å.

O–P–O = 99° ± 1°

P–O–P = 127.5 ± 1°

The results given by Maxwell, Hendricks and Deming[1] are:

P–P = 3.00 ± 0.05 Å.

P–O = 1.67 ± 0.03 Å.

P–O–P = 128.5 ± 1.5°

Radial distribution calculations result in a curve (Fig. 2) with maxima corresponding to interatomic distances of 1.66 and 3.03 Å. The theoretical intensity curves for P_4O_6 are given in Fig. 4.

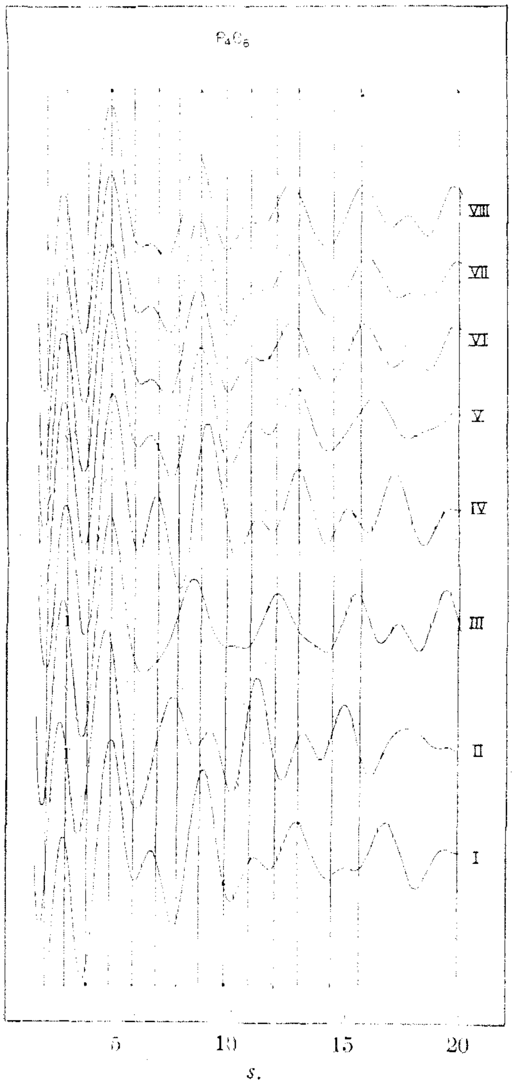

Fig. 4.—Calculated intensity curves for P_4O_6.

Phosphorus Pentoxide.—The photographs taken show eleven measurable maxima. The second maximum is the strongest and is followed by a shelf with no observable minimum interposed; and the third maximum is moderately strong and is followed by a broad shelf-like region. On photographs which were taken using a longer jet-to-camera distance (28.0 cm.) this shelf appears as two very weak maxima with poorly marked minima interposed. With the shorter camera distance (10.85 cm.) the doublet is not resolved. Following the eighth measured maximum there is another doublet of which only the outer ring is measurable. The second ring of this doublet is followed by a fairly pronounced minimum and a much stronger maximum. The last measured maximum is broad, and is preceded by a well marked minimum. The minima immediately preceding and following the weak seventh maximum are both weak, the outermost being possibly a little deeper. The measured values of s_0 of the maxima and minima and the estimated intensities of the maxima are listed in Table V. In Table VI the models for which theoretical intensity curves were calculated are listed.

TABLE V

Max.	Min.	I	c	s_0	s (XIV)	s_{XIV}/s_0
1		10	2	2.823	2.82	(0.999)
	1			3.965	3.75	(.946)
2		15	17	5.015	4.91	.979
	2 Absent					
3		5	10	6.300	6.20	.984
	3			7.215	7.05	.977
4		8	35	8.345	8.50	1.019
	4			9.86		
5		2	16	11.102	11.00	0.991
	5			12.097	11.72	.969
6		3	31	12.922	12.76	.988
	6			13.730	13.72	.999
7		1	12	14.491	14.25	.983
	7			15.351	14.84	.967
8		2	27	16.043	15.86	.989
	8 Not measurable					
9		1	14	18.645	18.46	.990
	9			19.662	19.24	.979
10		2	27	20.470	20.23	.988
	10			21.525	21.38	.993
11		1	12	22.943	23.00	1.003
					Mean	0.9873

TABLE VI

Model	a	b	c	P–P	P–O	P–O′	OPO	POP
I	1.064	1.820	2.011	3.01	1.68	1.64	99°41′	126°39′
III	0.910	1.820	1.926	2.57	1.58	1.76	109°28′	109°28′
IV	.903	1.867	1.919	2.56	1.60	1.76	111°12′	106°4′
V	.923	1.785	1.943	2.61	1.57	1.77	107°24′	112°50′
VI	1.030	1.785	1.830	2.91	1.64	1.39	100°38′	125°24′
VII	1.018	1.805	1.844	2.88	1.64	1.43	102°18′	122°40′
VIII	0.992	1.720	2.008	2.81	1.58	1.76	100°36′	125°15
IX	.993	1.840	1.795	2.81	1.64	1.39	104° 0′	117°46′
X	1.045	1.750	1.830	2.96	1.64	1.36	98° 0′	129°14′
XI	1.022	1.795	1.829	2.89	1.64	1.40	101°30′	123°42′
XII	1.040	1.795	1.829	2.94	1.65	1.40	100°18′	125°39′
XIII	1.020	1.800	1.836	2.88	1.64	1.41	101°49′	123°12′
XIV	1.018	1.792	1.827	2.88	1.63	1.40	101°39′	123°28′

All of the models are for the four P atoms at positions (a,a,a), ($\bar{a}$,$\bar{a}$,a), ($\bar{a}$,a,$\bar{a}$), and (a,$\bar{a}$,$\bar{a}$), six O atoms at positions (±b,0,0), (0,±b,0), and (0,0,±b), and the remaining four O atoms at the positions (c,c,c), ($\bar{c}$,$\bar{c}$,c), ($\bar{c}$,c,$\bar{c}$), and (c,$\bar{c}$,$\bar{c}$). Models XI, XIII and XIV are all satisfactory in their qualitative agreement with the photographs. Model XIV is roughly the mean of models XI and XIII, and it has been used for the final calculations of the interatomic distances of the molecule. The following distances result from these calculations:

P–P = 2.84 ± 0.03 Å. OPO = 101.5 ± 1°
P–O = 1.62 ± 0.02 Å. POP = 123.5 ± 1°
P–O′ = 1.39 ± 0.02 Å. OPO′ = 116.5 ± 1°

The angle designated by OPO′ is the angle formed by the P atom at (a,a,a) and the O atoms at (b,0,0) and (c,c,c) (Fig. 5). It may be seen from an inspection of the models listed that the valence angles are very closely limited. Model XII differs from model XI only in the phosphorus coördinates, causing a change in the P valence angle of only about one degree, but it is not in qualitative agreement with the photographs in that for it the shelf-like region following the fourth maximum has become a real maximum with a preceding minimum. The short P–O′ distance is also fixed closely by the disagreement of model VII. This model differs from the satisfactory models only in that the coördinates of the outer four O atoms are changed by a very small amount.

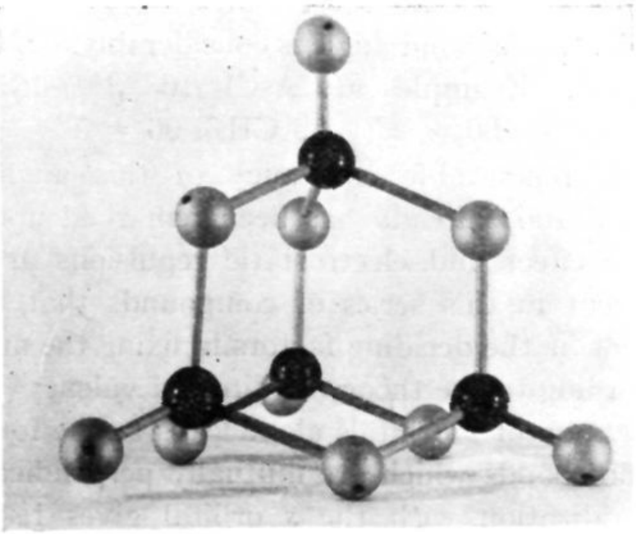

Fig. 5.—Photograph of model of P_4O_{10}. The black balls represent P; the silver balls represent O.

The modified radial distribution method suggested by Dr. Schomaker gave a remarkably good resolution of the various peaks, nearly all the interatomic distances in the molecule appearing as separate maxima. The curve is shown in Fig. 2. From the data which it provided, the three parameters could be determined within narrow limits, these parameters agreeing well with those chosen for the final model.

The theoretical intensity curves for the models of Table VI are shown in Fig. 6.

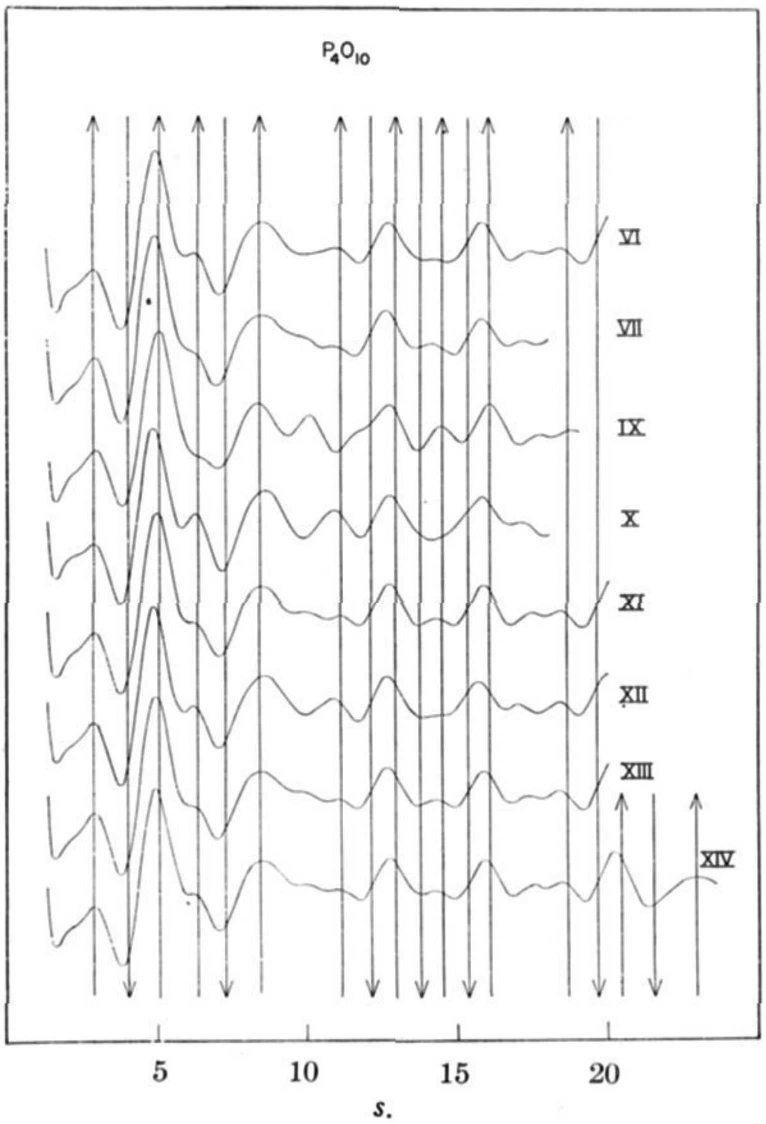

Fig. 6.—Calculated intensity curves for P_4O_{10}.

Hexamethylenetetramine.—The photographs of this substance were taken using a long jet-to-camera distance and show six maxima. The first two are strong, the third broad and diffuse, the fourth very weak, the fifth fairly strong and the sixth very weak.

The hexamethylenetetramine model is essentially the same as that for P_4O_6 and As_4O_6. Four N atoms are in positions (v,v,v), $(\bar{v},\bar{v},v)$, $(\bar{v},v,\bar{v})$ and $(v,\bar{v},\bar{v})$, six C atoms in positions $(\pm u,0,0)$, $(0,\pm u,0)$ and $(0,0,\pm u)$ and the twelve H atoms in positions $(x,\bar{x},z)$, $(\bar{x},x,z)$, etc. The hydrogen parameter could not be deduced from the photographs and an assumed value of 1.09 Å. for the C–H distance was used in computing the theoretical intensity curves. A model in which all the angles had the regular tetrahedral value of 109.5° and with a C–H distance of 1.48 Å. (N–N or C–C = 2.42 Å.) was found to agree well with the photographs. The curve for this model is shown in Fig. 7. Table VII gives the measured values of

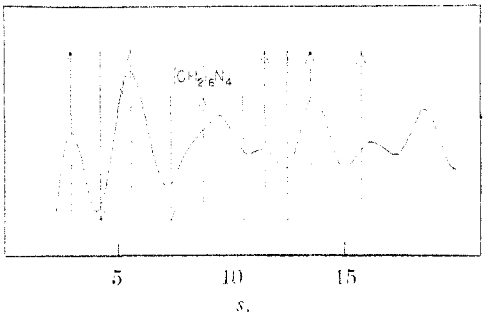

Fig. 7.—Calculated intensity curve for $(CH_2)_6N_4$.

s_0 for the maxima and minima together with the estimated intensities of the maxima; the *s* values for the above model are also listed, and the average value of s/s_0 is seen to be practically unity.

TABLE VII

Max.	Min.	I	c	s_0	s	s/s_0
1		10	2	2.966	2.93	0.988
	1			4.261	4.06	.953
2		8	15	5.606	5.56	.992
	2			7.303	7.15	.979
3		4	5	8.774	9.41	1.073
	3			10.54	10.75	1.020
4		2	2	11.47	11.40	0.995
	4			12.49	12.35	0.989
5		4	10	13.52	13.68	1.012
6		1	4	15.79	16.25	1.029
					Mean	1.003

The radial distribution curve shown in Fig. 2 gives C–N = 1.47 Å. and C–C or N–N = 2.43 Å. agreeing well with the above model.

Discussion of Results

Of the substances reported in this paper, two, hexamethylenetetramine and arsenious oxide, have been studied in the solid form. Hexamethylenetetramine crystallizes in a body-centered cubic lattice, Dickinson and Raymond[7] reporting a regular tetrahedral arrangement of valences with C–N = 1.44 Å. Gonell and Mark[8] gave C–N = 1.48 Å. and C–C = 2.58 Å., and this same type of structure has also been confirmed by Wyckoff and Corey,[9] who give C–N = 1.42 ± 0.08 Å. The sum of the covalent single-bond radii[10] of carbon and nitrogen is 1.47 Å. in good agreement with the value which we find here.

Arsenolite, cubic As_4O_6, was reported by Bozorth[11] to be a lattice of As_4O_6 molecules in a diamond-type arrangement. Both the As and the O valence angles are tetrahedral in this solid, the As–As distance 3.28 Å. and the As–O distance 2.01 Å. There are two strong bonds for each O atom to two As atoms in the same molecule, and two weak bonds to two As atoms of a neighboring molecule. This attraction between neighboring molecules apparently draws the O atom out, increasing the As–O distance and decreasing the oxygen valence angle from the values observed for the vapor molecule to those observed in the solid. To a smaller extent this applies to the As atoms too, since each forms three strong bonds to oxygens in the same molecule and three weak bonds to oxygens of adjacent molecules. A redetermination of the crystal parameters was made by Harker and Eskijian[12] in these Laboratories confirming the older values but fixing them more closely (to within about 0.03 Å.).

Arsenic apparently has a tendency to form bonds at angles smaller than the tetrahedral angle, as As_4O_6 is not unique in this respect. In this compound where the atoms form closed rings it might be thought that the As valences are strained into taking up this angle because of the tendency of the oxygen angle to expand beyond the tetrahedral value[13] but even in compounds where the groups attached to the As atom form no other bonds, the As bond angle is considerably less than 109°28′. Examples are $AsCl_3$ 103°,[14,15] 101 ± 4°,[16] $AsBr_3$ 100 ± 2°,[16] $As(CH_3)_3$ 96 ± 5°.[17]

The remarkable constancy of this angle of around 100° already has been remarked upon.[16] Steric effect and electrostatic repulsions are so different in this series of compounds that they cannot be the deciding factors in fixing the angle. According to the theory of directed valency[18] the utilization of *p* orbitals alone leads to the formation of bonds which are mutually perpendicular. Hybridization with the *s* orbital gives rise to stronger bonds which, if hybridization is complete, as with carbon compounds, are at an angle of 109°28′. If, however, there are unshared electrons, as in the case we are considering, hybridization may not be complete, for there are two opposing tendencies. On the one hand, hybridization tends to stabilize the bonds but at the same

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[7] Dickinson and Raymond, THIS JOURNAL, **45**, 22 (1923).

[8] Gonell and Mark, *Z. physik. Chem.*, **107**, 181 (1923).

[9] Wyckoff and Corey, *Z. Krist.*, **89**, 462 (1934).

[10] Pauling and Huggins, *ibid.*, **87**, 205 (1934).

[11] Bozorth, THIS JOURNAL, **45**, 1621 (1923).

[12] Unpublished work.

[13] Sutton and Hampson, *Trans. Faraday Soc.*, **31**, 945 (1935).

[14] Brockway and Wall, THIS JOURNAL, **56**, 2373 (1934).

[15] Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[16] Gregg, Hampson, Jenkins, Jones and Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

[17] Springall and Brockway, THIS JOURNAL, **60**, 996 (1938).

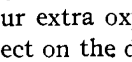
[18] Pauling, *ibid.*, **53**, 1367 (1931).

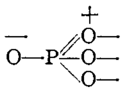
time this means that the unshared electrons also tend to become hybridized between the *s* and *p* orbitals, whereas the unshared pairs of electrons are always most stable when they occupy the *s* orbitals. As usual the actual configuration taken up is that which gives the lowest energy.

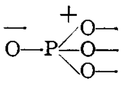
The sum of the covalent single-bond radii[10] of arsenic and oxygen is 1.87 Å. The decrease from the sum of the radii to the observed value of 1.80 Å. may be explained as the result of double bond character caused by unshared pairs from the oxygen atoms forming double bonds with the As atoms.[14–16] The value 126 ± 3° which is observed for the oxygen angle is close to 125°16′, the angle between a double and a single bond on the regular tetrahedral model.

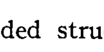
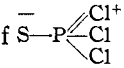
Phosphorus, like arsenic, shows a tendency to form bond angles less than the tetrahedral angle. In P_4O_6 it is found to be 99°. In other substances where the groups attached form no other bonds the same behavior is noted. Examples are PF_3 99 ± 4°,[14] PCl_3 100 ± 2°,[14] PBr_3 100 ± 2°,[16] PI_3 98 ± 4°,[16] $POCl_3$ 104°,[19] $P(CH_3)_3$ 100 ± 4°.[17]

The sum of the covalent radii[10] for phosphorus and oxygen is 1.76 Å. Again the observed value is lower presumably because of double-bond character, as with As_4O_6.

In P_4O_{10} the phosphorus angles are 101.5 and 116.5°. The latter angle is that between an outer oxygen atom and one within the P_4O_6 "kernel." Addition of this outer oxygen atom has had very little effect on the other bond angles and this might have been anticipated from the values given for PCl_3 and $POCl_3$. The most startling feature of the P_4O_{10} molecule is the unusually short distance of 1.39 Å. between each P atom and the "extra" O atom. The value found is about 79% of the sum of the single bond radii (1.76 Å.) and is approximately that expected for a triple bond between the two atoms. A similar anomaly has been observed in thiophosphoryl chloride, $PSCl_3$,[20] where the P–S distance is found to be 1.94 Å. instead of the normal single bond distance of 2.14 Å. It is clear that double bond character in a structure such as  $O{=}P(-O-)_3$, I, is not sufficient to explain such a large shortening as is observed. The addition of four extra oxygen atoms to P_4O_6 has very little effect on the dimensions of this P_4O_6 "kernel," and since we have postulated single-double bond resonance in P_4O_6, it seems reasonable to conclude that it also occurs in P_4O_{10}. The important systems are probably II and III in resonance with I.


II


III

There is another piece of evidence which favors this conclusion. In P_4O_6 the contribution of a double-bonded structure IV  $\overset{-}{P}(=\overset{+}{O}-)(-O-)_2$ was postulated to explain the shortening of the P–O bond below the single bond value. In this structure the phosphorus and oxygen atoms carry opposite charges and so there is no "formal charge effect"[21] influencing the bond length. On the other hand, in structures II and III of P_4O_{10} the positive charge on the oxygen or phosphorus atom is not compensated by a negative charge within the P_4O_6 "kernel" and hence because of the increased effective nuclear charge we should expect the bond length to be diminished. The P–O distance in P_4O_6 is 1.65 Å. and the corresponding distance in P_4O_{10} is indeed shorter, being 1.62 Å. The difference may be due to experimental error, although in view of the above argument it may be of some significance. As regards the other P–O distance having the extremely low value of 1.39 Å., the "formal charge effect" in structure II (negative charge on the oxygen, no charge on the phosphorus) would lead one to expect an increase rather than a decrease. One is forced to conclude that the predominant factor here must be the polar character of the bond. In discussing $PSCl_3$, Beach and Stevenson[20] ruled out any effect of ionic character and formal charges on the length of the bond, but concluded that the shortening of the P–S distance must be due to a considerable (about one half) contribution of  $\overset{-}{S}-P(=Cl^+)(-Cl)(-Cl)$ without, however, giving any reasons. The short P–O distance in P_4O_{10} is in accord with the chemical properties of this molecule. Such short bonds are presumably extremely stable, and the thermal stability and resistance to reduction of P_4O_{10} are well known.

We wish to express our thanks to Professor Brockway, Professor Pauling and Professor Sidgwick for their help and interest in this work,

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[19] Brockway and Beach, THIS JOURNAL, **60**, 1836 (1938).

[20] Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

[21] Elliott, THIS JOURNAL, **59**, 1380 (1937).

and the Commonwealth Fund for a Fellowship to one of us (G. C. H.).

Summary

Electron diffraction measurements on arsenious oxide, phosphorus trioxide and hexamethylenetetramine show that the molecules consist of four phosphorus or nitrogen atoms in positions (vvv) ($\bar{v}\bar{v}v$) ($\bar{v}v\bar{v}$) and ($v\bar{v}\bar{v}$) and six oxygen atoms or methylene groups in the positions ($\pm$u00) (0$\pm$u0) and (00$\pm$u). In phosphorus pentoxide there are four additional oxygen atoms in the positions (www) ($\bar{w}\bar{w}w$) ($\bar{w}w\bar{w}$) and ($w\bar{w}\bar{w}$).

The interatomic distances and angles are: for As_4O_6, As–O = 1.80 ± 0.02 Å., O–As–O = 100 ± 1.5°, As–O–As = 126 ± 3°, for P_4O_6, P–O = 1.65 ± 0.02 Å., O–P–O = 99 ± 1°, P–O–P = 127.5 ± 1°, for $N_4(CH_2)_6$, C–N = 1.47 ± 0.02 Å., C–N–C = N–C–N = 109.5°, for P_4O_{10}, P–O = 1.62 ± 0.02 Å., P–O′ = 1.39 ± 0.02 Å., O–P–O = 101.5 ± 1°, P–O–P = 123.5 ± 1° and O–P–O′ = 116.5 ± 1°.

The shortening of the bond distances in As_4O_6, P_4O_6 and P_4O_{10} below the theoretical single-bond values is attributed to single-bond double-bond resonance. It is concluded that the abnormally low value of 1.39 Å. for the P–O′ bond in P_4O_{10} is due to the polar character of the bond.

Pasadena, Calif. Received May 31, 1938

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 647]

The Properties of Osmium Tetroxide in Carbon Tetrachloride Solutions. The Thermodynamic Constants of Osmium Tetroxide[1]

By LeRoy H. Anderson and Don M. Yost

Introduction

Osmium tetroxide is known to be moderately soluble in water and very soluble in carbon tetrachloride. Von Wartenberg[2] determined the solubility to be 6.47 g. per 100 g. of water, and about 250 g. per 100 g. of carbon tetrachloride, at 20°. The distribution ratio of osmium tetroxide between carbon tetrachloride and water was determined by Yost and White[3] for dilute solutions to be 13 when the concentrations are expressed in moles per liter of both solvents. Distribution ratios were determined independently, and at about the same time, by Tschugajeff and Lukashuk[4] with essentially the same results. These authors also made solubility determinations in water but the result, 6.23 g. per 100 g. of water at 25°, does not seem to be consistent with that of Von Wartenberg.

The distribution ratio calculated from solubilities is much higher than that found in the experiments on dilute solutions. This fact indicated that either the concentrated solutions in carbon tetrachloride were exhibiting some abnormal behavior, or that in the distribution experiments water possibly was associated with the tetroxide in carbon tetrachloride layer, thus forming a different solute. In order to settle this point, distribution experiments were made with solutions whose concentrations varied from very dilute to saturation, the solubilities of osmium tetroxide in both water and carbon tetrachloride were redetermined, and the vapor pressures of carbon tetrachloride above solutions of osmium tetroxide in it were measured for the range of concentrations up to saturation.

Preparation of Materials and Experimental Methods

Osmium Tetroxide.—Osmium metal freed from ruthenium was heated to 300–400° in a glass tube in a stream of dried oxygen. The vapors of osmium tetroxide (b. p. 130°) were condensed in the distribution vessel or capsules by means of a solid carbon dioxide–alcohol bath.

All other chemicals used were of the best grade obtainable. The carbon tetrachloride was further purified by fractional distillation.

Analytical Methods.—Osmium tetroxide is frequently determined iodimetrically,[4,5] but the colored tetravalent osmium solutions hide the end-point in all but rather dilute solutions, and atmospheric oxygen affects the results. After some experimentation the following procedure was

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(1) Presented at the Second Annual Symposium of the Division of Physical and Inorganic Chemistry on the Less Familiar Elements, Cleveland, Ohio, December 27, 28 and 29, 1937.

(2) Von Wartenberg, *Ann. Chem.*, **440**, 97 (1924); **441**, 318 (1925); Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 82.

(3) Yost and White, This Journal, **50**, 81 (1928).

(4) Tschugajeff and Lukashuk, *Z. anorg. Chem.*, **172**, 223 (1928).

(5) For other methods see Crowell, This Journal, **54**, 1324 (1932).