

i. e., 1.47 Å. The value 1.22 Å. found for the N-O distance is considerably less than the sum of the single bond radii for nitrogen and oxygen, which is equal to 1.36 Å. This value found in this investigation is within 0.01 Å. of 1.23 Å., the value expected for 50% double bond character for the bond on the basis of resonance between the structures I and II. There is apparently no pronounced additional shortening of the N-O bond caused by the formal change of the nitrogen atom.

Acknowledgment.—The author wishes to express his appreciation to Dr. Buchman for suggesting the problem, to Dr. Schomaker for suggesting the temperature factor treatment used, and to Professor Pauling for helpful discussions.

Summary

A structure for tetranitromethane is proposed which is in agreement with electron diffraction data. In the model there are four nitro groups attached to the carbon atom at tetrahedral angles, the C-N distance is 1.47 ± 0.02 Å., the N-O distance is 1.22 ± 0.02 Å., and the angle O-N-O in the nitro group is 127° . In order to obtain satisfactory intensity agreement it was necessary to assume the nitro groups to be undergoing rotatory oscillation about the C-N bonds in such a way as to keep the oxygen-oxygen repulsions essentially minimized, and to include the usually omitted temperature factor in the approximate intensity formula.

PASADENA, CALIF.

RECEIVED FEBRUARY 7, 1939

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 689]

The Electron Diffraction Investigation of Phosphorus Sulfoxide, $P_4O_6S_4$

BY A. J. STOSICK

Phosphorus sulfoxide, $P_4O_6S_4$, was first reported by Thorpe and Tutton¹ in a paper giving the method of preparation of the compound and the results of vapor density measurements. Its mode of formation by direct reaction of P_4O_6 and the stoichiometric equivalent of free sulfur (a reaction paralleling the reaction of P_4O_6 and O_2) suggests that $P_4O_6S_4$ should be structurally similar to P_4O_{10} . The $P_4O_6S_4$ used in this investigation was prepared by the method referred to above, and was purified by a vacuum distillation, crystallization from carbon disulfide, and a second vacuum distillation.

Electron diffraction photographs of the compound were made in the usual way, and were found to be excellent, showing thirteen measurable rings. The measured values of $s_0 = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$ for the maxima and minima (in which λ is the de Broglie wave length of the electrons (about 0.06 Å.), and θ the scattering angle), the visual intensities I_0 , and the coefficients C_0 of the modified radial distribution function are listed in Table I. These coefficients are the visually estimated intensities multiplied by $s_k^2 e^{-as_k^2}$, where s_k is the s_0 value for the k 'th ring, and "a" is chosen such that e^{-as^2} is equal to 0.1 for the last ring. The resulting

TABLE I

Max.	Min.	I_0	c_0	s_0	s_0/s_0
	1			2.43	(0.827)
1	2	10	1	3.10	(.929)
2	3	15	4	3.83	(.948)
	3			4.64	.974
3	4			Absent	
	4			Shelf; not measured	
	4	5	4	06.45	0.960
4	5	5	4	7.09	.994
	5			8.01	.986
5	6	10	14	8.87	.991
	6			10.21	.979
6	7	4	9	11.26	.995
	7			12.28	.998
7	8	5	16	13.14	.987
	8			13.87	.984
8	9	2	7	14.49	.977
	9			15.12	.979
9	10	5	20	15.81	.992
	10			16.55	.995
10	11	3	14	17.26	.989
	11			17.90	.987
11	12	4	19	18.43	.989
	12			19.24	.986
12	13	5	24	20.49	.991
	13			21.73	1.002
13	14	1	5	22.68	0.988
	14			23.57	.977
14	15	2	8	24.46	.984
	15			25.77	.999
				Mean	.9867

(1) Thorpe and Tutton, *J. Chem. Soc.*, **59**, 1023 (1891).

numbers are normalized to one hundred for ease of computation. The radial distribution curve is presented in Fig. 1, the vertical lines indicating the distances found in the final model and their relative importance. The large peaks at 1.61 and 2.87 Å. were recognized immediately as due to the bonded P-O distance and the non-bonded P-P distance, respectively, since these are within a few hundredths of an ångström of the values found in a previous investigation of P₄O₁₀.²

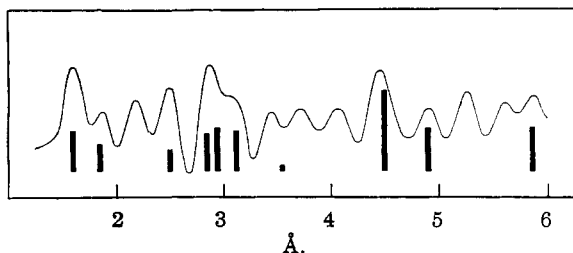


Fig. 1.

Making use of the information obtained from the radial distribution curve, a series of models was calculated using the values of the P and O parameters for the P₄O₆ "kernel" as found in P₄O₁₀ and varying only the S parameter. These models have four P atoms at (a, a, a), (a, \bar{a} , \bar{a}), (\bar{a} , \bar{a} , a), and (\bar{a} , a, \bar{a}); six O atoms at ($\pm b$, 0, 0), (0, $\pm b$, 0), and (0, 0, $\pm b$); and four S atoms at (c, c, c), (c, \bar{c} , \bar{c}), (\bar{c} , \bar{c} , c), and (\bar{c} , c, \bar{c}). In P₄O₆S₄ the four S atoms are substituted for four O atoms in similar positions in P₄O₁₀, the molecule exhibiting symmetry T_d. A list of the models for which intensity calculations were made is presented in Table II. In making the intensity calculations the approximate intensity formula $I = \sum_{ij} \sum_{k,l} \frac{\sin s r_{ij}}{s r_{ij}}$ was used. The curves resulting from these calculations are shown in Fig. 2, the vertical arrows indicating the measured positions of the maxima and minima.

Model	a	b	c	P-S	P-O	P-P
I	1.018	1.792	2.040	1.77	1.63	2.88
II	1.018	1.792	2.155	1.97	1.63	2.88
III	1.018	1.792	2.132	1.93	1.63	2.88
IV	1.018	1.792	2.115	1.90	1.63	2.88
V	1.018	1.792	2.098	1.87	1.63	2.88

In all models $\angle OPO = 101.5^\circ$, $\angle POP = 123.5^\circ$, $\angle OPS = 116.5^\circ$.

Characteristic features of the photographs are: a weak shelf following the second maximum; a marked broadness and asymmetry of the third,

(2) Hampson and Stosick, *This Journal*, **60**, 1814 (1938).

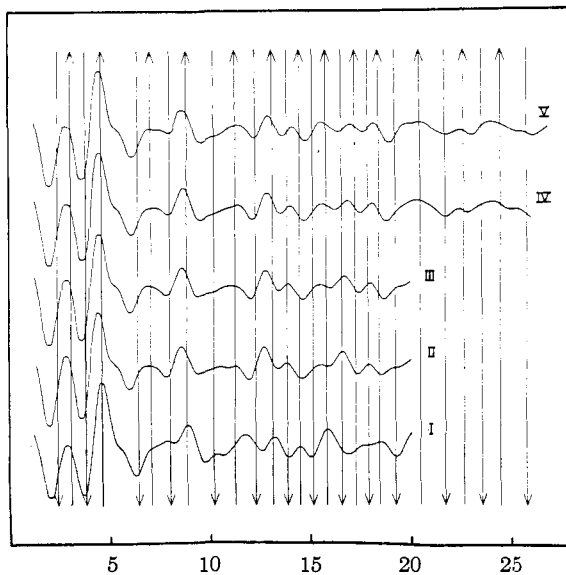


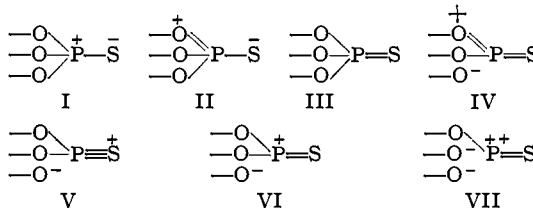
Fig. 2.

fifth, eleventh, and thirteenth maxima; a relatively closely spaced "triplet" between $s_0 = 15$ and 19, with the middle ring slightly weaker than the outer two; and a very weak but measurable twelfth ring. It may be seen from the curves that model V best reproduces these features. The quantitative comparison of $s_{\text{calcd.}}$ and s_0 was made for model V, the values of s_c/s_0 being listed in Table I. After changing the scale of the model as indicated by the s_c/s_0 ratio the following distances are found for P₄O₆S₄

P-O = 1.61 \pm 0.02 Å.	O-P-O = 101.5 \pm 1°
P-P = 2.85 \pm 0.03 Å.	P-O-P = 123.5 \pm 1°
P-S = 1.85 \pm 0.02 Å.	O-P-S = 116.5 \pm 1°

Discussion

The bonded distances P-O and P-S at 1.61 and 1.85 Å. are both less than the respective covalent single bond values³ of 1.76 and 2.14 Å. The shortening of the P-O distance to 1.61 Å. is to be ascribed to partial double bond character of the bond. Since the octet rule need not rigorously apply to elements beyond the first row of the periodic table, the following structures are permissible. It may be seen that none of them is in



(3) Pauling and Huggins, *Z. Krist.*, **87**, 205 (1934).

disagreement with the adjacent charge rule.⁴ Since the P-S distance is considerably less than the double bond value of 1.95 Å., and since the P-O distance is also considerably shorter than the single bond value of 1.76 Å.,³ it is probable that structure III represents to the first approximation the bonding arrangements, with considerable contributions of structures such as IV and V. Structures such as I and II probably do not contribute appreciably since these would tend to increase the P-S distance to the single bond value. It would appear that structure V must contribute to the resonance system if the shortening of the P-S bond below the double bond value is to be explained simply. Structures VI and VII could also result in a shortening of the P-S distance by a formal charge effect.

A comparison of the P=O and P=S distances in various other phosphorus compounds is instructive.

Compound	P=O	Compound	P=S
P ₄ O ₁₀	1.39 ²	P ₄ O ₆ S ₄	1.85
POCl ₃	1.58 ⁶	PSCl ₃	1.94 ⁶
POFCl ₃	1.54 ⁶		
POF ₂ Cl	1.55 ⁶		
POF ₃	1.56 ⁶		

It is evident from the above table that the P=O and P=S bond type in P₄O₁₀ and P₄O₆S₄, respectively, is different from that in the phosphoryl and thiophosphoryl halides, and the inclusion of structure V may be considered justifiable.

(4) Pauling and Brockway, *THIS JOURNAL*, **59**, 13 (1937).

(5) Brockway and Beach, *ibid.*, **60**, 1836 (1938).

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

The O-P-O valence angle of 101.5° is close to the value of the phosphorus angle in several other compounds, the decrease below the tetrahedral value of 109°28' being explainable by a greater degree of *p* orbital character than in normal *sp*³ tetrahedral bonds. The change of the O-P-O angle from 99° in P₄O₆²⁻ to 101.5° in P₄O₆S₄ and P₄O₁₀ indicates that increasing the coordination of the phosphorus atom from three to four tends to make the valence angles become more like those of the tetrahedral PO₄³⁻.

Acknowledgment.—The author wishes to acknowledge the helpful criticisms of Professor Linus Pauling.

Summary

The structure of P₄O₆S₄ has been determined by electron diffraction in the gas phase. The molecule consists of four P atoms at (a, a, a), (a, \bar{a} , \bar{a}), (\bar{a} , \bar{a} , a), and (\bar{a} , a, \bar{a}); six O atoms at ($\pm b$, 0, 0), (0, $\pm b$, 0), and (0, 0, $\pm b$); and four S atoms at (c, c, c), (c, \bar{c} , \bar{c}), (\bar{c} , \bar{c} , c) and (\bar{c} , c, \bar{c}). The valence angles and the principal interatomic distances are: P-O = 1.61 ± 0.02 Å., P-S = 1.85 ± 0.02 Å., P-P = 2.85 ± 0.03 Å., O-P-O = 101.5 ± 1°, P-O-P = 123.5 ± 1°, and O-P-O = 116.5 ± 1°. Single-double bond and double-triple bond resonance is considered to be the cause of the shortening of the P-O and P-S bond distances below the single and double bond values, respectively.

PASADENA, CALIF.

RECEIVED FEBRUARY 7, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Structure of Gossypol. XIX.¹ Synthesis of 1,2-Dihydroxy-3-isopropyl-6-benzoic Acid

BY ROGER ADAMS AND MADISON HUNT

By the vigorous action of hydrobromic acid on gossic (I) or apogossypolic acid (II),² a dihydroxy isopropyl benzoic acid is obtained which might be, on the basis of formula I for gossic acid, the 6-, 5-, or 4-carboxylic acid (II, III, or IV) of 1,2-dihydroxy-3-isopropylbenzene.

If the postulated formula for apogossypolic acid (V), however, is correct, then the structure

(1) For previous paper see Adams, Hunt and Morris, *THIS JOURNAL*, **60**, 2972 (1938).

(2) Adams, Morris, Butterbaugh and Kirkpatrick, *ibid.*, **60**, 2191 (1938).

with the carboxyl group in the 6-position (II) is excluded since both gossic and apogossypolic acids degrade to the same product.

In order to confirm this assumption, the synthesis of 1,2-dihydroxy-3-isopropyl-6-benzoic acid (II) has been undertaken. The dihydroxy acid was not identical with the dihydroxy monobasic acid obtained from gossic or apogossypolic acid. Thus, it may be deduced that the dihydroxy monocarboxylic acid from the natural source has either formula III or IV.