

The Electron Diffraction Investigation of the Molecular Structures of Ketene and Thiophosphoryl Chloride

J. Y. Beach and D. P. Stevenson

Citation: *The Journal of Chemical Physics* **6**, 75 (1938); doi: 10.1063/1.1750206

View online: <http://dx.doi.org/10.1063/1.1750206>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/2?ver=pdfcov>

Published by the **AIP Publishing**

Articles you may be interested in

[On the molecular structure of methane sulfonyl chloride as studied by electron diffraction](#)

J. Chem. Phys. **59**, 2513 (1973); 10.1063/1.1680366

[Electron diffraction investigation of the molecular structure and amplitudes of vibration of gaseous thiazyl chloride, NSCl](#)

J. Chem. Phys. **58**, 2195 (1973); 10.1063/1.1679491

[Electron Diffraction Investigation of the Molecular Structure of Dichlorodifluoromethane](#)

J. Chem. Phys. **24**, 1283 (1956); 10.1063/1.1742797

[An Electron Diffraction Investigation of the Structures of Neopentyl Chloride and SilicoNeopentyl Chloride: The Determination of Intensities through the Use of a Rotating Sector](#)

J. Chem. Phys. **18**, 13 (1950); 10.1063/1.1747431

[Electron Diffraction Investigation of the Molecular Structure of Thioacetic Acid](#)

J. Chem. Phys. **14**, 560 (1946); 10.1063/1.1724194



The relations stated above suffice for the calculation of M_1 and M_2 . For the higher moments others of a similar nature would be needed.

We may calculate M_1 at once, using Eqs. (25) and (27), and obtain the result,

$$M_1 = \frac{2}{NZ} \sum_{a=1}^N \langle \nu_a \rangle_{Av} \langle n_a \rangle_{Av} = \frac{2 \langle \nu \rangle_{Av} \langle n \rangle_{Av}}{s} = (1-s^2)/2. \quad (31)$$

For the moment, M_2 , we may write, by virtue of the independence of averages on the separate lattices,

$$M_2 = \frac{4}{N^2 Z^2} [N \langle (\nu^2)_{Av} - \langle \nu \nu' \rangle_{Av} \rangle \langle n^2 \rangle_{Av} + \langle \nu \nu' \rangle_{Av} \langle (\sum_{a=1}^N n_a)^2 \rangle_{Av}]. \quad (32)$$

From Eq. (30) we find that n is equal to $z^2 r^2 + z r w$. This result together with Eqs. (27), (28), and (32) yields,

$$M_2 = M_1^2 + (4/NZ) r^2 w^2 + O(1/N^2) \\ = M_1^2 + (1-s^2)^2/4NZ + O(1/N^2). \quad (33)$$

The third moment, M_3 , may be obtained in a similar fashion, although the calculation is somewhat more tedious. When substituted in Eqs. (13), the moments so obtained yield Eqs. (19).

The moments may be calculated in another way if p is expressed in the form of Eq. (5). A method analogous to that employed by Van Vleck⁶ in his treatment of the Heisenberg theory of ferromagnetism may then be employed. This method, though somewhat simpler to state, involves about the same amount of computational labor as the one described above.

⁶ J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Vol. 12, § 78 (Clarendon Press, Oxford, 1932).

FEBRUARY, 1938

JOURNAL OF CHEMICAL PHYSICS

VOLUME 6

The Electron Diffraction Investigation of the Molecular Structures of Ketene and Thiophosphoryl Chloride¹

J. Y. BEACH² AND D. P. STEVENSON

Frick Chemical Laboratory, Princeton University, Princeton, N. J.

(Received November 23, 1937)

The structures of the gas molecules of ketene and thiophosphoryl chloride have been determined by the diffraction of 57 kilovolt electrons. The interpretation of the photographs was made by the visual method in conjunction with the radial distribution method. The results for ketene are: carbon-carbon distance $1.35 \pm 0.02\text{\AA}$, and carbon-oxygen distance $1.17 \pm 0.02\text{\AA}$. The carbon-hydrogen distance was assumed to be 1.07\AA . The results for thiophosphoryl chloride are: phosphorus-chlorine distance $2.01 \pm 0.02\text{\AA}$, phosphorus-sulphur distance $1.94 \pm 0.03\text{\AA}$, and the Cl-P-Cl angle $107 \pm 3^\circ$. The results are discussed in terms of covalent radii and the resonance of molecules among several electronic structures.

THE apparatus used in this investigation is closely similar to the one described by Brockway³ and used by Pauling, Brockway *et al.* for determining the structures of gas molecules. The electrons were accelerated by a potential of roughly 57 kilovolts. The wave-length of the electrons was 0.0515\AA . This wave-length was found accurately by taking transmission pictures of gold foil, the structure of which is known. In interpreting the photographs we have used the visual method and the radial distribution method. Both of these procedures have been

described by Pauling and Brockway.⁴ Bauer⁵ has developed an analytic method, based on visual measurement, for interpreting photographs. The method consists of differentiating the theoretical scattering curve and setting the derivative equal to zero at each of the measured maxima and minima. The interatomic distances are then obtained by solving a set of simultaneous equations.

The formula used in the visual method for calculating the intensity of the scattered elec-

¹ Presented before the American Chemical Society, Rochester, September, 1937.

² National Research Fellow in chemistry.

³ For a general review of the experimental procedure and a summary of electron diffraction results see L. O. Brockway, *Rev. Mod. Phys.* **8**, 231 (1936).

⁴ The visual method of interpretation, originally developed by R. Wierl, *Ann. d. Physik* **8**, 531 (1931) and **13**, 453 (1932), has been tested and discussed by L. Pauling and L. O. Brockway, *J. Chem. Phys.* **2**, 867 (1934). The radial distribution method was developed, tested and applied to a large number of compounds by L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **57**, 2684 (1935).

⁵ S. H. Bauer, *J. Chem. Phys.* **4**, 406 (1936).

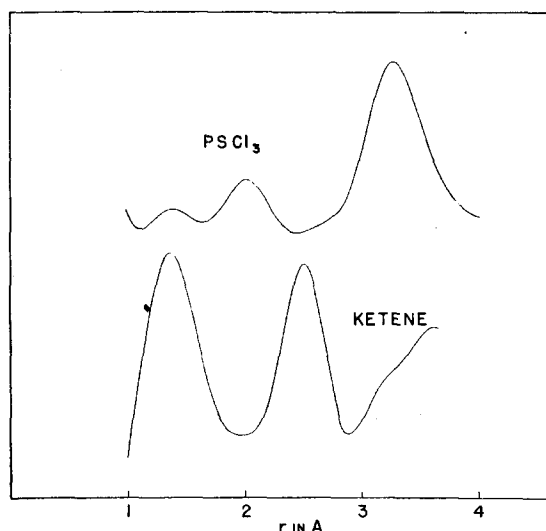


FIG. 1. Radial distribution curves for ketene and thiophosphoryl chloride.

trons as a function of the scattering angle is

$$I = \sum_i \sum_j Z_i Z_j (\sin sr_{ij} / sr_{ij}), \quad (1)$$

where Z_i and Z_j are the atomic numbers of the i th and j th atoms, r_{ij} is the distance between the i th and j th atoms, and s is

$$(4\pi \sin \theta/2)/\lambda.$$

Both summations are taken over every atom in the molecule. λ is the wave-length of the electrons and θ is the angle through which the electrons are scattered. To evaluate Eq. (1) a model for the molecule is assumed, the r_{ij} 's are calculated from the geometry of the model and put into the formula. The intensity, in arbitrary units, is calculated and plotted in terms of s . This procedure is repeated for a number of molecular models, the number depending on the complexity of the molecule and on the pre-existent ideas regarding its structure. The shape of the intensity curve, that is the relative heights and spacings of the maxima and minima, is dependent only on the shape assumed for the molecule and not on the assumed size. The size assumed affects only a scale factor which is automatically corrected when the ring diameters of the maxima and minima on the films are compared quantitatively with the positions of the maxima and minima on the theoretical curve. In general many of the models for the molecule can be eliminated from a qualitative comparison

of the photographs with the calculated curves. By qualitative comparison is meant a comparison of the relative heights and spacings of maxima and minima between photographs and curves without resorting to measurement of the photographs. The final results are obtained from a quantitative comparison of the photographs with the qualitatively acceptable calculated curves.

The radial distribution method consists of inverting the intensity formula. Instead of calculating the intensity of scattering as a function of the structure, the density of atoms in the molecule is calculated in terms of the observed scattering. This distribution function is obtained directly from measurements on the photographs, no assumption of molecular model being involved. These functions for ketene and thiophosphoryl chloride are shown in Fig. 1.

KETENE

The ketene used in this investigation was prepared by Dr. W. E. Vaughn, Dr. Elgene A. Smith and Mr. M. A. Dolliver of Harvard University. From the time the preparation was made until the photographs were taken it was kept in an evacuated vessel at the temperature of solid carbon dioxide and alcohol. During all of the time the ketene was kept cold it remained a clear colorless liquid. Just before it was discarded the dimer began to deposit as a colorless solid on the bottom of the container. The polymer remained colorless until allowed to warm up to room temperature in the presence of air, at which time it turned brown. The presence of some of the dimer at the time the last pictures were taken could not influence the photographs because of the low vapor pressure of the dimer at low temperatures. The boiling point of the dimer is about 128°C. The pictures were taken with the sample at -75°C.

Visual inspection of the photographs shows five maxima. In addition, on some of the photographs, there is a spurious maximum close to the intense central image. When this occurs it is easy to detect as its position is well inside the possible position of diffraction maxima and is quite variable. The first maximum is very intense. The second appears to be a small

maximum or shelf on the outside of the first. The third maximum is sharp. The fourth is less sharp and is close to the third. The fifth is sharp but is very faint and is farther from the fourth than the fourth is from the third. The visually estimated intensities along with the measured values of s are given in the third and fourth columns on Table I.

TABLE I. *Ketene*.

MAX.	MIN.	I	s_{obs}	s_{calc}	C—CA
1		20	5.657	5.93	1.442
2 (shelf)		7	8.193		
	3		9.578	8.96	1.291
3		10	10.53	10.43	1.367
	4		12.04	11.42	1.308
4		4	12.91	12.30	1.315
5		1	15.45	15.35	1.371
				Ave.	1.349

Results: C—C $1.35 \pm 0.02\text{\AA}$
 C—O $1.17 \pm 0.02\text{\AA}$
 C—H 1.07\AA (assumed) H—C—H angle $109^\circ 28'$ (assumed)

The five term radial distribution function is shown in Fig. 1. It possesses maxima at 1.37\AA and at 2.51\AA . The first peak represents the carbon-carbon and the short carbon-oxygen distances unresolved. The second peak gives the long carbon-oxygen distance.

To calculate the theoretical scattering curves it is necessary to evaluate Eq. (1) for several models. No attempt is made to determine the position of the hydrogen atoms. In calculating intensities it was assumed that the carbon-hydrogen distance is 1.07\AA , which is intermediate between the carbon-hydrogen distance in acetylene (1.06\AA) and the carbon-hydrogen distance in methane (1.09\AA). The angle between the carbon-hydrogen bonds was assumed to be tetrahedral. The scattering from the hydrogen atoms is such a small part of the total scattering that the assumptions regarding their position cannot affect the results obtained. There are two distances to be determined: the carbon-carbon distance and the carbon-oxygen distance. The scattering curve, except for a scale factor, is determined entirely by the shape of the molecule, in this case the ratio of the carbon-carbon distance to the carbon-oxygen distance. Accord-

ingly several intensity curves are calculated for ratios of the carbon-carbon distance to the carbon-oxygen distance varying from $1.38/1.13$ to $1.38/1.36$. These curves are shown in Fig. 2. From a qualitative comparison of the curves with photographs it is found that the most satisfactory curve is the one for which the ratio is $1.38/1.20$. The fifth maximum, counting the shelf on the first maximum as a separate maximum, on the $1.38/1.16$ curve is too low, while the second maximum (or shelf) on the $1.38/1.24$ curve is too low. Quantitative comparison of the photographs with the $1.38/1.20$ curve is given in Table I. The final values are: for the carbon-carbon distance, $1.35 \pm 0.02\text{\AA}$ and for the carbon-oxygen distance $1.17 \pm 0.02\text{\AA}$.

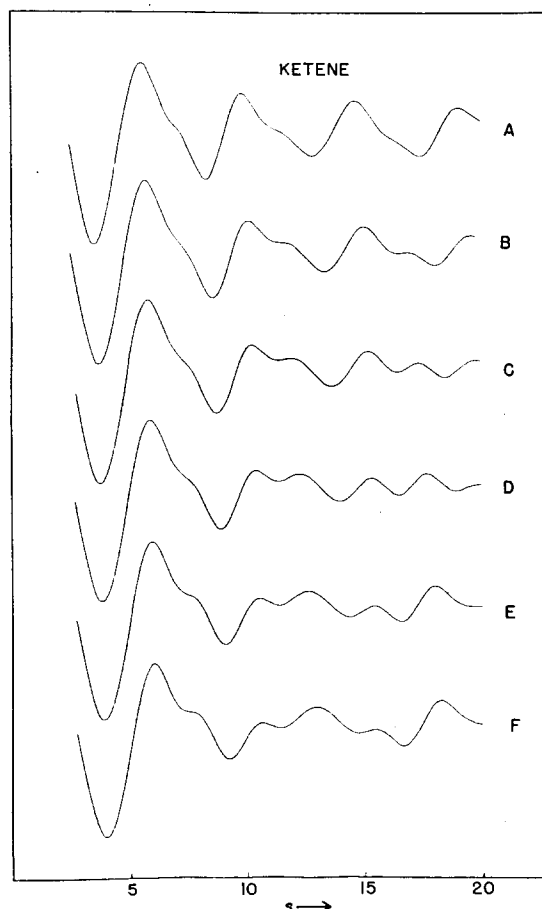


FIG. 2. Theoretical intensity curves for ketene. The ratios of the carbon-carbon distance to the carbon-oxygen distance are: curve A, $1.38/1.32$; curve B, $1.38/1.28$; curve C, $1.38/1.24$; curve D, $1.38/1.20$; curve E, $1.38/1.16$; curve F, $1.38/1.13$.

THIOPHOSPHORYL CHLORIDE

The thiophosphoryl chloride used in this investigation was an Eastman product purified by repeated fractional distillation in vacuo by Mr. F. B. Jennings. The photographs, taken with the sample at 50°C, show six rings. The first three are sharp, the second being the most intense. The fourth maximum is less intense than the third and is close to the third. The fifth is intense and sharp. The sixth is weak and is difficult to measure. The visually estimated intensities are given in Table II.

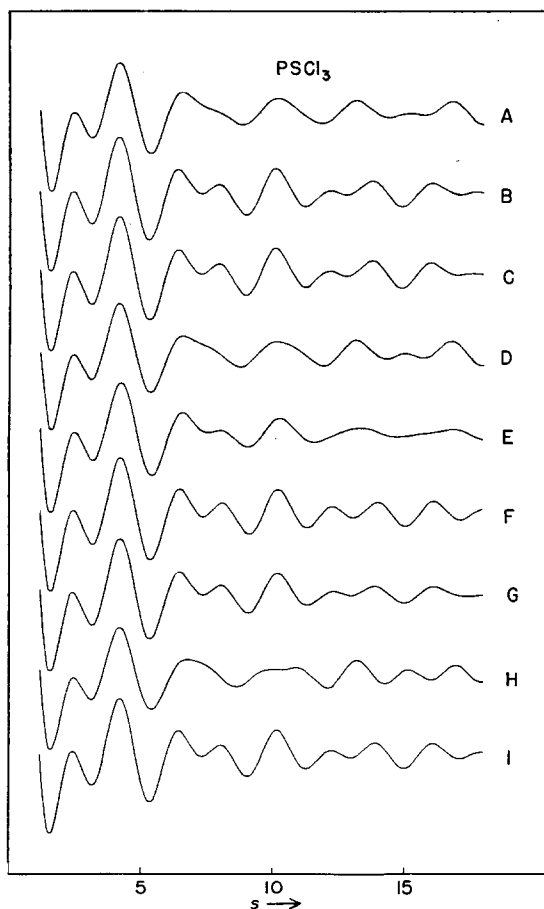


FIG. 3. Theoretical intensity curves for thiophosphoryl chloride. Denoting the Cl-P-Cl angle by α and the ratio of the phosphorus-chlorine distance to the phosphorus-sulfur distance by ρ , the curves are for the following models: curve A, $\alpha=100^\circ$ and $\rho=2.02/1.93$; curve B, $\alpha=105^\circ$ and $\rho=2.02/1.93$; curve C, $\alpha=109^\circ 28'$ and $\rho=2.02/1.93$; curve D, $\alpha=115^\circ$ and $\rho=2.02/1.93$; curve E, $\alpha=100^\circ$ and $\rho=2.02/1.85$; curve F, $\alpha=105^\circ$ and $\rho=2.02/1.85$; curve G, $\alpha=109^\circ 28'$ and $\rho=2.02/1.85$; curve H, $\alpha=115^\circ$ and $\rho=2.02/1.85$; curve I, $\alpha=105^\circ$ and $\rho=2.02/1.89$.

TABLE II. Thiophosphoryl chloride.

MAX.	MIN.	I	s_{obs}	s_{calc}	P-ClA
1	1	14	1.691	1.59	1.899
			2.442	2.43	2.010
			3.388	3.17	1.890
2	2	25	4.238	4.18	1.992
			5.449	5.33	1.976
3	3	17	6.290	6.42	2.062
			7.326	7.29	2.010
4	4	7	8.036	7.98	2.006
			9.132	8.98	1.986
5	5	12	10.12	10.11	2.017
			11.83		
6	6	2	13.19		
				Ave.	2.007

(1st max. and 1st and 2nd min. omitted)

Results: P-Cl $2.01 \pm 0.02\text{\AA}$
P-S $1.94 \pm 0.03\text{\AA}$
Cl-P-Cl angle $107^\circ \pm 3^\circ$.

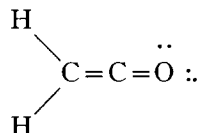
The five term radial distribution function is shown in Fig. 1. In calculating the radial distribution function the sixth maximum was omitted because of the difficulty in measuring it. The peak at 2.02Å represents the phosphorus-chlorine and the phosphorus-sulfur distances unresolved. The peak at 3.27Å represents the chlorine-chlorine and the sulfur-chlorine distances unresolved. The small peak at 1.38Å is without significance.

In calculating theoretical intensity curves the only models considered were those having the symmetry C_{3v} . Having made this assumption—that the three chlorine atoms are equivalent—two parameters are necessary to specify the shape of the molecule. These parameters are taken to be the angle between two phosphorus-chlorine bonds, α , and the ratio of the phosphorus-chlorine distance to the phosphorus-sulfur distance, ρ . Theoretical intensity curves were calculated for models having values of α ranging from 100° to 115° and ρ ranging from 2.02/2.10 to 2.02/1.77. Sixteen curves were calculated. Nine of these are shown in Fig. 3. The top four show the effect of changing α from 100° to 115° keeping ρ constant at 2.02/1.93. The next four show the effect of varying α with ρ constant at 2.02/1.85. Curve I is one of the qualitatively acceptable curves. From the curves shown and other curves it is seen that values of α of 100° or less and 115° or greater are unsatisfactory because of the prominence of the fourth maximum

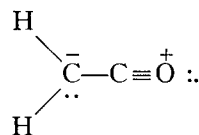
on the photographs. The 105° models are unsatisfactory when ρ is greater than 2.02/2.02 for the same reason. The tetrahedral models are unsatisfactory when ρ is greater than 2.02/2.10 because the average of the chlorine-chlorine and sulfur-chlorine distances is greater than the 3.27 Å required by the radial distribution curve. The tetrahedral and 105° curves are unsatisfactory when ρ is less than 2.02/1.77 because the average of the chlorine-chlorine and sulfur-chlorine distances is less than the 3.27 Å required by the radial distribution curve. All the curves within these limits are qualitatively acceptable. As the most probably correct model we have chosen the one for which α is 107° and ρ is 2.02/1.95. This curve is not shown in Fig. 3 but is practically identical in appearance with curve I. Quantitative comparison of the photographs with the 107° , 2.02/1.95 curve is shown in Table II. The final values are: for the phosphorus-chlorine distance 2.01 ± 0.02 Å, for the phosphorus-sulfur distance 1.94 ± 0.03 Å and for the Cl-P-Cl angle $107^\circ \pm 3^\circ$.

DISCUSSION

The distances found in ketene are not those that would be expected if ketene has the electronic structure



The expected distances for this structure, from Pauling and Brockway's⁶ recent revision of the covalent radius table of Pauling and Huggins,⁷ are 1.34 Å for the carbon-carbon bond and 1.24 Å for the carbon-oxygen bond. It is seen that the carbon-carbon distance is greater and the carbon-oxygen distance is less than expected. This is immediately accounted for by resonance of the molecule between the above structure and the structure

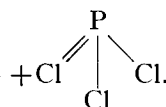


⁶ L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

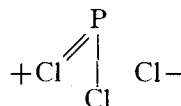
⁷ L. Pauling and M. L. Huggins, Zeits. f. Krist. **A87**, 205 (1934).

It is possible to estimate the extent of the resonance by using the relation between bond type and bond distance given by Pauling, Brockway and Beach⁸ and revised by Pauling and Brockway.⁶ This procedure leads to the result that the structure is three quarters double-bond, double-bond and one quarter single-bond, triple-bond.

The P-Cl distance in PSCl_3 (2.01 Å) is about the same as the P-Cl distance in PCl_3 (2.00 Å) obtained by Brockway and Wall⁹ and Pauling and Brockway.¹⁰ The sum of the single covalent radii for phosphorus and chlorine is 2.09 Å. The shortening of the bond is ascribed by Brockway and Jenkins¹¹ to partial double bond character due to resonance of the molecule to structures of the type



Structures of the type



may also contribute, as suggested by Gregg, Hampson, Jenkins, Jones and Sutton.¹² The possibility that the shortening is due to ionic character of the bonds was eliminated by Brockway and Jenkins by a study of several metal methyls. In these compounds, the atoms of which have greater relative electronegativities than phosphorus and chlorine, the distances are normal. Here, double bond formation cannot occur because of the necessity for observing the octet rule on carbon. It was therefore concluded that the shortening in PCl_3 (and other similar compounds) is due to partial double bond character and not to ionic character. In our discussion of PSCl_3 we shall accordingly assume that ionic character cannot affect the length of the bonds.

⁸ L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **56**, 2706 (1935).

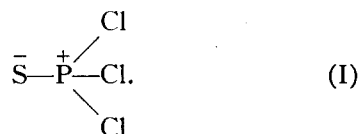
⁹ L. Brockway, and F. T. Wall, J. Am. Chem. Soc. **56**, 2373 (1934).

¹⁰ L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **57**, 2684 (1935).

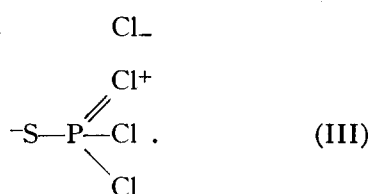
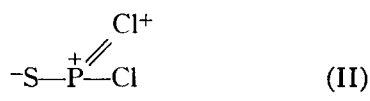
¹¹ L. O. Brockway and H. O. Jenkins, J. Am. Chem. Soc. **58**, 2036 (1936).

¹² A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. F. L. Jones and L. E. Sutton, Trans. Faraday Soc. **33**, 852 (1937).

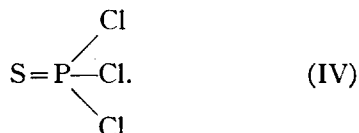
To a first approximation the structure of PSCl_3 is



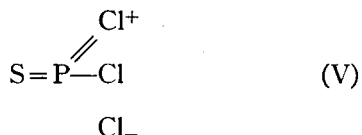
The contributing structures which will tend to shorten the P—Cl bond are of the following type:



Structure (II) will not contribute, however, because of the adjacent charge rule.^{12a} Probably a more important (lower energy) structure, tending to shorten the P—S bond, is



The structure



may also contribute to some extent.

In these last three structures the octet rule is not observed for phosphorus. However, violation of the octet rule in atoms in other than the first row of the periodic table is permissible; for example PF_5 , etc. The structures that shorten the P—Cl bond in PSCl_3 are less numerous and probably less important than the ones for PCl_3 . It is therefore surprising that the P—Cl distance in PSCl_3 is not substantially greater than in PCl_3 . The answer to this question is found in the discussion of the short N—O distance in nitrate

ion given by Elliott.¹³ The short distance is attributed to the resultant positive charge on the nitrogen atom. In the most important structure for PSCl_3 there is a resultant charge of plus one on the phosphorus atom which by analogy with the small radius for nitrogen in nitrate ion leads one to expect a short P—Cl distance in PSCl_3 . This effect apparently just offsets the lack of suitable contributing double P—Cl bond structures mentioned above, leaving the P—Cl distance in PSCl_3 the same as in PCl_3 .

If the electronic structure of PSCl_3 is simply structure (I) written above, the P—S bond being a single bond between oppositely charged atoms; the considerations of Elliott would predict that the bond distance is the single bond distance. The increase in the single bond radius of the negative sulfur atom would be offset by the decrease in the radius of the positive phosphorus atom. That this prediction leads to correct results is seen in the case of a large number of tetrahedral crystals. In these crystals the most important electronic structure, responsible for the tetrahedral orientation of bonds, is one in which bonded atoms have equal and opposite formal charges. In these cases the interatomic distances are observed to be just the interatomic distances for normal valence bonds for which there are no resultant charges on bonded atoms. The observed P—S distance in PSCl_3 is 1.94Å, nearly the same as the double bond distance for this bond (1.95Å). Having ruled out any effect of ionic character and formal charges on the length of this bond, the shortening below the single bond distance must be due to a considerable (about one-half) contribution of structure (III). It is difficult to see how the P—S distance can be less than the double bond distance. This effect is also observed in the case of sulfate and phosphate crystals. In the cases investigated the distance between the central atom of the anion and the oxygen atom is found to be roughly the double bond distance.

We wish to express our appreciation to Professor C. P. Smyth for suggesting that the apparatus be built and for his continued interest in the research.

^{12a} L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **59**, 13 (1937).

¹³ Norman Elliott, *J. Am. Chem. Soc.* **59**, 1380 (1937).