Studies of the Representation of Interatomic Distances in Molecules and Crystals as Sums of Atomic Radii

Thesis by

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Abstract

The electron diffraction investigation of the following compounds has been carried out: sulfur, sulfur nitride, realgar, arsenic trisulfide, spiropentane, dimethyltrisulfide, cis and trans lewisite, methylal, and ethylene glycol.

The crystal structures of the following salts have been determined by x-ray diffraction: silver molybdateand hydrazinium dichloride.

Suggested revisions of the covalent radii for B, Si, P, Ge, As, Sn, Sb, and Pb have been made, and values for the covalent radii of Al, Ga, In, Tl, and Bi have been proposed.

The Schomaker-Stevenson revision of the additivity rule for single covalent bond distances has been used in conjunction with the revised radii. Agreement with experiment is in general better with the revised radii than with the former radii and additivity.

The principle of ionic bond character in addition to that present in a normal covalent bond has been applied to the observed structures of numerous molecules. It leads to a method of interpretation which is at least as consistent as the theory of multiple bond formation.

The revision of the additivity rule has been extended to double bonds. An encouraging beginning along these lines has been made, but additional experimental data are needed for clarification.

I. Ionic and Covalent Radii, and Their Application to the Discussion of Interatomic Distances in Molecules and Crystals.

Introduction.- The concept of atoms as essentially rigid spheres probably originated concurrently with the concept of atoms themselves. It was not possible to apply this concept to the problems of chemistry until the modern methods of structural investigation were developed, although it is evident, for example from the work of Barlow[1], that the now familiar way of representing crystals was not unknown to early investigators. The great activity in the x-ray field which followed the discovery in 1912 of interference phenomena in crystals and its application to structure determination by the Braggs resulted in the accumulation of a large amount of data concerning interatomic distances in numerous crystals. That it should have been possible to introduce some sort of logical explanation to the observed distances was recognized by most of the workers in the field, for example Landé[2], who derived a set of atomic radii for the alkali metals and the halogens on the assumption that in the lithium halides the anions were contiguous, but it was not until 1920, when W. L. Bragg analyzed the available data[3], that a systematic attempt was made to correlate interatomic distances in crystals by assigning values to the radii of the various atoms. This work by Bragg was wholly empirical in its approach and he found that he could not satisfactorily relate the quantities he obtained to the modern developments of the theory of valence which had been proposed some years previously by Lewis[4]. The starting point used by Bragg was the carbon-carbon distance in diamond and the sulfur-sulfur distance in pyrite. Since these values were next used in interpreting the distances in the alkali halides and the alkaline earth oxides, halides, and sulfides, the discrepancies which exist between Bragg's radii and those now commonly accepted arose mainly from the fact that no distinction was then made between the three general extreme types of chemical bonds. Bragg was aware however that some such difficulty existed, for he stated that: "Sodium, for instance, has been given a diameter much larger than that of chlorine, yet it will be seen that there is every reason for supposing that the group of electrons surrounding the sodium nucleus in sodium chloride has smaller dimensions than that surrounding the chlorine nucleus in the same crystal."[3]

Because of their relative simplicity, the alkali halides were generally chosen for subsequent discussions of the properties of crystals which involved the radii of the constituent ions. In 1920 Fajans and Herzfeld[5] developed a theory which connected the potential energy of the crystal and the sizes of the ions; their theory gave the correct values for the compressibilities, but the radii they obtained in this way were not consistent with the distances in other types of crystals. Grimm[6] in 1921 modified and extended the work of Fajans and Herzfeld, and obtained a set of ionic radii by consideration of the molecular volumes of isomorphous compounds and various other physical properties. Both of the above discussions were based on the cubical model of the atom, now considered unsatisfactory.

Additional examples of the methods which were used are found in the work of Eve[7], Saha[8], and Richards[9]. Saha explained, on the basis of the old quantum theory, a relation pointed out by Eve which stated that the product of the ionization potential and the atomic radius is constant. The radii calculated by the Saha formula are considerably in error. Richards calculated the radii of the atoms in the alkali halides, making use of compressibility data. He too based his interpretation of the data on the cubical atom, and moreover did not consider the change in bond type which occurs in the reaction of the free elements to form salts.

A considerably more accurate set of radii was then given by Wasastjerna[10] who had done a large amount of work on ionic refractivity; on certain theoretical grounds he related refraction equivalents to ionic volumes and hence ionic radii. These values are perhaps more significant than those mentioned above because Wasastjerna was interested primarily in the prediction of interatomic distances in crystals, comparing his values with those observed in various substances. The values of Wasastjerna were then refined by Goldschmidt[11] who also determined, from the available x-ray data, empirical values for a large number of additional radii.

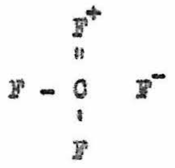
In spite of the great amount of effort expended on this subject in the years 1920 to 1926, only a part of which has been referred to above, no completely satisfactory set of radii for use in interpreting crystal structure data was formulated, for the simple reason that even in the simplest salts, the alkali halides, the interatomic distances do not satisfy the criterion of additivity which had been tacitly assumed in all of the foregoing. Another, and probably more important reason for this failure was the underlying principle used by most of the investigators, viz., the derivation of atomic radii from one particular property of the crystals under examination. Thus, Bragg made use of x-ray data, Fajans and Herzfeld, potential energy relationships, Saha, ionization potentials, Wasastjerna, mole refractions, and so on. A far more logical procedure is to assign radii which, with sound theoretical refinements, will account satisfactorily for all of the observed properties of the crystals. Although this method is difficult if not impossible in practice, a practical approach to it is capable of being carried out. This was done by Pauling[12] in 1927.

The experimental basis of Pauling's radii is the observed interatomic distances in the five crystals, NaF, KCl, RbBr, CsI, and Li_2O. From these were calculated, by the use of theoretical screening constants and coulomb repulsive coefficients, a set of crystal radii. Suitable considerations allow these radii to be used in the different types of structures involving varying environments of the ions. Agreement between observed and calculated interatomic distances and other quantities is in general very good[13].

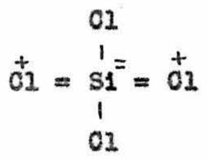
The cognizance that the radius of an atom is dependent on the type of bonding was more or less gradual during this period. Since most of the data which were being examined were obtained from the results of x-ray examination of ionic crystals, little or no difficulties were encountered. Some radii for use in predicting covalent bond distances were given in 1926 by Huggins[14], although Huggins himself applied these radii to the ionic fluorite-type crystals also. The stipulation that ionic radii should be used only for ionic bonds was made by Goldschmidt[11] and by Pauling[12]. By 1934 sufficient additional data had been obtained to allow Pauling and Huggins[15] to set up a table of covalent radii for use in predicting the lengths of single and multiple bonds between atoms in various covalent configurations, namely, tetrahedral, square, and octahedral.

The Pauling-Huggins table, as corrected in 1937 by Pauling and Brockway[16] has been widely used in the interpretation of experimental values of interatomic distances, by the application of the resonance principle, double bond character, and so forth. It is perhaps unfortunate that in general the discussions of the bond type in a molecule were usually based upon but one experimental quantity, the interatomic distance. The explanation of anomalous distances in a wide variety of compounds was nevertheless based on the deviations from the distances predicted by the Pauling-Huggins radii, which were considered to give the normal distances.

In the majority of cases in which anomalously short distances have been observed the discussion rested upon the contribution to the normal state of the molecule of structures involving multiple bonds. Thus, in the fluorinated methanes and the chlorinated silanes the structures



$$\begin{array}{ccc} & F^{+} & \\ & \| & \\ F - & C & F^{-} \\ & | & \\ & F & \end{array}$$



$$\begin{array}{ccccc} & & Cl & & \\ & & | & & \\ \overset{+}{Cl} & = & Si^{=} & = & \overset{+}{Cl} \\ & & | & & \\ & & Cl & & \end{array}$$

and many others similar to these were suggested. It was then possible to explain the trends observed in such series as CF_xCl_{4-x}, SiH_xCl_{4-x}. Most of the discussions, exemplified by the work of Brockway and coworkers in the period following the publication of the Pauling-Huggins radii, made use of this explanation. An alternative suggestion, that of significant ionic character of the bonds, was considered as being of only secondary importance by these workers.

Although most of the experimental data could be discussed on a consistent basis by the application of the above principle, there remained a major defect in the Pauling-Huggins table, its inability to predict accurately the lengths of bonds between the very electronegative atoms, F, O, N, and Cl, as illustrated in Table 1.

Table 1

bond	compound	obs. distance*	calc. distance
F-O	FNO_3	1.42	1.30
	OF_2	1.41	1.30
F-F	F_2	1.45	1.28
O-O	H_2O_2	1.47	1.32
N-O	CH_3ONH_2	1.43	1.36
N-Cl	$(CH_3)_2NCl$	1.77	1.69
Cl-O	Cl_2O	1.68	1.65

*The units of distance are Å in this and all subsequent tables.

The suggestion that the radii are in error and that agreement could be achieved with revised radii might be proferred, but this view is scarcely tenable since the data indicate that often, even in the simplest cases, the additivity rule is not obeyed. For example:

$\frac{1}{2}$F-F(in fluorine) + $\frac{1}{2}$C-C(in diamond) = 1.49

$\frac{1}{2}$C-C + $\frac{1}{2}$O-O(in hydrogen peroxide) = 1.50

$\frac{1}{2}$Cl-Cl(in chlorine) + $\frac{1}{2}$Si-Si(in silicon) = 2.16

whereas the observed values of C-F, C-O, and Si-Cl in methyl fluoride, methylal, and chlorosilane are 1.36, 1.43, and 2.06 respectively. This state of affairs need not surprise us, since an analogous situation was found to prevail in the case of the distances in ionic crystals. It might therefore be expected that suitable refinements of a similar nature might bring about a satisfactory basis for discussion of the distances in molecules also.

Many of these discrepancies were removed by the suggestion of Schomaker and Stevenson[17] that the additivity rule be replaced by the relation

$$r_{AB} = r_A + r_B - 0.09 \left| x_A - x_B \right| \; .$$

where x_A is the electronegativity and r_A the radius of the atom A. The final term corrects for the extra ionic character of the bond A-B. Simultaneously, Schomaker and Stevenson gave revised values for the radii of F, O, and N. It thus appears that the agreement obtained by the use of the former radii and the additivity rule was largely fortuitous in the case of bonds (other than those in Table 1) involving these three elements, especially since Pauling and Huggins used the inappropriate value of Gale and Monk[17] for the fluorine-fluorine distance in fluorine.

In 1944 Skinner and Sutton[18] pointed out that a straightforward explanation of the small but progressive contraction which occurs in the bond lengths when more halogens are added to the central atom in the halides of the fourth and fifth group elements is difficult in terms of either bond multiplicity, as was done by Brockway, or ionic character of bonds. They concluded that, contrary to the previous prevalent opinion, the latter effect was the more important, since the multiple bond theory leads in some cases to direct contradiction with experiment.

Since the notion of ionic character is going to be more fully explored in subsequent sections of this Thesis, it is perhaps important to give in full one of the points raised by Skinner and Sutton: "In its original simple form, the theory [of multiple bond formation] took no account of the effects of charge distribution to which this process would give rise. Each coordinate link [double bond] from a halogen atom to the central atom increases the negative charge on the latter [see above structures] . Now if the formation of these multiple bonds by each halogen were to be more favoured the more halogen atoms there are, this would mean that the more negative charge the central atom has, the more it wants. The exact opposite would, however, be expected."

Skinner and Sutton did not favor the Schomaker-Stevenson revision of the additivity rule. In fact, they did not attempt a discussion of absolute bond distances, being interested mainly in the changes which are observed in series of the type $Sn(CH_3)_xCl_{4-x}$.

Many of the distances calculated by the Schomaker-Stevenson relation are still discrepant. In the following sections we shall attempt to remove these discrepancies by a logical extension of the application of their relation. It is found that this procedure necessitates the revision of additional of the covalent radii, as will be seen.

A. Revisions of Covalent Radii and the Ionic Character of Single Covalent Bonds

The values of Pauling and Huggins (PH) for the single bond covalent radii were taken from the interatomic distances in the elementary substances, with the exception of derived radii for N, O, and F. The revised values of Schomaker and Stevenson (SS) were obtained from interatomic distance determinations of N_2H_4, H_2O_2, and F_2. If, as seems likely, the equation of Schomaker and Stevenson is significant, then further revisions in the table must be made.

Let us calculate a set of single bond radii on the basis of the Schomaker-Stevenson relation, using the experimental interatomic distances in the compounds $M(CH_3)_n$; the radii for the four halogens however will be taken as half the separation in the gaseous elements. The results of these calculations are presented in Table 2, together with the two previous sets of radii for comparison. The electronegativities in the compilation of Gordy[19] were used in the calculations.

Table 2

Covalent Radii for Atoms

	H 0.36 .30 .37			
B 0.85 .88	C 0.77 .77 .77	N 0.74 .70 .74	O 0.73[a] .66 .74	F 0.72 .64 .72
Al 1.33	Si 1.19 1.17 1.17	P 1.14 1.10 1.10	S 1.04 1.04 1.04	Cl 0.99 .99 .99
Ga 1.38[b]	Ge 1.28 1.22 1.22	As 1.26 1.21 1.21	Se 1.17[b] 1.17 1.17	Br 1.14 1.14 1.14
In 1.49	Sn 1.48 1.40 1.40	Sb 1.45[b] 1.41 1.41	Te 1.37[b] 1.37 1.37	I 1.33 1.33 1.33
Tl 1.61[b]	Pb 1.61 1.46	Bi 1.58[b]		

The upper values are the radii as revised in this work; in many cases no revision was required. The second values are the Pauling-Huggins radii, the third values the Schomaker-Stevenson radii.

[a] The revision of r_0 from the original Schomaker-Stevenson value of 0.74 was suggested by Giguere and Schomaker[20].

[b] No determination of interatomic distances in the methyl derivatives of these elements has been reported. The radii given were obtained from other compounds, the corrections from the older radii being suggested by analogy with other elements in the same group.

The Pauling-Huggins radii for P and As, which are 0.04 and 0.05 smaller than those in the new table, were obtained from the tetrahedral molecules P_4 and As_4. Since recent experiments on spiropentane (see part II of this Thesis) have suggested that the bond distances in highly strained molecules may be shorter than those in normal molecules, it is not surprising to find this effect present in these molecules. Some support is lent to this view by the results of Fourier analysis of x-ray data obtained from several of the forms of phosphorus[21], which indicate a phosphorus-phosphorus distance of 2.28, exactly twice the phosphorus radius derived above, in both the "amorphous" and crystalline forms of red and black phosphorus, neither of which consists of P_4 molecules. Moreover, in crystalline arsenic, which likewise does not consist of As_4 molecules, the arsenic-arsenic separation is 2.51[22], within 0.01 of twice the new radius.

The inappropriateness of some of those Pauling-Huggins values which were derived from x-ray determinations on the crystalline elements is suggested by the difference of 0.05 between the sulfur-sulfur distances in gaseous and solid S_8, the value in rhombic sulfur being 2.12, and in gaseous sulfur, 2.07. It is possible that the proximity of the atoms of neighboring molecules in crystalline elements weakens the bonds somewhat. At any rate, the cause of this effect does not concern us: we need only be aware of its presence.

We shall now make extensive comparisons of observed and calculated interatomic distances in order to test exhaustively the usefulness of the various sets of radii and the revision of the additivity rule. In the cases where no revision of the Schomaker-Stevenson radii was made, only the new radii and the Pauling-Huggins radii are used in the comparison. In fact, the present discussion may be regarded as a critical survey of the applicability of the equation of Schomaker and Stevenson.

1. Hydrides

The comparison of observed and calculated distances for fifteen hydrides is presented in Table 3.

Table 3

Interatomic Distances in Hydrides

bond	obs. distance in MH_n	calc. distance this work	PH	SS
H-H	0.74	0.72	0.60	0.74
B-H	1.20[a]	1.19	1.18	
C-H	1.09	1.09	1.07	1.10
N-H	1.01	1.02	1.00	1.03
P-H	1.45	1.50	1.40	1.47
As-H	1.56	1.61	1.51	1.57
O-H	.96	.96	.96	.98
S-H	1.33	1.36	1.34	1.37
Se-H	1.53	1.50	1.47	1.51
F-H	.92	.91	.94	.92
Cl-H	1.28	1.27	1.29	1.28
Br-H	1.41	1.44	1.44	1.45
I-H	1.60	1.66	1.63	1.67
average deviation from obs.		0.024	0.035	0.021

[a] in BH_3CO

The revised radii are apparently somewhat less accurate than the Schomaker-Stevenson radii for this set of compounds. Both revised sets give better agreement than the original Pauling-Huggins set and additivity.

2. Halogen Compounds

(a) Monohalides

The comparison of observed and calculated distances for fourteen monohalides is presented in Table 4.

Table 4

Interatomic Distances in Monohalides

bond	compound	obs. distance	calc. distance		
			this work	PH	SS
C-F	CH_3F	1.39	1.36	1.41	1.35
C-Cl	CH_3Cl	1.77	1.72	1.76	1.72
C-Br	CH_3Br	1.90	1.89	1.91	1.89
N-Cl	$N(CH_3)_2Cl$	1.77	1.73	1.69	1.73
F-Cl	ClF	1.64	1.62	1.63	1.62
Si-Cl	SiH_3Cl	2.06	2.07	2.16	2.05
Cl-I	ICl	2.32	2.28	2.32	2.28
As-Cl	$As(CH_3)_2Cl$	2.18	2.16	2.20	2.11
As-Br	$As(CH_3)_2Br$	2.34	2.33	2.35	2.28
As-I	$As(CH_3)_2I$	2.52	2.55	2.54	2.50
Sn-Cl	$Sn(CH_3)_3Cl$	2.37	2.35	2.39	2.27
Sn-Br	$Sn(CH_3)_3Br$	2.49	2.53	2.54	2.45
Sn-I	$Sn(CH_3)_3I$	2.72	2.74	2.73	2.66
	average deviation from obs.		0.026	0.028	0.045

From these data it is apparent that, if the Schomaker-Stevenson revision of the additivity rule has any validity for correcting the discrepancies which suggested it, the revised radii should be used. The agreement they give in the case of the arsenic and tin compounds is very much improved.

(b) Trihalides of the Fifth Group Elements

The comparison of observed and calculated distances for the compounds MX_3 is presented in Table 5.

Table 5

Interatomic Distances in the Fifth Group Trihalides

bond	obs. distance	calc. distance		
		this work	PH	SS
N-F	1.37	1.37	1.34	1.37
P-F	1.56	1.69	1.74	1.65
P-Cl	2.03	2.05	2.09	2.01
P-Br	2.20	2.22	2.24	2.18
P-I	2.45	2.44	2.43	2.40
As-F	1.72	1.80	1.85	1.75
As-Cl	2.16	2.16	2.20	2.11
As-Br	2.33	2.33	2.35	2.28
As-I	2.54	2.55	2.54	2.50
Sb-Cl	2.37	2.33	2.40	2.29
Sb-Br	2.50	2.50	2.55	2.46
Sb-I	2.71	2.72	2.74	2.68
Bi-Cl	2.48	2.46		
Bi-Br	2.63	2.63		
average deviation from obs.		0.026	0.055	0.042

In this case the revised radii are much superior to either of the old sets. The discrepancies for PF_3 and AsF_3 are rather large with all three sets. This point is discussed in the following section.

(c) Polyhalides of the Fourth Group Elements

Considerable work has been done on the fourth group halides. The data are presented in Table 6.

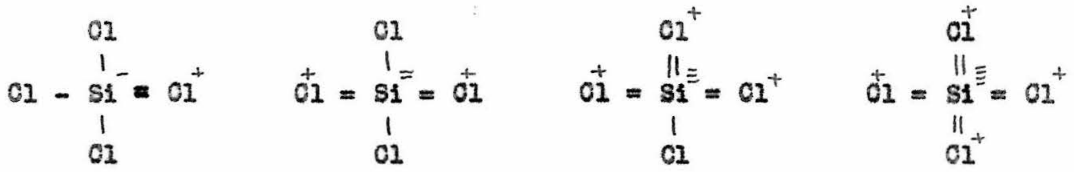
Table 6

Interatomic Distances in Fourth Group Halides

	obs. distance in:				calc. distance		
bond	MX_4	MCH_3X_3	$M(CH_3)_2X_2$	$M(CH_3)_3X$	this work	PH	SS
C-F	1.36		1.36[a]	1.39[a]	1.36	1.41	1.36
C-Cl	1.76	1.78	1.77[a]	1.77	1.72	1.76	1.72
C-Br	1.91	1.91[a]	1.91[a]	1.90[a]	1.89	1.91	1.89
C-I	2.12	2.12[a]			2.09	2.10	2.09
Si-F	1.54				1.72	1.81	1.70
Si-Cl	2.00	2.01[a]	2.02[a]	2.06[a]	2.07	2.16	2.05
Si-Br	2.15	2.16[a]			2.24	2.31	2.22
Si-I	2.43				2.46	2.50	2.44
Ge-Cl	2.08				2.15	2.21	2.09
Ge-Br	2.29				2.33	2.36	2.27
Ge-I	2.50				2.54	2.55	2.48
Sn-Cl	2.29	2.32	2.34	2.37	2.35	2.39	2.27
Sn-Br	2.44	2.45	2.48	2.49	2.53	2.54	2.45
Sn-I	2.64	2.68	2.69	2.72	2.74	2.74	2.66
Pb-Cl	2.43				2.46	2.45	

[a] CH_3 replaced by H

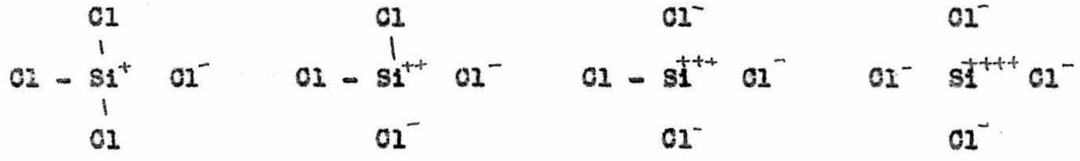
The distances in the polyhalides, except those of carbon, are shorter than both the distances in the corresponding monohalides and the calculated distances. This shortening has been discussed in terms of double bond character, structures like the following being assumed to contribute to the state of the molecule[23]:



Since stable d orbitals are not available to the carbon atom, no such effect is possible in the carbon polyhalides.

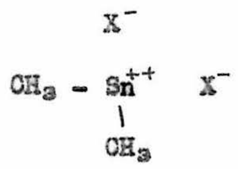
Several objections may be offered to the above interpretation: 1) It requires an unreasonably large amount of multiple bond character in SiF_4. 2) It does not account for the gradual shortening of the tin-halogen bonds in the stannic polyhalides inasmuch as the conclusion that bromine and iodine have small power of double bond formation follows from the interpretation. 3) It requires that structures in which the halogen atoms have a positive formal charge contribute to the state of the molecule, a condition which seems rather improbable.

A second class of contributing structures, discussed with the above[23] is

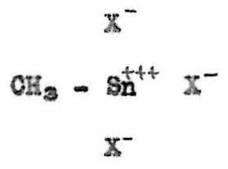


If these structures are considered the only important ones, a reasonable explanation may be offered (cf. ref. 18). The bonds in $(CH_3)_3SnX$, for example, are considered as normal, and the contribution of $(CH_3)_3Sn^+X^-$

is taken into account by the Schomaker-Stevenson correction term. But in $(CH_3)_2SnX_2$ and $(CH_3)SnX_3$, the following situation may prevail:



$$\begin{array}{ccc} & X^- & \\ CH_3 - & Sn^{++} & X^- \\ & \backslash & \\ & CH_3 & \end{array}$$



$$\begin{array}{ccc} & X^- & \\ CH_3 - & Sn^{+++} & X^- \\ & X^- & \end{array}$$

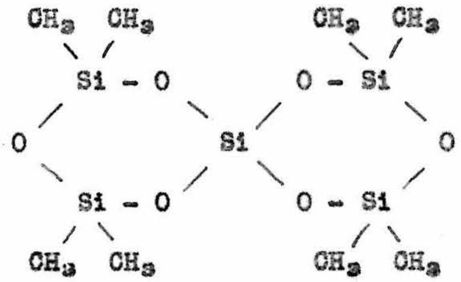
The removal of electrons not only reduces the radius of the central atom, but the resulting opposite charges would tend to draw the negative atoms in closer, by simple coulomb attraction. The second effect is apparently far more important than the first, since the C-Sn distance is the same in $(CH_3)_4Sn$ and $(CH_3)_3SnX$, X = Cl or Br.

It is possible, with this scheme, for the carbon compounds to exhibit the same effect. The reason that it is not observed may follow from the fact that the X...X distances in CX_4 are already much less than the van der Waals diameters, making additional shortening impossible.

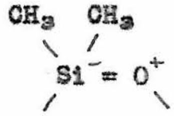
The shortening in the fluorides would thus be expected to be the greatest, as is observed. The trihalides of the fifth group elements, with the exception of PF_3 and AsF_3, show normal distances, a condition corresponding to little or no additional ionic character to the bonds.

Electron diffraction investigations of the compounds $Si(CH_3)_nX_{n-4}$ and $Ge(CH_3)_nX_{n-4}$ would provide a valuable check on the above interpretation.

Additional evidence against the formation of multiple bonds is to be found in the recent x-ray investigation of the crystal structure of octamethylspiro[5.5]pentasiloxane[24]:



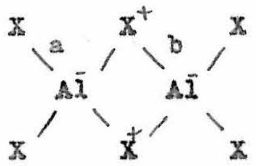
The preliminary results indicate that free rotation of the $Si(CH_3)_2$ groups occurs, the silicon atom being free to move in the ring, "as in a ball and socket joint." Structures such as



would certainly be expected to inhibit rotation to an even greater extent than the normal valence bond structure.

(d) Halides of the Third Group Elements

The halides of aluminum are dimeric, with two types of Al-X distances:



Comparison of observed and calculated distances is shown in Table 7.

Table 7

Interatomic Distances in Aluminum Halides

	obs. distance		calc. distance	
bond	a	b	this work	PH*
Al-Cl	2.06	2.21	2.18	2.25
Al-Br	2.21	2.33	2.36	2.40
Al-I	2.53	2.58	2.57	2.59

*Calculated by the use of the Pauling-Huggins tetrahedral radius for aluminum.

The distances b are longer than the distances a, just the reverse of what is expected on the basis of the new interpretation. The structures of the Al_2X_6 molecules were determined on the assumption that the bonds are predominantly ionic -- under which assumption the quoted results were obtained. There may be some doubt, however, concerning the correctness of the assumption. It is generally observed that tetrahedra do not share edges except in the case of covalent complexes; for example, the ionic character of the silicon-sulfur bond is about the same as that of an aluminum-iodine bond, and crystalline SiS_2 consists of SiS_4 tetrahedra with shared edges. Incidentally, the observed Si-S distance in SiS_2, 2.14, is in satisfactory agreement with the calculated value of 2.16 (Pauling-Huggins radius sum, 2.21). It is possible that models of the Al_2X_6 molecules with distances b shorter than distances a could be constructed to give agreement with the observed electron diffraction data.

The distances reported for the trihalides of gallium and indium, the structures of which are in doubt, are compared with the calculated distances in Table 8.

Table 8

Interatomic Distances in Gallium and Indium Trihalides

bond	obs. distance	calc. distance this work	 PH*
Ga-Cl	2.22	2.23	2.24
Ga-Br	2.34, 2.41	2.40	2.40
Ga-I	2.50	2.62	2.59
In-Cl	2.46	2.34	2.43
In-Br	2.58	2.51	2.58
In-I	2.76	2.73	2.77

*Calculated by the use of the Pauling-Huggins tetrahedral radii for gallium and indium

In this case the interpretation is rendered difficult by the large uncertainties which must be ascribed to the observed distances. The agreement in the case of GaI_3 is especially poor. On the other hand, the values of In-X in the diatomic indous halides calculated by Stevenson[25], viz., In-Cl = 2.39, In-Br = 2.53, and In-I = 2.72, are in good agreement with the calculated values.

The observed values in the thallous halides, Tl-Cl = 2.55, Tl-Br = 2.68, and Tl-I = 2.87 are in only fair agreement with the calculated values of 2.45, 2.62, and 2.84 respectively. The Pauling-Huggins radius sums are 2.46, 2.61, and 2.80.

(e) Halides of the Sixth Group Elements

The observed and calculated distances in the sixth group dihalides are presented in Table 9.

Table 9

Interatomic Distances in Sixth Group Dihalides

bond	obs. distance	calc. distance this work	calc. distance PH
O-F	1.41	1.40	1.30
O-Cl	1.68	1.68	1.65
S-Cl	1.99	1.99	2.03
Se-Cl	2.13	2.11	2.16
Te-Cl	2.36	2.28	2.36
Te-Br	2.49	2.45	2.51
average deviation from obs.		0.028	0.040

Again the agreement is better with the revised radii. The data suggest that the experimental value for $TeCl_2$ may be in error.

3. Boron Compounds

The available data for various boron compounds are presented in Table 10.

Table 10

Interatomic Distance in Boron Compounds

			calc. distance	
bond	compound	obs. distance	this work	PH
B-B	CaB_6	1.72	1.70	1.76
B-H	BH_3CO	1.20	1.19	1.18
	B_5H_9	1.17	1.19	1.18
B-F	$B(CH_3)_2F$	1.29	1.39	1.52
	BCH_3F_2	1.30		
	BF_3	1.30		
B-Cl	BCL_3^{l}	1.74	1.74	1.87
B-Br	BBr_3	1.87	1.91	2.02
B-Al	$Al(BH_4)_3$	2.14	2.14	2.14
B-O	$B(OCH_3)_3$	1.38	1.44	1.54
	average deviation from obs.		0.031	0.093

For this set of compounds the Pauling-Huggins radii are in such great disagreement that a special discussion was made in explanation[26]. On the new basis, no such explanation is necessary, although the discrepant values for B-F and B-O remain. The series $B(CH_3)_nF_{n-3}$ shows no trend of shortening such as is observed for the methyl halides of the fourth group elements. A more extended discussion of the problem of the radius of boron and the applicability of the Schomaker-Stevenson relation to boron compounds has been made by Bauer and Beach[27].

B. Double Bonds

If the Schomaker-Stevenson equation is valid for single bonds, a relation of similar form might be expected to hold for multiple bonds. In this section a discussion of double bonds is developed. It might be possible to extend the treatment to triple bonds also, but the experimental data for molecules with triple bonds are too meager to determine whether the treatment is of value in the discussion of molecular structure.

Experimental double bond distances are available only for C = C (1.35 in ethylene), N = N (1.24 in azobenzene), and O = O (1.21 in aldehydes). The determination of the interatomic distances in compounds containing C = N bonds or N = O bonds would be of great value in settling some of the questions which arise in the discussion of double bond radii. The electron diffraction investigation of several of the simpler oximes such as formaldoxime and acetaldoxime would afford a direct measurement of the C = N distance.

The dependence of interatomic distances on resonance between single bond and double bond structures has been discussed in detail by Pauling, Brockway, and Beach[28]. The equation which relates interatomic distance with double bond character is

$$r = r_s - (r_s - r_d)\,\frac{3x}{2_x + 1}$$

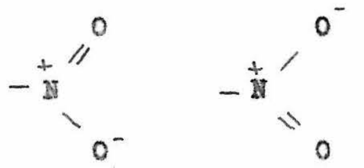
where r_s and r_d are the distances for pure single and double bonds respectively, and x is the amount of double bond character. Thus, the carbon-carbon distances in benzene ($x = \frac{1}{2}$) and graphite ($x = \frac{1}{3}$) are predicted to be 1.38 and 1.41 respectively, which compare well with the observed values of 1.39 and 1.41. Similarly, the carbon-oxygen distance in the carboxyl group ($x = \frac{1}{2}$) and the carbonate ion ($x = \frac{1}{3}$) are predicted to be 1.26 and 1.30, the observed values being 1.26 and 1.31.

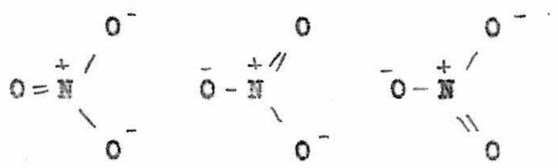
A plausible C = N distance of 1.25 may be calculated with the above equation and the carbon-nitrogen distance in melamine ($x = \frac{1}{2}$). The C = N distance which is calculated assuming additivity is 1.28. Now, if the lengths of double bonds follow the same law as do single bonds, we have:

$$1.25 = 1.28 - k\Delta x$$

from which we obtain k = 0.07. The double bond radius of oxygen of 0.61 can then be calculated from the observed C = O distance of 1.21 in aldehydes. We then obtain 1.22 for O = O and 1.20 for N = O.

Accurate experimental values are available for the nitrogen-oxygen distances in the nitro group and in the nitrate ion. They are 1.22 and 1.21 respectively. The resonating structures of these groups are





so that the respective values of x are $\frac{1}{2}$ and $\frac{1}{3}$, leading to calculated distances of 1.26 and 1.29. However, in both groups there are bonds with ionic character over and above that corrected for by the Schomaker-Stevenson rule. There are twice as many such bonds in the nitrate ion as in the nitro group, so that the observed deviation of -0.04 in the latter case and of -0.08 in the former supports the conclusion reached in the consideration of the fourth group halides, that additional ionic character shortens the bonds.

The nitrogen-oxygen distance in the nitrite ion, which resonates between the two structures

is predicted to be 1.26; the reported distance is 1.14 ± 0.2[29].

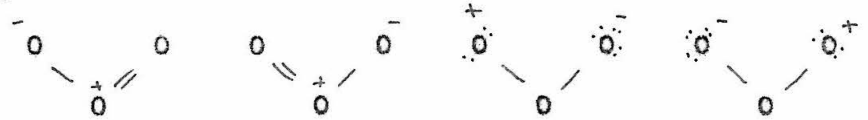
The distances observed in the methyl nitrite molecule are: C - O = 1.44, N - O = 1.37, and N = O = 1.22. These indicate that resonance occurs between the structures:

$CH_3 - O - N = O$ $\qquad$ $CH_3 - \overset{+}{O} = N - \overset{-}{O}$

A $\qquad$ B

Structure B would be expected to contribute only a small amount to the ground state. The distance predicted for $\frac{7}{8}$A, $\frac{1}{8}$B are N - O = 1.37, N = O = 1.21.

The oxygen-oxygen distance in ozone, which has the following resonating structures[30]

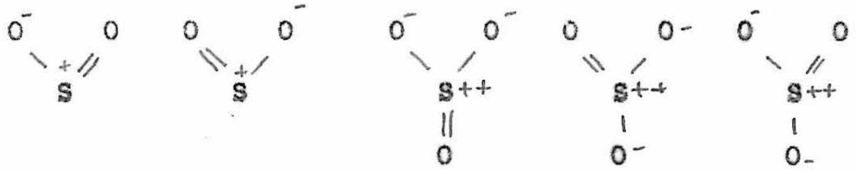


is predicted, on the basis of $x = \frac{1}{2}$ and an extra ionic character correction of -0.06 (intermediate between those observed in $-NO_2$ and NO_3^-), to be 1.26, in excellent agreement with the observed value, 1.26.

Since no revision of the double bond radius of carbon has been made, the previous interpretations of the distances in aromatic hydrocarbons remains unaltered.

The observed internuclear separation in the oxygen molecule is 1.21, close to twice the double bond radius obtained above. This suggests that half the interatomic distance in the S_2 molecule may be taken as a good approximation to the sulfur double bond radius, since both O_2 and S_2 have the ground state ${}^3\Sigma$. The distance predicted for O=S is then 1.61, in satisfactory agreement with the observed distance of 1.64 in thiourea. The distance observed in SO, 1.49, is in good agreement with the calculated value of 1.49.

The observed distances in SO_2 and SO_3, which have the following structures:



are the same, 1.43. Calculated distances for $x = \frac{1}{2}$ and $\frac{1}{3}$ are 1.54 and 1.57 respectively. The corrections due to extra ionic character are greater than those observed in NO_2 and NO_3^-, as might be expected from the greater electronegativity difference in the sulfur oxides.

Addendum: After the above section on multiple bonds was essentially completed, a paper by Gordy[31] was published in which many of the above conclusions were reached. Gordy also extended the Schomaker-Stevenson equation to double bonds, obtaining 0.06 for the value of k, as compared with the value 0.07 obtained above. A comparison of the double bond radii of Gordy, Pauling-Huggins-Brockway, and this work appears in Table 11.

Table 11

Values Proposed for Double Bond Radii

	this work	PHB	Gordy
C	0.675	0.665	0.675
N	.62	.60	.62
O	.61	.55	.604
F	-	.54	.60
S	.94	.94	.94

Summary

1. Suggested revisions of the covalent radii for B, Si, P, Ge, As, Sn, Sb, and Pb have been made, and values for the covalent radii of Al, Ga, In, Tl, and Bi have been proposed.

2. The Schomaker-Stevenson revision of the additivity rule for single covalent bond distances has been used in conjunction with the revised radii. Agreement with experiment is in general better with the revised radii than with the former radii and additivity.

3. The principle of ionic bond character in addition to that present in a normal covalent bond has been applied to the observed structures of numerous molecules. It leads to a method of interpretation which is at least as consistent as the theory of multiple bond formation.

4. The revision of the additivity rule has been extended to double bonds. An encouraging beginning along these lines has been made, but additional experimental data are needed for clarification.

Conclusion

The application of certain principles differing from the original method of Pauling and Huggins which was extended and widely applied by Brockway has, I believe, led to better agreement and more consistent interpretation of interatomic distances in molecules. In order to simplify the exposition of these principles I have based my discussion almost solely upon them without introducing the complication of applying the former method simultaneously in the cases where it is almost certainly demanded by the data. Nevertheless I believe that the success of the new principles is great enough to warrant their serious consideration in future discussions of molecular structure.

Sources of Interatomic Distances Used in the Tables

References to the literature for each of the compounds in the respective tables are given in the following table. The designations M and W refer respectively to the compilations of L. R. Maxwell, J. Opt. Soc. America 30, 374 (1940) and G. W. Wheland, "The Theory of Resonance," Wiley and Sons, New York, 1944, p. 286 ff. No attempt has been made to cite the original reference for each compound.

Table 1

compound	reference
FNO_2	M
OF_2	M
F_2	ref.17
H_2O_2	ref.20
CH_3ONH_2	ref.17
$(CH_3)_2NCl$	W
Cl_2O	M

Table 2

CH_4	
$B(CH_3)_3$	M
$C(CH_3)_4$	M
$N(CH_3)_3$	M
$O(CH_3)_2$	M
F_2	ref.17
$Al_2(CH_3)_6$	ref.32
$Si_2(CH_3)_6$	ref.32
$P(CH_3)_3$	M
$S(CH_3)_2$	M
Cl_2	M
$Ge(CH_3)_4$	M
$As(CH_3)_3$	M
Br_2	M
$In(CH_3)_3$	ref.33
$Sn(CH_3)_4$	M
I_2	M
$Pb(CH_3)_4$	M

Table 3

H_2	ref.13, p.168
BH_3CO	M
CH_4	ref.19
NH_3	ref.19
PH_3	ref.19
AsH_3	ref.19
H_2O	ref.19
H_2S	ref.19
H_2Se	ref.19
HF	ref.19
HCl	ref.19
HBr	ref.19
HI	ref.19

Table 4

$B(CH_3)_2F$	ref.34
CH_3F	W
CH_3Cl	W
CH_3Br	M
$N(CH_3)_2Cl$	W
ClF	ref.17
SiH_3Cl	M
ICl	M
$As(CH_3)_2Cl$	ref.18
$As(CH_3)_2Br$	ref.18
$As(CH_3)_2I$	ref.18
$Sn(CH_3)_3Cl$	ref.18
$Sn(CH_3)_3Br$	ref.18
$Sn(CH_3)_3I$	ref.18

Table 5

NF_3	ref.35
PF_3	ref.36
PCl_3	ref.37
PBr_3	ref.37
PI_3	ref.37
AsF_3	ref.13, p.234
$AsCl_3$	ref.13, p.234
$AsBr_3$	ref.13, p.234
AsI_3	ref.13, p.234
$SbCl_3$	ref.13, p.234
$SbBr_3$	ref.13, p.234
SbI_3	ref.13, p.234
$BiCl_3$	M
$BiBr_3$	M

Table 6

CF_4	W
CH_2F_2	W
CH_3F	ref.17
CCl_4	W
CCH_3Cl_3	M
CH_2Cl_2	W
$C(CH_3)_3Cl$	W
CBr_4	W
$CHBr_3$	W
CH_2Br_2	W
$C(CH_3)_3Br$	W
CI_4	M
CHI_3	W
SiF_4	M
$SiCl_4$	M

Table 6 continued

$SiHCl_3$	M
SiH_2Cl_2	M
SiH_3Cl	M
$SiBr_4$	ref.38
$SiHBr_3$	ref.38
$GeCl_4$	M
$GeBr_4$	ref.39
GeI_4	ref.39
$SnCl_4$	M
$SnCH_3Cl_3$	ref.18
$Sn(CH_3)_2Cl_2$	ref.18
$Sn(CH_3)_3Cl$	ref.18
$SnBr_4$	ref.39
$SnCH_3Br_3$	ref.18
$Sn(CH_3)_2Br_2$	ref.18
$Sn(CH_3)_3Br$	ref.18
SnI_4	M
$SnCH_3I_3$	ref.18
$Sn(CH_3)_2I_2$	ref.18
$Sn(CH_3)_3I$	ref.18
$PbCl_4$	ref.39

Table 7

Al_2Cl_6	M
Al_2Br_6	M
Al_2I_6	M

Table 8

$GaCl_3$	ref.40
$GaBr_3$	ref.40
GaI_3	ref.40
$InCl_3$	ref.40
$InBr_3$	ref.40
InI_3	ref.40
TlCl	M
TlBr	M
TlI	M

Table 9

OF_2	M
Cl_2O	M
SCl_2	M
$SeCl_2$	ref.39
$TeCl_2$	M
$TeBr_2$	M

Table 10

see ref.27

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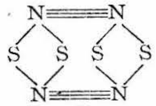
An Electron Diffraction Investigation of Sulfur Nitride, Arsenic Disulfide (Realgar), Arsenic Trisulfide (Orpiment) and Sulfur

BY CHIA-SI LU AND JERRY DONOHUE

Although sulfur nitride, S_4N_4, has been known for over fifty years and is the parent substance of several compounds, its molecular structure has remained an unsolved problem. Its molecular formula is derived from ebullioscopic and cryoscopic measurements; but neither the methods of preparation nor its chemical properties give any important clue to its chemical constitution. Schenck[1] and Muthmann and Clever[2] proposed, respectively, the stereochemically similar structural formulas I and II, which are rather improbable because of the four rings and the small distances. Later Ruff and Geisel[3] proposed the formulas III and IV. They gave preference to the latter formula, which was also supported by Meuwsen.[4] None of these formulas seems to account for the chemical properties of sulfur nitride satisfactorily. In 1931 Jaeger and Zanstra,[5] on the basis of their x-ray investigation of the crystals of sulfur nitride, reported that the molecules had the configuration of two interpenetrating concentric bisphenoids (tetragonal bisphenoids) of sulfur and nitrogen atoms (formula V). The N-S bond length of their model was only about 1.2 Å., which seems to be far too short. Their results are rendered more doubtful, inasmuch as they regarded the crystals as being orthorhombic, by the fact that the crystals have been shown to possess only monoclinic symmetry by means of both goniometric and x-ray methods[6,7] but usually twin themselves to exhibit orthorhombic symmetry. In 1936 Arnold, Hugill and Hutson[8] proposed formula VI, which would involve resonance among several bond structures. They also considered formula VII, which would easily account for the formation of the thiotrithiazyl ion[9] $(N_3S_4)^+$ from sulfur nitride but would not readily account for the other reactions. Formula VI was supported by Phalnikar and Bhide,[10] although their argument on the basis of their dipole moment measurements is not at all convincing.



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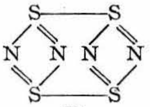

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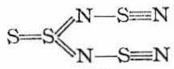

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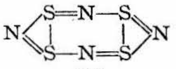

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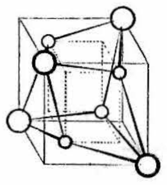

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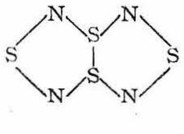

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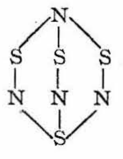

VII

The molecular structure of arsenic disulfide (realgar) has been another unsolved problem in structural chemistry. The possibility of isomorphous structures of sulfur nitride and realgar was first suggested by Szarvasy and Messinger.[11] They determined the vapor densities of realgar at several temperatures, and found that the measured vapor density would correspond to As_4S_4 at temperatures below 550° but dissociation into As_2S_2 molecules became appreciable at higher temperatures. They proposed a structure similar to I for the As_4S_4 molecule except with single bonds between the arsenic atoms instead of the triple bonds. Recently Buerger[12] determined the dimensions of the unit cell in the realgar crystal and compared them with those in the crystal of sulfur nitride,[7] and suggested that the difference in the length of the monoclinic *b*-axis might be attributed to the difference in the sizes of the arsenic and nitrogen atoms. However, no complete structure investigation for either substance has been reported in the literature.

Burt[13] reported in 1910 that sulfur nitride can be sublimed readily *in vacuo* at as low a temperature as 100°. Realgar also sublimes readily *in vacuo* at temperatures below its melting point (307°); and excellent realgar crystals can be grown in this way.[14] We have therefore undertaken an electron diffraction investigation of these

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[7] M. J. Buerger, *Am. Min.*, **21**, 575 (1936). His results are quoted as follows: $a_0 = 8.74$ Å., $b_0 = 7.14$ Å., $c_0 = 8.645$ Å., $\beta = 92°21'$; $C_{2h}^5 - P2_1/n$; $Z = 4$ (S_4N_4).

[8] M. H. M. Arnold, J. A. C. Hugill and J. M. Hutson, *J. Chem. Soc.*, 1645 (1936).

[9] W. Muthmann and E. Seitter, *Ber.*, **30**, 627 (1897).

[10] N. L. Phalnikar and B. V. Bhide, *Current Science*, **8**, 473 (1939).

[11] E. Szarvasy and C. Messinger, *Ber.*, **30**, 1343 (1897).

[12] M. J. Buerger, *Am. Min.*, **20**, 36 (1935). His results are quoted as follows: $a_0 = 9.27$ Å., $b_0 = 13.50$ Å., $c_0 = 6.56$ Å., $\beta = 106°37'$; $C_{2h}^5 - P2_1/n$; $Z = 4$ (As_4S_4).

[13] F. P. Burt, *J. Chem. Soc.*, **97**, 1171 (1910).

[14] A. Schuller, *Z. Krist.*, **27**, 97 (1897).

two substances in the vapor state. In the course of our investigation we began to feel the desirability of examining arsenic trisulfide (orpiment) and sulfur by means of similar experimental techniques. In the case of orpiment, which exhibits rather large birefringence in the crystal, it might be expected that the crystal structure would be different from that of arsenolite,[15] which consists of As_4O_6 molecules. However, orpiment can be distilled unchanged,[16] although it does not sublime as readily as realgar.[14] It is thus of interest to find out whether it could have the As_4O_6 structure in the vapor state.[17] In the case of sulfur a puckered ring structure has been established in the rhombic crystals[18] as well as in the vapor.[19] Since the electron diffraction photographs of Howe and Lark-Horovitz[19] apparently were not taken to show features beyond $q = 30$ ($q = 40/\lambda \sin \theta/2$), their patterns are not capable of giving as complete information with regard to the size, configuration, and rigidity of the ring as we have been able to obtain.

We have accidentally taken some excellent photographs of arsenic trioxide, which apparently contaminated a sample of stockroom-grade "pure" arsenic trisulfide. Five more features could be seen and measured than those reported by Hampson and Stosick.[20] Our final parameters are as follows: As–O = 1.78 ± 0.02 Å., As–As = 3.20 ± 0.02 Å. and ∠ As–O–As = 128 ± 2° (∠O–As–O = 99 ± 2°). These agree very well with the values of Hampson and Stosick:[20] namely, As–O = 1.80 ± 0.02 Å., As–As = 3.20 ± 0.03 Å. and ∠ As–O–As = 126 ± 3°. It should be noted that both the As–O bond length and the oxygen bond angle indicate large amounts of double bond character in the As–O bonds arising from the unshared electrons on the oxygen atoms.

Experimental.—The sample of sulfur nitride used in this investigation was prepared by the method described by Arnold, Hugill and Hutson.[8] The sample was recrystallized twice from chloroform. It burned quietly in air and left no residue on sublimation *in vacuo*. The samples of realgar and orpiment were purchased from a mineralogical supply service in Pasadena. According to Mr. Grieger of this supply service, the sources of these mineral specimens are: realgar, White Caps mine, Manhattan, Nevada; orpiment, Mercur, Utah. Both specimens are of very high quality. The realgar was purified by sublimation *in vacuo* at a temperature of *ca.* 300°. Orpiment would not sublime so readily; hence it was fused *in vacuo* to a glassy mass at a temperature of 300–400° to remove both arsenic trioxide and realgar, and was then pulverized. The powdered sample had a dark yellow color. Another sample of arsenic trisulfide was prepared artificially by precipitation by hydrogen sulfide from a solution of arsenic trichloride in hydrochloric acid. The sample of sulfur was obtained from the chemical stockroom. It was apparently of very high purity, and it left practically no residue on sublimation *in vacuo*.

The electron diffraction apparatus used for this investigation has been described by Brockway.[21] The camera distance used was about 11 cm. The wave length of the electrons (*ca.* 0.06 Å.) was determined against zinc oxide smoke[22] (a_0 = 3.2426 Å., c_0 = 5.1948 Å.) with a camera of about 40 cm. distance.

The metal high-temperature nozzle of Brockway and Palmer[23] was found to be unsuitable for sulfur nitride and realgar. With this nozzle no photographs could be obtained below a certain heating current; while at higher heating current only photographs of decomposition or reaction products resulted. A glass high-temperature nozzle of very simple design was made to meet this difficulty and was used throughout this investigation. It consists of a small sample tube (diameter 6 mm.; length 2.5 cm.) with a male ground joint, and a capillary chimney (O. D. 6 mm.; I. D. 2 mm.; length 2.5 cm.) with a female ground joint on one end and a constricted bore of 0.5 mm. diameter on the other. Each of these two parts is wound with a few turns of no. 26 nichrome wire. Of the four substances studied (aside from arsenic trioxide), sulfur nitride required the lowest heating current and orpiment the highest. No attempt was made to measure the temperature of the vapor in the nozzle; evidently it was never as high as the softening point of Pyrex glass. A diagram of the nozzle is shown in Fig. 1.

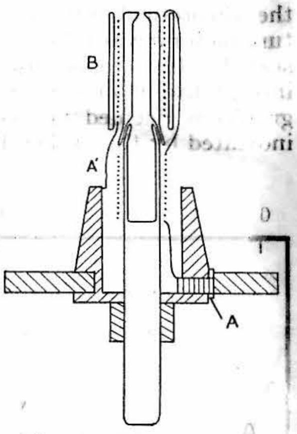

Fig. 1.—Diagram of the high temperature nozzle: A,A′, leads for heating coil; B, glass shield for upper part of chimney. In actual practice the entire chimney was wrapped in asbestos.

The photographs were examined on a viewing box, and, for the outer rings, two or more good, heavy photographs were superimposed and examined on a Triplett and Barton viewing lamp of adjustable illumination aperture and intensity. Measurements of the diffraction features were made on a comparator in the usual manner. All the intensity patterns could be observed up to or beyond $q = 80$. The photographs were all corrected for film expansion by measuring two fiducial distances on the film.

Interpretation.—Both the radial distribution method[24] and the correlation method[25] were used in interpreting the photographs. The radial distribution functions were calculated from the visual intensity curves by means of the following equation

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[15] R. M. Bozorth, This Journal, **45**, 1621 (1923); K. E. Almin and A. Westgren, *Arkiv Kemi, Mineral. Geol.*, **15B**, No. 22 (1942), abstracted in *Chem. Abs.*, **36**, 5688 (1942).

[16] E. Mitscherlich, *Ges. Wiss. Göttingen*, **12**, 137 (1834), quoted in Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, London, 1929.

[17] Szarvasy and Messinger (ref. 10) reported that their vapor density measurements on orpiment indicated appreciable dissociation at 1000°. They did not mention, however, whether it was from As_2S_3 or from As_4S_6 that orpiment dissociated.

[18] B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

[19] J. D. Howe and K. Lark-Horovitz, *Phys. Rev.*, **51**, 380A (1937).

[20] G. C. Hampson and A. J. Stosick, This Journal, **60**, 1814 (1938).

[21] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[22] C. S. Lu and E. W. Malmberg, *Rev. Sci. Instr.*, **14**, 271 (1943).

[23] L. O. Brockway and K. J. Palmer, This Journal, **59**, 2181 (1937).

[24] L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935); R. Spurr and V. Schomaker, *ibid.*, **64**, 2693 (1942).

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

$$rD(r) = \sum_{q=1} I(q)e^{-aq^2} \sin\left(\frac{\pi}{10}qr\right)$$

where a was so determined that e^{-aq^2} was 1/10 or 1/20 at $q = 90$. The unobservable first feature of the visual curve (dotted part) was introduced arbitrarily. (In the case of sulfur, this first feature was taken from the theoretical intensity curves, *cf.* Fig. 2.) On the other hand, for the correlation treatment the simplified theoretical scattering formula,[24] was used to calculate

$$I^\circ(q) = \sum_{i,j}{}' \frac{Z_iZ_j}{r_{ij}} e^{-b_{ij}q^2} \sin\left(\frac{\pi}{10}r_{ij}q\right)$$

the theoretical intensity curves. The temperature factor b was taken to be zero unless otherwise stated. It is to be noted that sometimes a reinterpretation of certain features of the photographs is deemed necessary. Such a change is indicated by the broken lines on the visual curve.

We shall describe our results obtained in this investigation in the following order: sulfur, orpiment, sulfur nitride and realgar.

Sulfur.—The electron diffraction pattern of the sulfur molecule S_8 is depicted in curve V of Fig. 2. The radial distribution function R calculated for this visual curve gives two sharp peaks at 2.07 and 3.28 Å. and a broad peak at 4.3–4.4 Å. From these we obtain S.S = 2.07 ± 0.02 Å. and ∠ S–S–S = 105 ± 2°. The broad peak should then arise from the longer S–S terms, which, for a regular puckered eight-ring, would be 4.34 and 4.67 Å., with weights *ca.* 2:1. Several configurations derivable from a regular puckered ring by systematic distortions, such as the "tub" form, the "chair" form, the "cradle" form and the "butterfly" form (Fig. 3), have been shown to be incompatible with the radial distribution peak at 4.3–4.4 Å. Therefore the fraction of sulfur molecules having these configurations in the vapor phase must be small.

Four theoretical intensity curves A–D were calculated for regular puckered ring models with S–S = 2.07 Å. and ∠ S–S–S = 100°, 103°, 106° and 109°, respectively. In order to estimate the thermal vibration of the ring two more theoretical curves (dotted curves) including only the two shortest terms were calculated for the models B and C. Qualitative comparison reveals at once that there is a rather large thermal vibration associated with the puckered ring structure. (We estimate from the curves B and C that $\sqrt{\overline{\delta r^2}} \cong 0.15$ Å. for the two longer S–S terms. Curve E calculated with S–S = 2.07 Å., ∠S–S–S = 104°50′, and this amplitude of vibration (corresponding to $b = 0.0009$) for the two long terms is seen to agree very well with the visual curve.) Quantitative comparison of the observed and the calculated features is given in Table I.

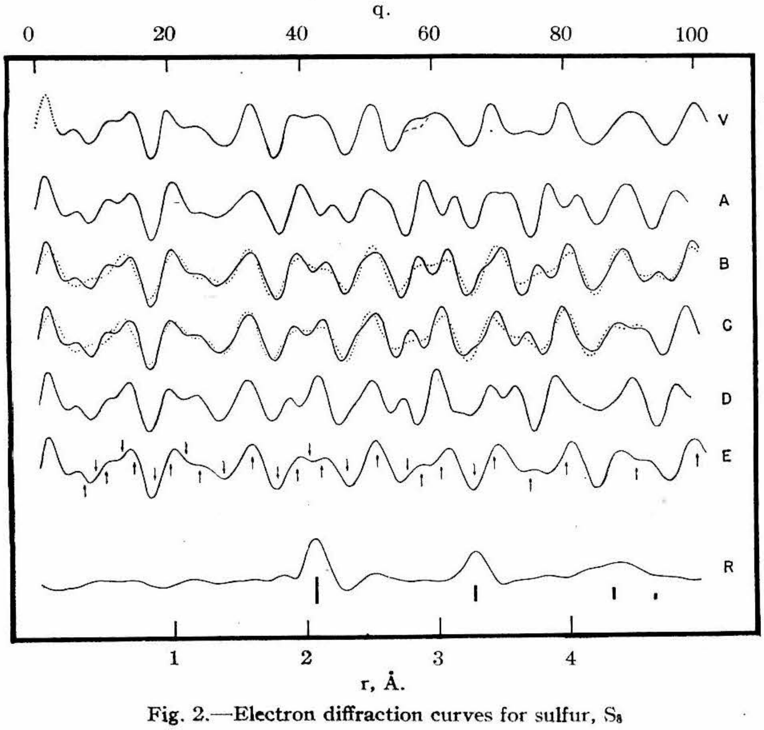

Fig. 2.—Electron diffraction curves for sulfur, S_8

	S.S, Å.	<S.S.S	Remarks
A	2.07	100°	
B	2.07	103°	
C	2.07	106°	
D	2.07	109°	
E	2.07	104°50′	Temperature factor (b = 0.0009) for two longer terms

Both the electron diffraction values of Howe and Lark-Horovitz[19] (S–S = 2.08 ± 0.02 Å.) and the x-ray values of Warren and Burwell[18] (S–S = 2.12 Å., ∠ S–S–S = 105°) for the sulfur molecule agree satisfactorily with our present results.

Orpiment.—The fused orpiment and the precipitated arsenic trisulfide gave identical electron diffraction patterns, which are depicted in curve V of Fig. 4. The radial distribution function R calculated for this visual curve gives a sharp peak at 2.25 Å. and a peak at 3.46 Å. with a broad shoulder on the outside. The first peak (2.25 ± 0.02 Å.) corresponds to a single-bond As–S distance.[26] No

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[26] See L. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, New York, 1940.

TABLE I

SULFUR

Min.	Max.	$q_{obs.}$	q_E	$q_E/q_{obs.}$
	1	6.87	5.6	(0.815)
2		8.51	7.6	(.893)
	2	10.05	10.5	(1.045)
3		12.41	11.5	(0.927)
	3	14.29	13.6	(.952)
4		17.27	16.7	(.967)
	4	19.68	20.1	(1.021)
5		22.05	21.8	0.989
	5	24.08	24.3	1.009
6		27.65	27.7	1.002
	6	32.08	31.8	0.991
7		35.77	35.6	.995
	7	38.75	39.0	1.006
8		40.63	41.0	1.009
	8	42.40	43.0	1.014
9		46.26	46.6	1.007
	9	50.89	50.5	0.992
10		55.54	54.2	.976
	10	57.46	57.5	1.001
11			48.8	
	11	60.47	61.7	1.020
12		65.60	65.4	0.997
	12	68.64	69.2	1.008
13			73.0	
	13	74.10	74.3	1.003
14			76.6	
	14	79.60	80.2	1.008
	15	90.3	88.0	(0.975)
	16	99.6	99.2	0.996
		Average		1.001
		Average deviation		0.008

plausible model, however, can be constructed for As_2S_3 such that the As−S bonds would be expected to be essentially single bonds and such that the peaks in the radial distribution function are satisfactorily accounted for. Hence, it is likely that the orpiment molecule in the vapor phase is As_4S_6 and has the As_4O_6 structure. For As_4S_6 with this structure, with As−S = 2.25 Å. and ∠ As−S−As = 100°, we would expect a large As−As peak at 3.45 Å., a small S−S peak at 3.77 Å. (which possibly falls in the shoulder of the As−As peak), a large As−S peak at 4.25 Å., and a negligibly small S−S peak at 5.33 Å. Theoretical intensity curves calculated for this model with As−S = 2.25 Å. and ∠ As−S−As = 97°, 100°, and 103°, respectively, are shown in curves A−C of Fig. 4. In order to estimate the thermal effect on such a rigid model, we calculated two more theoretical curves (dotted curves) including only the three shorter terms for the models B and C. From a qualitative comparison of the curves B and C with the visual curve it is easily seen that if As_4S_6 molecules do exist in the vapor phase they cannot be as rigid as the As_4O_6 molecules. This loss of rigidity is probably due to the high temperature used in our investigation.

Curve D was calculated for an As_4S_6 model with As−S = 2.25 Å. and ∠ As−S−As = 101° and a temperature factor (b = 0.0009) for the two longest terms. Quantitative comparison of the

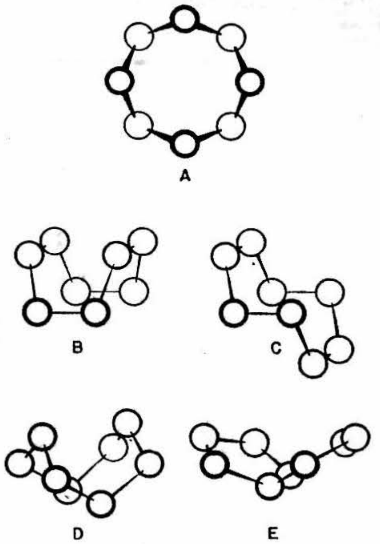

Fig. 3.—Some configurations of the eight ring: A, regular puckered ring (S_8 molecule); B, "tub" form; C, "chair" form; D, "cradle" form; E, "butterfly" form.

TABLE II

ORPIMENT

Min.	Max.	$q_{obs.}$	q_D	$q_D/q_{obs.}$
	1	6.82	6.5	(0.953)
2		9.80	8.6	(.878)
	2	12.48	11.7	(.938)
3		15.93	15.8	.992
	3	18.78	19.3	1.028
4		22.23	22.3	1.003
	4	24.15	24.3	1.006
5		26.09	26.3	1.008
	5	29.66	29.5	0.995
6		33.22	32.9	.990
	6	35.85	37.0	(1.032)
7		39.55	41.0	(1.037)
	7	41.37	42.5	(1.027)
8		43.55	43.7	1.003
	8	47.10	47.3	1.004
9		51.80	50.8	0.981
	9	54.87	54.3	.990
10			57.0	
	10	59.15	58.5	.989
11		61.71	61.5	.997
	11	64.05	64.5	1.007
12		68.26	68.3	1.001
	12	71.34	71.3	0.999
13		73.28	73.5	1.003
	13	76.95	75.6	0.982
	14	82.71	82.4	.996
	15	89.8	88.8	.989
	16	95.4	93.0	.975
		Average		.997
		Average deviation		.009

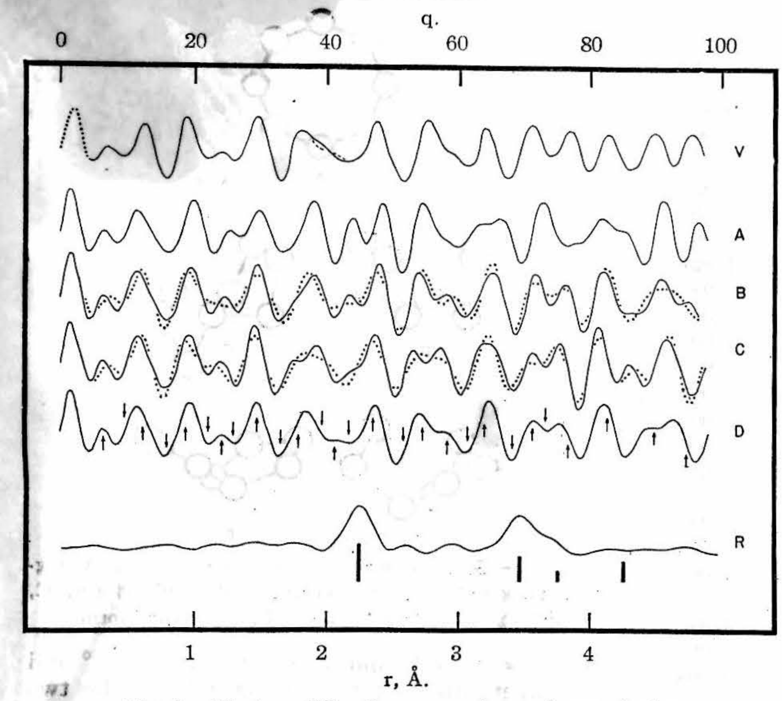

Fig. 4.—Electron diffraction curves for orpiment, As_4S_6:

	As-S, Å	<As-S-As	Remarks
A	2.25	97°	
B	2.25	100°	
C	2.25	103°	
D	2.25	101°	Temperature factor (b = 0.0009) for two longest terms

observed and the calculated features is given in Table II. Our final parameters are as follows: As—S = 2.25 ± 0.02 Å., $\angle$ As—S—As = 100 ± 2° ($\angle$ S—As—S = 114 ± 2°). The As_4S_6 molecules exhibit large thermal vibration under our experimental conditions.

The orpiment crystal probably bears a similar relationship to As_4S_6 molecules as orthorhombic antimony trioxide (valentinite)[27] does to Sb_4O_6, and possibly even as monoclinic arsenic trioxide (claudetite) does to As_4O_6, although the crystal structure of claudetite is not yet known.

It is interesting to note that Medlin[28] obtained for orpiment the following interatomic distance peaks: 2.24 Å. (somewhat asymmetric), 3.46 Å., and 4.39 Å., from the radial distribution treatment of x-ray powder photographs. Although the close agreement with our radial distribution function is apparently coincidental, this tends to indicate that the bond lengths and bond angles in the orpiment crystal are not subject to severe deformation during the process of volatilization.

Sulfur Nitride.—The electron diffraction pattern of the sulfur nitride molecule S_4N_4 is represented by curve V of Fig. 5. The radial distribution function R calculated for this visual intensity curve gives a sharp peak at 1.62 Å., another equally sharp but somewhat stronger peak at 2.69 Å. with a slight asymmetry on the inside, followed by a small shouldering peak at about 3.1 Å., a small peak at 3.78 Å., and possibly another small but broad peak at about 4.2 Å. The first peak at 1.62 Å. undoubtedly arises from the N—S bonds in the sulfur nitride molecule. Since the length of a single S—N bond is expected to be *ca.* 1.74 Å. while that of a double bond is *ca.* 1.54 Å.,[26] it seems that practically all the S—N bonds in the sulfur nitride molecule would have considerable amounts of double bond character. The second peak at 2.69 Å. might be interpreted as due mostly to the S—S intractions; if this is the case, the bond angle $\angle$ S—N—S would be close to 112°. Meanwhile, the relative sizes of the first two peaks might have some significance which must be taken into consideration. At any rate, our radial distribution function indicates that the sulfur nitride molecule is rather compact, since no important long distance in the molecule is shown by it.

The height of the first peak and its shape would exclude all models involving either more than one direct bond between the sulfur atoms or more than two N—N bonds. Hence the structural formulas II and IV are very improbable. Formula III, on the other hand, is not likely to be correct since the radial distribution function indicates that there is no important distance longer than 3.1 Å. in the molecule. Jaeger and Zanstra's model (V) is also not acceptable, because even if the N—S bond length and the size of the nitrogen bisphenoid should be made more reasonable, the interatomic distance spectrum of the radial distribution function could not be fitted at all. As a matter of fact, we have not been able to find any satisfactory models consisting of two interpenetrating concentric bisphenoids of nitrogen and sulfur atoms.

Formula VI represents a limiting case of one of the several plausible configurations which can be derived from a regular puckered eight-ring of alternate sulfur and nitrogen atoms by systematic distortions. Calculations were made for two planar models of formula VI with N—S = 1.62 Å. and S—S = 2.08 Å. and 1.88 Å., respectively. The theoretical curves A_1 and A_2 are shown in Fig. 5; and the corresponding interatomic distance spectra are shown under R. Since the

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(27) M. J. Buerger and S. B. Hendricks, *Z. Krist.*, **98**, 1 (1937).
(28) W. V. Medlin, THIS JOURNAL, **58**, 1590 (1936).

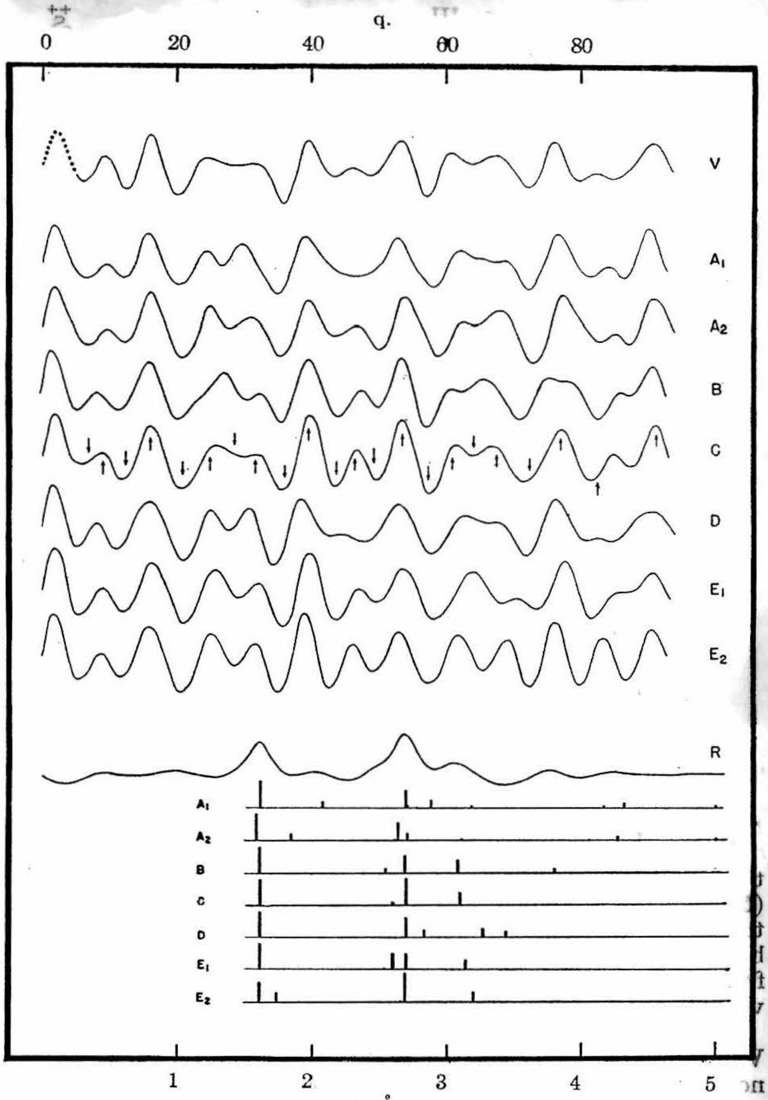

Fig. 5.—Electron diffraction curves for sulfur nitride, S_4N_4:

Configuration

A_1	formula VI, planar, S–S = 2.08 Å.
A_2	formula VI, planar, S–S = 1.88 Å.
B	"cradle," bisphenoid of nitrogen atoms, N–N = 2.55 Å.
C	Our proposed structure (*cf.* Fig. 7)
D	"tub" form
E_1	"cage" form (formula VII), intervening N–S = 1.62 Å.
E_2	"cage" form (formula VII), intervening N–S = 1.74 Å.

inter-ring distances contribute less than one-fifth of the total molecular scattering, the analysis of these two planar models suffices to show that such a configuration, suggested by Arnold, Hugill and Hutson,[8] is not likely, insofar as it is impossible to get a sufficiently important term at about 3.1 Å. The counterpart of such a configuration obtained by the exchange of the sulfur and nitrogen atoms is equally unsatisfactory.

An irregular puckered ring model was also investigated. With N–S = 1.62 Å. and ∠S–N–S = 112°, and the angle ∠N–S–N taken as a variable parameter, satisfactory agreement with the radial distribution function can be obtained (although the relative heights of the peaks are not correct), but only with the unreasonably small value 70° for the sulfur bond angle.

Two other simple "cradle" models, one the counterpart of the other, can be derived from the puckered ring configuration. One consisting of a bisphenoid of nitrogen atoms and a square of sulfur atoms was found to be unlikely by comparison with the radial distribution function and by calculation of a theoretical curve for a model (curve B, Fig. 5) of this type which most nearly agrees with the radial distribution function. The limiting form of this structure, obtained by reducing the N–N distance across the "cradle" to 1.47 Å., the N–N single bond distance,[29] cannot be made to fit the radial distribution function and at best demands unreasonably small nonbonded N–N distances and sulfur bond angles. Essentially the same difficulties are encountered with the less symmetrical model analogous to this which would be taken as the modern realization of formula I. The counterpart of this "cradle" configuration, consisting of a bisphenoid of sulfur atoms and a square of nitrogen atoms, is, on the other hand, a promising configuration. A model with N–S = 1.62 Å., ∠S–N–S = 112°, and ∠N–S–N = 105° (the distribution of the sulfur atoms is tetrahedral in this model) gives curve C of Fig. 5; the corresponding interatomic distance spectrum is shown under R. Quantitative comparison of the observed features and those calculated for this model is given in Table III.

Models of the "chair" and of the "tub" forms derived from the puckered ring configuration were also considered but were found to be unsatisfactory. Curve D of Fig. 5 was calculated for a "tub" model involving four coplanar

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(29) V. Schomaker and D. P. Stevenson, THIS JOURNAL, 63, 37 (1941); P. A. Giguère and V. Schomaker, *ibid.*, 65, 2025 (1943).

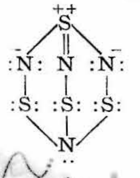
TABLE III

SULFUR NITRIDE

Min.	Max.	$q_{obs.}$	q_C	$q_C/q_{obs.}$
	1	8.90	9.0	(1.011)
2		12.24	11.7	(0.956)
	2	16.02	16.0	.999
3		20.60	20.6	1.000
	3	24.83	25.7	(1.035)
4		28.32	29.3	(1.034)
	4	31.53	31.8	1.009
5		35.95	35.6	0.990
	5	39.42	39.7	1.007
6		43.54	43.5	0.999
	6	46.23	46.8	1.012
7		49.14	49.6	1.009
	7	53.51	53.6	1.002
8		57.12	57.6	1.008
	8	60.85	61.5	1.011
9		63.96	64.0	1.001
	9	67.43	67.0	0.994
10		72.33	71.5	.989
	10	75.92	77.3	1.018
11			81.3	
	11	81.67	84.3	(1.032)
12			87.2	
	12	91.2	91.1	0.999
			Average	1.003
			Average deviation	0.007

"*cis*" groupings S–N–S–N with N–S = 1.62 Å. and ∠ S–N–S = ∠ N–S–N = 112°. In order to obtain fair agreement with the radial distribution function it is necessary to distort this configuration toward the "cradle" form (Model C), and good agreement with respect to the relative heights of the peaks of R cannot be obtained without approaching the "cradle" form very closely. Similar difficulties were involved in the "chair" structure.

The "cage" structure represented by formula VII should consist of two interpenetrating but not concentric trigonal pyramids of nitrogen and sulfur atoms. Calculations were made for models with N–S = 1.62 Å., ∠ S–N–S = ∠ N–S–N = 112° for the two end groups NS_3 and SN_3 and the intervening N–S = 1.62 Å. and 1.74 Å., respectively. The theoretical intensity curves E_1 and E_2 are given in Fig. 5 together with the corresponding interatomic distance spectra. Since five parameters (namely, three distances for the S–N bonds and two pyramidal angles) are required to describe this structure if it has symmetry C_{3v}, it should be possible to construct models with this "cage" configuration in satisfactory agreement with the diffraction pattern. Nevertheless we believe that this configuration may be rejected by consideration of the following plausible bond structures which makes it difficult to understand how the N–S bonds could have such a considerable amount of double bond character as is indicated by the short average bond length 1.62 Å. It is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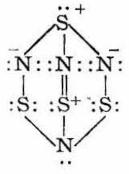
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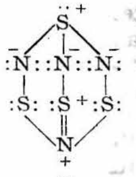
C

also to be noted that this structure could hardly account for most of the chemical properties of sulfur nitride.

The electron diffraction data alone are not sufficient to establish with certainty the "cradle" model for sulfur nitride, and, as a matter of fact, it would seem to be not altogether impossible to construct models of other configurations which would be compatible with the diffraction pattern. We shall, however, make no further attempt to exhaust all the possibilities.

Realgar.—The electron diffraction pattern of the realgar molecule As_4S_4 is represented by the curve V of Fig. 6. The radial distribution function R calculated for this visual intensity curve gives a sharp peak at 2.23 Å., a small peak at 2.55 Å., a strong but broad peak at 3.50 Å., and a very weak and broad peak at about 4.75 Å.; it resembles the radial distribution function for orpiment (Fig. 4) to a certain extent. The first peak at 2.23 Å. must arise from the As–S bonds. Since 2.23 Å. is very close to the single bond value 2.25 Å. found in the orpiment molecule, the As–S bonds in the realgar and the orpiment molecules probably have comparable amounts of double bond character. The small peak at 2.55 Å., if it is significant, may be interpreted as due to As–As bonds. The next peak seems to consist of at least two unresolved interatomic distances, one of which is an As–As term. According to this interpretation the bond angle ∠ As–S–As is apparently not greater than 106°. This may be taken as an indication that as far as bonding is concerned the sulfur atoms in the realgar molecule are more like those in dimethyl disulfide (107°)[30] and in sulfur (105°) than like those in sulfur dioxide (120°).[31] It is interesting to note that there is no important long distance in the realgar molecule.

The formulas II–IV suggested for the sulfur nitride molecule could also be formulated for the realgar molecule. None of them, however, could be made to fit the radial distribution function. A regular puckered eight-ring of alternate arsenic and sulfur atoms is also not acceptable. Since the bond angle ∠ As–S–As is small relative to the tetrahedral angle we were unable to construct a satisfactory "cage" model.

On the other hand, a "cradle" configuration consisting of a bisphenoid of arsenic atoms and a

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(30) D. P. Stevenson and J. Y. Beach, THIS JOURNAL, **60**, 2872 (1938).

(31) P. C. Cross and L. O. Brockway, *J. Chem. Phys.*, **3**, 821 (1935); V. Schomaker and D. P. Stevenson, THIS JOURNAL, **62**, 1270 (1940).

square of sulfur atoms (involving rearrangement of bonds in the formula proposed by Szarvasy and Messinger[11]) was found to be plausible. Theoretical intensity curves A–C were calculated for such "cradle" models with As–S = 2.23 Å., As–As = 2.44, 2.49, and 2.55 Å., respectively, and the weighted average value of the longer As–As and As–S terms at about 3.50 Å. These are shown in Fig. 6. Curve B reproduces the qualitative features rather satisfactorily. Quantitative comparison of the observed and the calculated features is given in Table IV. As in the case of sulfur nitride, no attempt is made to exhaust all the possible models of other configurations that are compatible with the diffraction pattern.

Incidentally it is to be noted that Medlin,[28] from the radial distribution treatment of x-ray powder photographs, obtained for realgar the following interatomic distance peaks: 2.16 (somewhat asymmetric), 3.54 and 4.52 Å. The agreement with our finding is not at all disappointing.

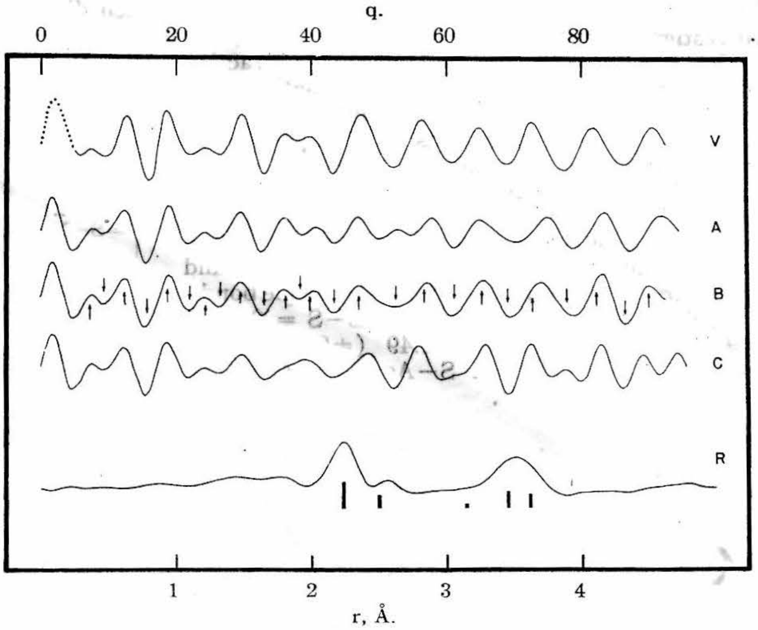


Fig. 6.—Electron diffraction curves for realgar, As_4S_4:

	As-As, Å.	non-bonded As-As, Å.	non-bonded As-S, Å.
A	2.44	3.45	3.58
B	2.49	3.45	3.61
C	2.55	3.43	3.66

All models have configuration as in Fig. 7, bonded As–S = 2.23 Å.

TABLE IV

REALGAR

Min.	Max.	$q_{obs.}$	q_B	$q_B/q_{obs.}$
	1	7.29	7.6	(1.043)
2		9.75	9.4	(0.964)
	2	12.45	12.3	.988
3		15.79	15.6	.988
	3	18.49	18.7	1.011
4		21.94	22.0	1.003
	4	24.13	24.3	1.007
5		26.28	26.5	1.008
	5	29.75	29.5	0.992
6		33.09	32.6	.985
	6	36.15	35.7	.988
7		38.08	38.3	1.006
	7	39.74	40.5	1.019
8		43.47	43.4	0.998
	8	46.91	47.0	1.002
9		52.22	52.5	1.005
	9	56.65	57.1	1.008
10		61.06	60.7	0.994
	10	65.21	65.6	1.006
11		69.05	69.5	1.007
	11	72.69	74.0	1.018
12		77.63	78.9	1.016
	12	82.12	83.1	1.012
13		86.71	86.5	0.998
	13	90.2	90.0	0.998
		Average		1.002
		Average deviation		0.008

Discussion

The structure of the sulfur molecule is essentially the same as that in the crystal, as was to be expected. The large thermal libration of the puckered sulfur molecule is apparently associated with the flexibility of the eight-ring structure. In orpiment the bond angle ∠ As–S–As (100 ± 2°) is found to be much smaller than the corresponding angle ∠ As–O–As (128 ± 2°) in the As_4O_6 molecule. This effectively draws the neighbors to the arsenic atoms closer without perturbing the coördination of the sulfur atoms to an unnecessary extent. The double bond character of the As–S bonds is also diminished.

Our results on the sulfur nitride and realgar molecules are gratifying insofar as these help to make another step forward in the solution of these two unsolved problems in structural chemistry. These structures cannot yet be established with certainty, although several of the structures proposed by previous workers are definitely eliminated. We believe that a detailed analysis of the crystal structures of sulfur nitride and realgar, which should be simplified by our present results, will lead to the ultimate solution of these two problems. (The ease of sublimation of these substances and their solubility in several organic solvents indicate that the crystals are molecular. It seems likely that the structures in vapor and crystal are similar.) Wartime duties, however, prevent us from undertaking an extensive x-ray investigation at this time.

We have shown from our electron diffraction data that "cradle" structures lead to satisfactory models (Fig. 7). For the sulfur nitride molecule this "cradle" model consists of a bisphenoid of sulfur atoms and a square of nitrogen atoms, with N–S = 1.62 Å., ∠ S–N–S = 112°, and ∠ N–S–N = 106°. For the realgar molecule the vertices of the bisphenoid are occupied by the arsenic atoms instead of the sulfur atoms, and these arsenic atoms are connected by single bonds. The dimensions are as follows: As–S = 2.23 Å. (±0.02 Å.), As–As = 2.49 (±0.04 Å.), ∠ As–S–As = 101°, ∠ S–As–S = 93°, and ∠ S–As–As = 100°.

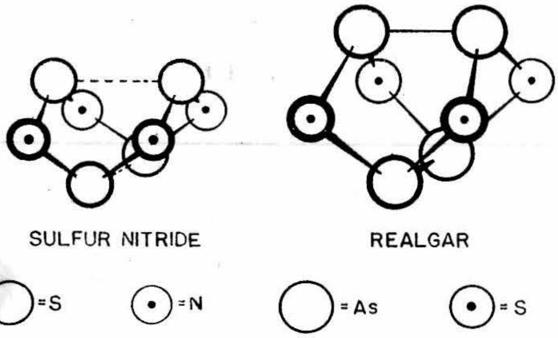
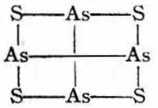


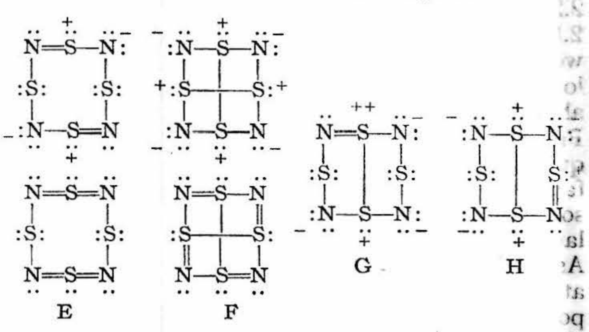
Fig. 7.—The molecular structures proposed for realgar and sulfur nitride.

Our "cradle" structure for the realgar molecule is conventional as is indicated by the bond structure D and the observed bond lengths. Its simple relationship to the structure of the As_4S_6 molecule is borne out by the fact that orpiment and realgar can be easily converted into one another at high temperatures. The conversion of realgar to orpiment would involve simply inserting a sulfur atom between each As–As pair. Moreover, the chemical reactions of realgar are in general typical of sulfides and trivalent arsenic compounds.



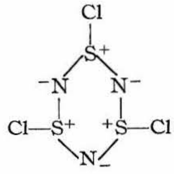
D.

If the arsenic atoms of this model for the realgar molecule were now replaced by nitrogen atoms and the N–N bonds across the "cradle" were made practically single bonds, then in order to make the side of the sulfur square *ca.* 2.7 Å. in length the non-bonded N–N distance and the sulfur bond angle would have to be too small to be reasonable; also, the stronger tendency of the sulfur atoms (compared with the nitrogen atoms) toward high coördination would never be realized. The "cradle" model for the sulfur nitride molecule, on the other hand, does not involve any such difficulty, although it should be noted that the S–S distances in this model are much shorter than the ordinary van der Waals separation (3.7 Å.[26]). Our structure probably involves resonance among the following bond structures, including some of those in which sulfur has a decet of electrons, and other less important ones.



Of these structures E is probably the most important. Hence each N–S bond is expected to have about 25% double bond character, which is borne out by the short bond length of 1.62 Å. The bond angles, *ca.* 112° for ∠ S–N–S and 106° for ∠ N–S–N, are also reasonable for this type of bond structure. However, it must be pointed out that the deviation of the S–N–S–N groupings from the "*cis*" configuration is great (*ca.* 58°). Since a similar situation is found in the similar compact structures of As_4O_6, P_4O_6 and P_4O_{10} molecules, where it has been argued[26] that the bonds have considerable amounts of double bond character, it may well be true that the coplanarity condition for the configuration of such groupings is not stringent when other than first first-row atoms are involved because of the available *d* orbitals for bond formation. It should also be noted that the short S–S distances across the "cradle" (*ca.* 2.69 Å.) give an indication of the importance of the bond structures F, G and H. We believe that the stability of such structures as these and the choice between the two "cradle" structures for the sulfur nitride and realgar molecules depends to a large extent upon a delicate balance between the difference in sizes, coördination tendencies, and multiple-bond-forming powers of the two kinds of atoms on one hand and the difference in their electronegativities and the distribution of formal charges on the other. This helps us to understand why such molecules as N_4O_4 and P_4S_4 are unstable and are not known to exist.

It may be mentioned that our "cradle" structure for the sulfur nitride molecule is rather closely related to Arnold, Hugill and Hutson's model,[8] and also to the formula IV proposed by Ruff and Geisel[3] and supported by Meuwsen.[4] It is accordingly not surprising that our structure accounts satisfactorily for the chemical considerations Ruff and Geisel,[3] Meuwsen,[4] and Arnold, Hugill and Hutson[8] brought forward to support their respective formulas. Thus when sulfur nitride is hydrogenated the resulting substance $H_4N_4S_4$,[4] presumably has a ring structure with alternate sulfur and (imino) nitrogen atoms. (The structure of $H_4N_4S_4$ reported by Jaeger and Zanstra[5] cannot be correct for the same reasons which we have discussed in regard to their structure of sulfur nitride.) In the formation of the thiotrithiazyl ion[9] $(N_3S_4)^+$ on boiling sulfur nitride with acetyl chloride, the "cradle" structure with its eight-ring is apparently torn open, giving rise to an ion having possibly the following chain structure: $S{=}N-{}^+S{=}N-S-N{=}S$, which derives its stability from resonance between two identical bond structures. The molecule is also degraded on chlorination with the formation of $(SNCl)_3$,[4] which possibly has the structure



The existence of $(SNCl)_4$ is probable, although it has not been definitely established. Regarding the formation of coördination compounds of sulfur nitride with metallic chlorides such as $SnCl_4$ and $MoCl_4$,[32] Arnold, Hugill and Hutson's explanation[8] in terms of a "unique" sulfur atom in the sulfur nitride molecule is by no means necessary.

We wish to thank Dr. V. Schomaker for helpful suggestions and illuminating discussions.

Summary

Sulfur (S_8), orpiment (As_4S_6), sulfur nitride (S_4N_4), and realgar (As_4S_4) were studied by the method of electron diffraction. The S_8 molecule is a regular puckered-ring with $S-S = 2.07 \pm 0.02$ Å. and $\angle S-S-S = 105 \pm 2°$, and it exhibits a rather large amplitude of thermal vibration. Orpiment sublimes at high temperatures, presumably to give As_4S_6 molecules which have the As_4O_6 structure and the following dimensions: $As-S = 2.25 \pm 0.02$ Å., $\angle As-S-As = 100 \pm 2°$ ($\angle S-As-S = 114 \pm 2°$). The molecular structures of sulfur nitride S_4N_4 and realgar As_4S_4 cannot be established with certainty from the electron diffraction data alone, although several structures proposed by previous workers are definitely eliminated. We have shown that cradle-shaped configurations of an alternating eight-ring lead to satisfactory models. For sulfur nitride this "cradle" model consists of a bisphenoid of sulfur atoms and a square of nitrogen atoms, with $N-S = 1.62 \pm 0.02$ Å., $S-S = 2.69$ Å., $\angle S-N-S = 112°$ and $\angle N-S-N = 106°$. For realgar the model consists of a bisphenoid of arsenic atoms and a square of sulfur atoms with $As-S = 2.23 \pm 0.02$ Å., $As-As = 2.49 \pm 0.04$ Å., and $\angle As-S-As = 101 \pm 4°$ ($\angle S-As-S = 93°$; $\angle S-As-As = 100°$). These results are discussed, special attention being given to the unconventional sulfur nitride structure and its relation to the realgar structure.

PASADENA 4, CALIFORNIA RECEIVED JANUARY 24, 1944

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[32] O. C. M. Davis, *J. Chem. Soc.*, 1575 (1906); H. Wöbling, *Z. anorg. Chem.*, **57**, 280 (1908).

[Reprinted from the Journal of the American Chemical Society, **67**, 332 (1945).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 988]

The Structure of Spiropentane

BY JERRY DONOHUE, GEORGE L. HUMPHREY AND VERNER SCHOMAKER

Murray and Stevenson[1] have prepared a C_5H_8 hydrocarbon by the debromination of pentaerythrityl bromide with zinc dust. They assigned to this substance the spiropentane structure (I) on the basis of its Raman spectrum, chemical properties, and method of preparation. We have confirmed this assignment of structure by an electron diffraction investigation carried out on a sample of the new hydrocarbon supplied us by Dr. Murray.

Experimental.—The electron diffraction apparatus used in this investigation has been described by Brockway.[2] The camera distance was 10.86 cm., and the wave length of the electrons, determined against zinc oxide smoke,[3] was 0.0609 Å. Photographs taken with the sample at 0° showed features extending to q values of about ninety-five ($q = 40/\lambda \sin \vartheta/2$).

Interpretation.—Both the radial distribution method[4] and the correlation method[5] were used in interpreting the photographs. The radial distribution curve was calculated with the equation

$$rD(r) = \sum_{q=1}^{q_{\max}} I(q)e^{-aq^2}\sin\left(\frac{\pi}{10}rq\right)$$

where a was so determined that e^{-aq^2} equals 1/10 at $q = 100$. The values of $I(q)$ were taken from curve V (Fig. 1), which was drawn to represent the appearance of the photographs. The unobservable first feature (dotted) was drawn to agree approximately with the theoretical curves.

Theoretical intensity curves for the correlation treatment were calculated using the simplified theoretical scattering formula

$$I(q) = \sum_{i,j} \frac{Z_iZ_j}{r_{ij}} e^{-b_{ij}q^2}\sin\left(\frac{\pi}{10}r_{ij}q\right)$$

The temperature factor b was given the value 0.00016 for bonded C–H terms, 0.0003 for nonbonded C–H terms, and zero for C–C terms. These calculations were made with punched cards on International Business Machines.

The radial distribution curve, R of Fig. 1, shows maxima at 1.09, 1.49, 2.19 and 2.77 Å., and a shelf at 3.0 Å. This curve is in complete agreement with the spiropentane structure, as shown by the heavy vertical lines representing the various distances and their amplitudes in the finally accepted model. Direct estimates of the angle parameters of the spiropentane structure (I) can easily be made with the information provided by the radial distribution function. The average C–C bond distance 1.49 Å. and the non-bonded C···C distance 2.77 Å. correspond to a $C_2C_3C_1$ bond angle of 61°. Taken with these data, the C–H distance 1.09 Å. and the shortest non-bonded C···H distance 2.19 Å. then imply an HCH bond angle of 121°.

Theoretical intensity curves were drawn (Fig. 1) for various models of the spiropentane structure (I) with a molecular symmetry of $D_{2d} - \bar{4}2m$, with the reasonable assumption that the plane of ∠ HCH bisects ∠ CCC. There are then three parameters which determine the configuration of the molecule. These were taken as $\angle C_2C_3C_1$, ∠HCH, and the ratio $C–H/C_2–C_3$. These parameters were varied in a systematic fashion. Since the curves are relatively insensitive to changes involving the hydrogen atoms only, the second and third parameters cannot be determined with great accuracy. Thus if $\angle C_2C_3C_1 = 61.5°$ and $C–H/C_2–C_3 = 1.08/1.48$, then comparison with the appearance of the photographs show that $\angle HCH = 120 \pm 8°$, whereas if $C–H/C_2–C_3 = 1.08/1.48$ and $\angle HCH = 120°$, $\angle C_2C_3C_1 = 61.5°$ with an uncertainty of only about one degree. With a longer or shorter C–H distance and/or an HCH angle differing considerably from 120°, however, the range of

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(1) M. J. Murray and E. H. Stevenson, THIS JOURNAL, **66**, 812 (1944).

(2) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(3) C. S. Lu and E. W. Malmberg, *Rev. Sci. Instr.*, **14**, 271 (1943).

(4) L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 2181 (1937); R. Spurr and V. Schomaker, *ibid.*, **64**, 2693 (1942).

(5) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

$\angle C_2C_3C_1$ in which agreement can be obtained is increased; for example, a C–H distance of 1.12 Å., a larger $\angle$HCH, and a larger $\angle C_2C_3C_1$ would give a curve in fairly satisfactory agreement with the photographs, as can be seen by referring to Fig. 1. But by virtue of the existing knowledge of hydrocarbon structures and the confirmation provided by the radial distribution, we believe it is reasonable to assume for the formal statement of our results that C–H/C_2–C_3 does not differ significantly from 1.08/1.48 and that $\angle$HCH lies somewhere within the range 120 ± 8°. With these restrictions qualitative consideration of all the theoretical scattering curves and quantitative comparison of the observed q values with the calculated q values for the best curve H as shown in Table I leads, in agreement with the radial distribution function, to the following structural parameters and probable limits of error: C–H = 1.08 Å. (assumed), $\angle$HCH = 120° ± 8° (assumed), $(C–C)_{av.}$ = 1.49 ± 0.01 Å., and $\angle C_2C_3C_1$ = 61.5 ± 2° (C_1–C_3 = 1.48 ± 0.03 Å., C_1–C_2 = 1.51 ± 0.04 Å.).

TABLE I

Min.	Max.	$q_{obs.}$	q_H	$q_H/q_{obs.}$
1		5.29	6.0	(1.134)
	1	7.86	7.6	(0.967)
2		11.91	11.5	(.966)
	2	16.94	17.0	1.004
3		19.66	19.6	(0.997)
	3	22.18	21.0	(.947)
4		26.00	25.5	.981
	4	30.42	29.8	.980
5		34.87	34.9	1.001
	5	38.81	40.0	(1.031)
6		41.84	41.8	(0.999)
	6	45.03	44.7	.993
7		49.62	49.7	1.002
	7	53.58	53.4	(0.997)
8		55.47	55.5	(1.001)
	8	58.25	58.4	1.003
9		63.95	63.1	0.987
	9	68.20	68.3	1.001
10		70.73	70.6	0.998
	10	73.60	72.4	.984
11		77.91	77.1	.990
	11	81.88	81.9	1.000
12		90.64	90.7	1.001
	12	95.50	96.0	1.005
		Average (fifteen features)		0.995
		Average deviation		.008

By means of the radial distribution function, and with the help of theoretical scattering functions, including those calculated for the investigation of methylenecyclobutane[6,7] and 1-methylcyclobutene,[6] we have attempted an exhaustive consideration of the possibility that some other plausible C_5H_8 structure might be in agreement with the diffraction data. On the basis of chemical and spectral evidence, Murray and Stevenson concluded that their substance contained no multiple bonds, and must therefore be bicyclic. Among the bicyclic C_5H_8 structures *there is none* except spiropentane which can be made to agree with the diffraction data. In particular, the configuration of 1,1,1-bicyclopentane (II), which

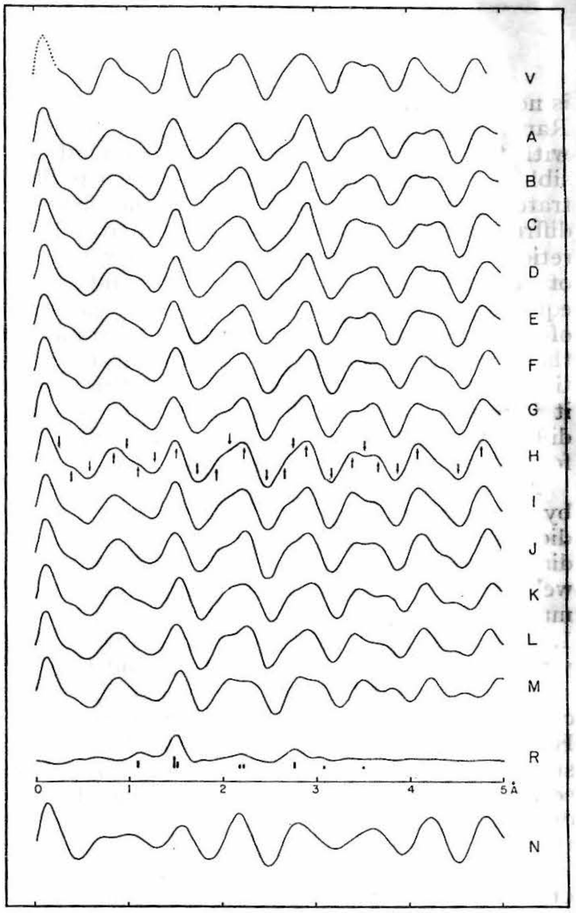

Fig. 1.—Electron diffraction curves for spiropentane (I):

$\angle C_2C_3C_1$	$\angle$HCH	C–H/C_1–C_3	
58.5°	130°	1.09/1.49	A
	120°	1.09/1.49	B
60°	130°	1.12/1.49	C
		1.09/1.49	D
	120°	1.06/1.49	E
61.5°	130°	1.09/1.49	F
	120°	1.12/1.49	G
		1.09/1.49	H
		1.06/1.49	I
	110°	1.09/1.49	J
63°	130°	1.09/1.49	K
	120°	1.06/1.49	L
64.5°	130°	1.09/1.49	M
1,1,1-Bicyclopentane (II)			N
Visual curve			V
Radial distribution curve			R

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[6] W. Shand, V. Schomaker and J. R. Fischer, THIS JOURNAL, 66, 636 (1944).

[7] S. H. Bauer and J. Y. Beach, *ibid.*, 64, 1142 (1942).

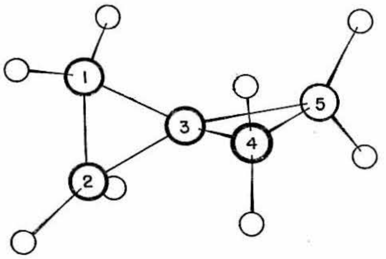
V

II

is not definitely excluded by consideration of the Raman spectrum,[8] is in marked disagreement with the radial distribution integral for all possible values of the bond angles. In order to illustrate the great disagreement with the observed diffraction pattern, we have calculated a theoretical scattering curve (N of Fig. 1) for a model of this molecule with all C–C–C bond angles equal. It is obvious that no reasonable variation of the angles would improve the appearance of the curve. (The stringent geometrical conditions on the C–C–C angles in the structure make it improbable that any of them could possibly differ by as much as 10° from the value 82° used for curve N.)

The radial distribution function, often merely by virtue of the large bond angle of *ca.* 138° indicated by the peaks at 1.49 and 2.77 Å., immediately excludes the other bicyclic structures, as well as all plausible C_5H_8 structures containing multiple bonds, except 1,2-dimethylcyclopropene-1, for which it is easy to set up a satisfactory planar model with C–C = 1.49 Å. and C=C = 1.34 Å. Nor is it entirely certain that agreement could not be obtained for 1-ethylcyclopropene-1. However, the evidence against a multiple bond structure presented by Murray and Stevenson seems conclusive, so that it and the electron diffraction data together afford definite proof of the spiropentane structure.

Discussion.—In spiropentane the deviations of the carbon bond angles from the normal tetrahedral values are most severe, the central carbon atom in particular being subject to the double constraint of having two of its bond angles fixed at approximately 60° by the three-rings of which it is the common member. It is of some interest to consider the structural results in relation to this condition of strain. In the first place, the average carbon–carbon bond distance, 1.49 Å., is significantly shorter than the usual single bond distance, 1.54 Å. In cyclopropane[9] the C–C distance is $1.52_5 \pm 0.03$ Å., also less than the standard distance but not certainly so. It is possible that there is indeed a general effect, correlatable with bond angle strain, which shortens the bond distances in three-membered rings by a barely detectable amount and in molecules with unusually great strain, such as spiropentane, shortens the bond distances considerably. This would be somewhat out of the ordinary (decrease in bond distance usually implies increase in bond energy or energetic stability and it is certain that these strained structures are energetically relatively unstable), but would perhaps not be entirely without precedent; ethylene with C=C = 1.353 Å.[10] and allene (to be regarded as more highly strained than ethylene) with C=C = 1.33_0 Å.[11] seem to present a fair analogy. It is not likely that the bonds in highly strained cyclic compounds should be readily comparable to those in open chain compounds and it seems probable that the full explanation of the properties of the bonds in highly strained molecules with our present language will be complex, with hyperconjugation playing an important role. In the second place, the interesting question of the distribution of the shortening of the bonds between the peripheral bonds C_1–C_2 and C_4–C_5 and the central bonds, to which they are of course not equivalent, is not completely answered by our results, which indicate that the peripheral bonds are somewhat longer than the others but do not exclude either the possibility that the bonds are all of the same length or the possibility that the peripheral bonds are not shortened at all. Finally, the indicated HCH angle of 120°, being considerably greater than the normal value of 109½°, suggests that the methylene carbon atoms relieve some of their bond angle strain by widening the HCH angle. If so, then it is possible that the indicated difference in bond distances, corresponding to the greater C–C–C angle of 61.5° in the ring at the central carbon atom, represents in part the effect of the greater net angle strain on this atom relative to the methylene carbon atoms with which it competes for the total angle of the ring.



I

The results of Rogowski,[12] who reported that he had prepared spiropentane by the conventional debromination of pentaerythrityl bromide and identified it by an electron diffraction investigation, are still puzzling. Whitmore and Williams,[13] repeating the preparation of Rogowski, reported that they obtained a mixture of methylene cyclobutane and 2-methyl-1-butene. Subsequent electron diffraction and chemical investigations confirmed the structure of the main product.[6,7] Comparison of Rogowski's *q* values with ours shows that ours are 3.7 ± 0.1% higher, a difference which is much larger than is usually

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[8] Private communication from Dr. Murray.

[9] L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).

[10] W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).

[11] E. H. Eyster, *J. Chem. Phys.*, **6**, 580 (1938). With the assumption of Gallaway and Barker's parameters for the CH_2 group (as found in ethylene) Eyster's value 97.0 × 10^{-40} g. sq. cm. for the large moment of inertia of allene leads to C=C = 1.33_5 Å.

[12] F. Rogowski, *Ber.*, **72**, 2021 (1939).

[13] See footnote 5 of ref. 7.

obtained in duplicate electron diffraction investigations. Moreover, if Rogowski actually did have spiropentane, his neglect to mention the asymmetries of the first and second minima and of the third maximum is very curious, inasmuch as these features show very clearly on our photographs. It is probably true, as would be indicated by the results of Whitmore and Williams,[13] that Rogowski's preparation was a mixture of hydrocarbons.

We are indebted to Dr. E. R. Buchman for interesting discussion, and to Dr. M. J. Murray for the sample of spiropentane.

Summary

The results of an electron diffraction investigation of the C_5H_8 hydrocarbon prepared by Murray and Stevenson[1] confirm their assignment of the spiropentane structure made on the basis of the Raman spectrum. The dimensions for this molecule are C–H = 1.08 Å. (assumed), C_1–C_3 = 1.48 ± 0.03 Å., C_1–C_2 = 1.51 ± 0.04 Å., $\angle C_2C_3C_1 = 61.5 \pm 2°$, and $\angle HCH = 120° \pm 8°$ ($(C–C)_{ave.}$ = 1.49 ± 0.01 Å.).

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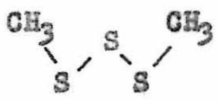
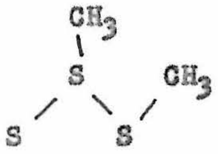
The Molecular Structure of Dimethyltrisulfide, $(CH_3)_2 S_3$

The present electron diffraction investigation was undertaken mainly to determine whether dimethyltrisulfide is a simple trisulfide (I), a thiodisulfide (II), or a dithiosulfone (III).



I



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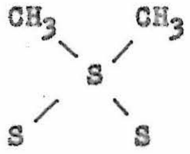

III

Knowledge of this structure is of interest in connection with the problems of the constitutions of the inorganic persulfides and polythionates[1] as well as of the alkyl polysulfides[2], and the Thiokols[3]. With the exception of the trithionate ion[4], $O_3S{-}S{-}SO_3^{=}$, there is no direct structural evidence which settles the question of whether the molecules of these substances have the chain configuration or are related to II or III. In the case of the disulfides H_2S_2, S_2Cl_2, and $(CH_3)_2S_2$, the existing evidence from electron diffraction favors chain structures for all three molecules[5,6,7].

<u>Experimental</u>.- The sample used in this investigation was provided by Professor R. C. Fuson. It was pale yellow in color and was used without further purification. Excellent electron diffraction photographs were made in the apparatus described by Brockway[8] with the use of the high temperature nozzle[9]. At the end of each run the boiler and remaining liquid were examined; no corrosion of the boiler and only slight darkening

of the liquid were observed, indicating that very little decomposition occurred.

Interpretation of the Photographs.- The characteristic features of the photographs are represented by curve of Fig. 1, which was drawn, in accordance with the measured ring diameters, so as to have the general properties of theoretical intensity curves calculated with the simplified expression

$$I\ (q) = \sum_{i,j} \frac{Z_i Z_j}{r_{ij}} \exp(-b_{ij} q^2) \sin\left(\frac{\pi}{10}\, r_{ij}\ q\right).$$

The radial distribution integral[10], curve RD of Fig. 1, was calculated by use of the formula $rD(r) = \sum\limits_{q=1} I(q) \exp(-aq^2) \sin\left(\frac{\pi}{10}\ qr\right)$. with $\exp(-a(100)^2) = 0.1$. The integral has maxima at 1.78 Å, 2.04 Å, 2.45 Å, 3.02 Å (very broad, asymmetric peak), and 4.0 Å (very broad, small peak). Of these peaks the first two may be interpreted as representing respectively the bonded C-S and S-S distances, the third the non-bonded S...H distance, and the asymmetric fourth the non-bonded C...S and S...S interations. The interpretation of the weak maximum at 4.0 Å is discussed below.

An extensive investigation of the straight chain structure I by the correlation procedure was made. For structure I four parameters are required to define the structure if the positions of the hydrogen atoms are assumed and if the long, rotation-dependent, C...S distance is neglected. These may be chosen as: 1) bonded C-S; 2) bonded S-S; 3) non-bonded S...S; and 4) non-bonded C...S.

The first two of these parameters may be determined directly from the radial distribution integral. As a check on the accuracy of this

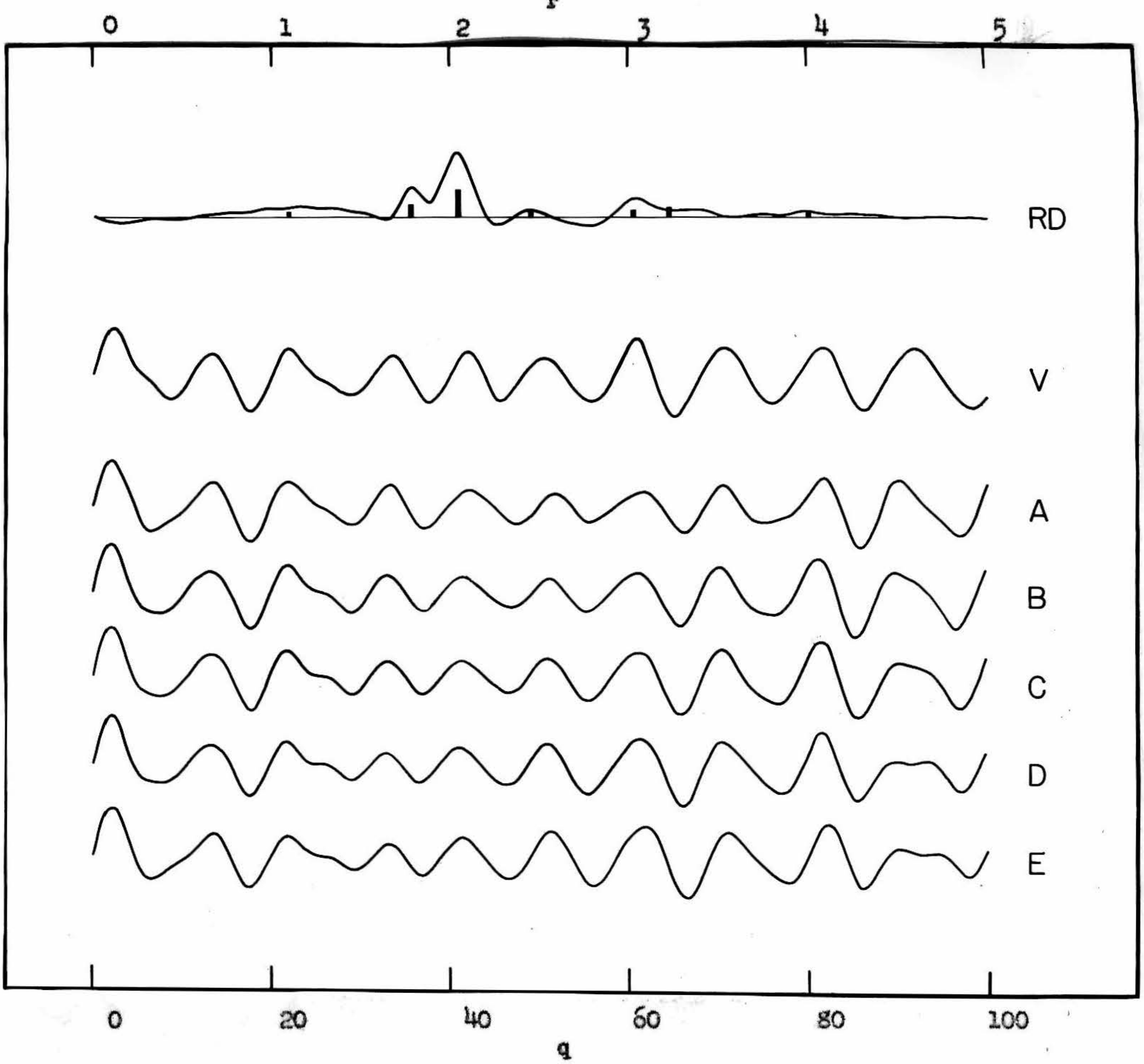

Fig. 1. Electron diffraction curves for dimethyltrisulfide. Chain models, molecular parameters for the various models are: for all models, C-H = 1.09 Å; S-S = 2.04 Å; S...H = 2.45 Å; C...S = 3.02 Å; S...S = 3.22 Å (∠ S-S-S = 104°); $b_{C...H}$ = 0.00016; other parameters varied as follows:

models	C-S	$b_{S...H}$	(∠ C-S-S)
A	1.83	0	102°45'
B	1.81	0.0003	103°30'
C	1.78	0.0003	104°
D	1.75	0.0003	105°
E	1.73	0	106°30'

All other b_{ij} = 0. The long C...S term, with b = 0.0009, was included for models B, C, and D, and neglected for the other models.

determination, twenty-one intensity curves, some of which shown in Fig. 1, were calculated for models with varying ratios between these two distances. In these models the S-S distance was held at 2.04 Å and the average of the non-bonded C...S and S...S distances was kept in agreement with the broad maximum of the integral at 3.0-3.2 Å. Best agreement between the calculated curves and the appearance of the photographs was obtained for models with C-S = 1.78 Å as was expected, changes of 0.03 Å giving marked discrepancies.

The determination of the two remaining parameters is a more difficult problem since the terms which are involved in their variation contribute only about 20% of the total scattering. Since the term representing the two non-bonded C...S distances and the term for the non-bonded S...S distance are of nearly equal weight, it is impossible to distinguish between them. For example, a curve calculated for a model with ∠ S-S-S = ∠ S-S-C = 104° is indistinguishable from one calculated for a model with ∠ S-S-S = 95½°, ∠ S-S-C = 115°. However, it is appropriate to choose S...S > C...S so that the sulfur bond angles ∠ S-S-S and ∠ S-S-C have similar values, and this is done in the following analysis.

Twenty-two scattering curves, some of which are shown in Fig. 2, were calculated for models with varying values of these distances. It was found that it is not possible to obtain theoretical scattering curves in agreement with the appearance of the photographs unless 1) a distance at 4.0 Å as suggested by the radial distribution integral is included in the intensity formula and 2) the S...S distance is given a rather severe temperature factor. The distance at 4.0 Å corresponds to the two longer non-bonded C...S distances in a non-planar model with the C-S bonds

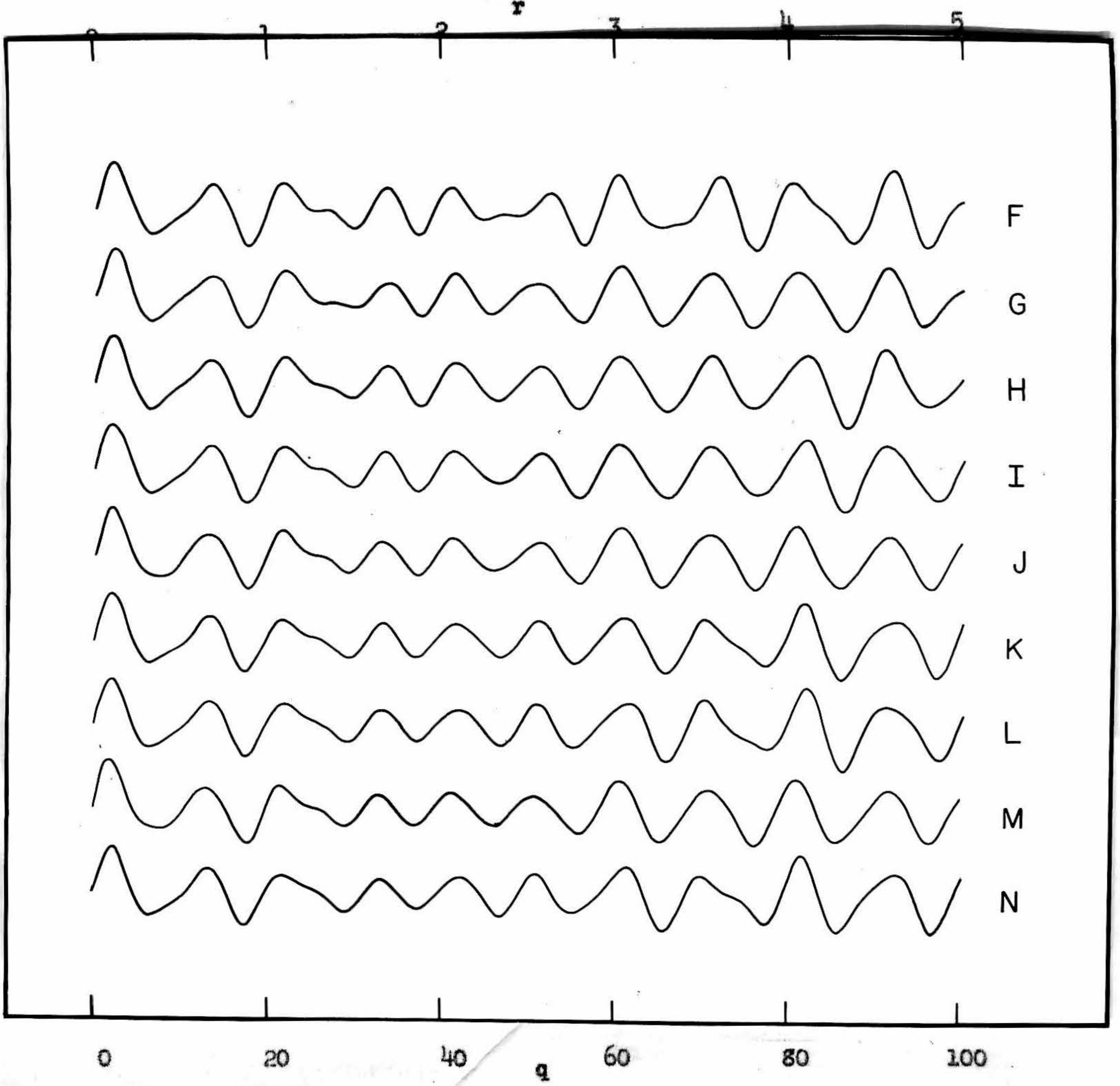

Fig. 2. Electron diffraction curves for dimethyltrisulfide chain models; molecular parameters for the various models are: for all models, C-H = 1.09 Å; C-S = 1.78 Å; S-S = 2.04 Å; S...H = 2.45 Å; $b_{C...H}$ = 0.00016; all other b_{ij} = 0 except for models J and M, for which $b_{S...S}$ = 0.0003; other parameters varied as follows:

model	C...S	S...S	(∠ S-S-S)	(∠ C-S-S)
F	3.10	3.10	99°	108°20'
G	2.96	3.10	99°	101°30'
H	2.97	3.14	100°30'	101°
I	3.02	3.17	102°	104°
J	3.05	3.20	103°	105°40'
K	3.02	3.22	104°	104°
L	2.98	3.22	104°	102°
M	3.05	3.25	105°30'	105°40'
N	3.00	3.25	105°30'	103°20'

The long C...S term, with b = 0.0009, was included for models J and M, and neglected for the other models.

rotated by 106° out of the plane containing the three sulfur atoms. This is just the angle of twist between the O-H bonds in hydrogen peroxide, as deduced from the crystal structure of H_2O_2.urea[11]. Unless this distance is included in the calculation, the character of the first maximum and adjacent minima is in definite disagreement with the appearance of the photographs and curve V, the theoretical curves having their sharp first minima just at the observed position of the weak first maximum, and a weak shoulder (which might be interpreted as corresponding to the observed first minimum) at the observed position of the second minimum. This discrepancy can not be regarded as merely a difficulty in interpretation, in view of our knowledge of the appearance of electron diffraction photographs and their interpretation, but must be regarded as conclusive. On the curve for the accepted model, O, on the other hand, the positions of the features corresponding to the measured first and second minima and the first maximum are satisfactory. The relative depths of the indicated first and second minima, also, are in better agreement with curve V than on the curves calculated without a 4.0 Å term. The agreement is not perfect either in this respect or for the magnitude of the first maximum, which on the photographs is clearly visible, although very weak, but on curve O is indicated only as a region of unusually small upward curvature; however these discrepancies do seem to represent difficulties of interpretation.

Similar differences between the correct and the obvious interpretation of a weak inner ring — the ring appearing stronger on the photographs than would be suggested by the correct theoretical curve, or the apparent relative depths of the adjacent minima being different from that shown by the theoretical curve — have been previously observed in the case of numerous other compounds of which propane[12] is an example. Curve Z_iZ_j, for which the customary coefficients Z_iZ_j/r_{ij} were replaced by Z_iZ_j was calculated to illustrate the notion that the apparent strength of the weak — and also relatively sharp — inner ring may be enhanced by a tendency of the eye to detect more readily the higher frequency components of the pattern.

It appears that in general the appearance of the innermost rings of electron diffraction photographs can not be so simply interpreted in terms of simplified theoretical intensity curves as can the rest of the pattern, perhaps in part because of the very rapid change of total intensity with change in scattering angle at small scattering angles, and that it is never justifiable to make important use of an inner feature — such as weak inner ring — without reference to similar features on the photographs of other substances of known structure. In addition to propane, we have here made particular reference to the photographs and curves of cyclopropane, ethylene imine, and ethylene oxide[13], which show somewhat similar inner rings to that of dimethyltrisulfide.

Curve O was calculated with the following values of the temperature factor b: C-H : 0.00016; S...H : 0.0003; S...S : 0.0003; long C...S : 0.0009; all others : zero, except for the remaining distances involving hydrogen, which were neglected. Curves C and P are identical with curve O except that the values zero and 0.0009, respectively were used for $b_{S...S}$. Curve C is unsatisfactory in regard to a number of minor details in the region $35 < Q < 60$ of which one regarding the relative intensity of the fourth ring can be seen most clearly in Fig. 3. Curve P is

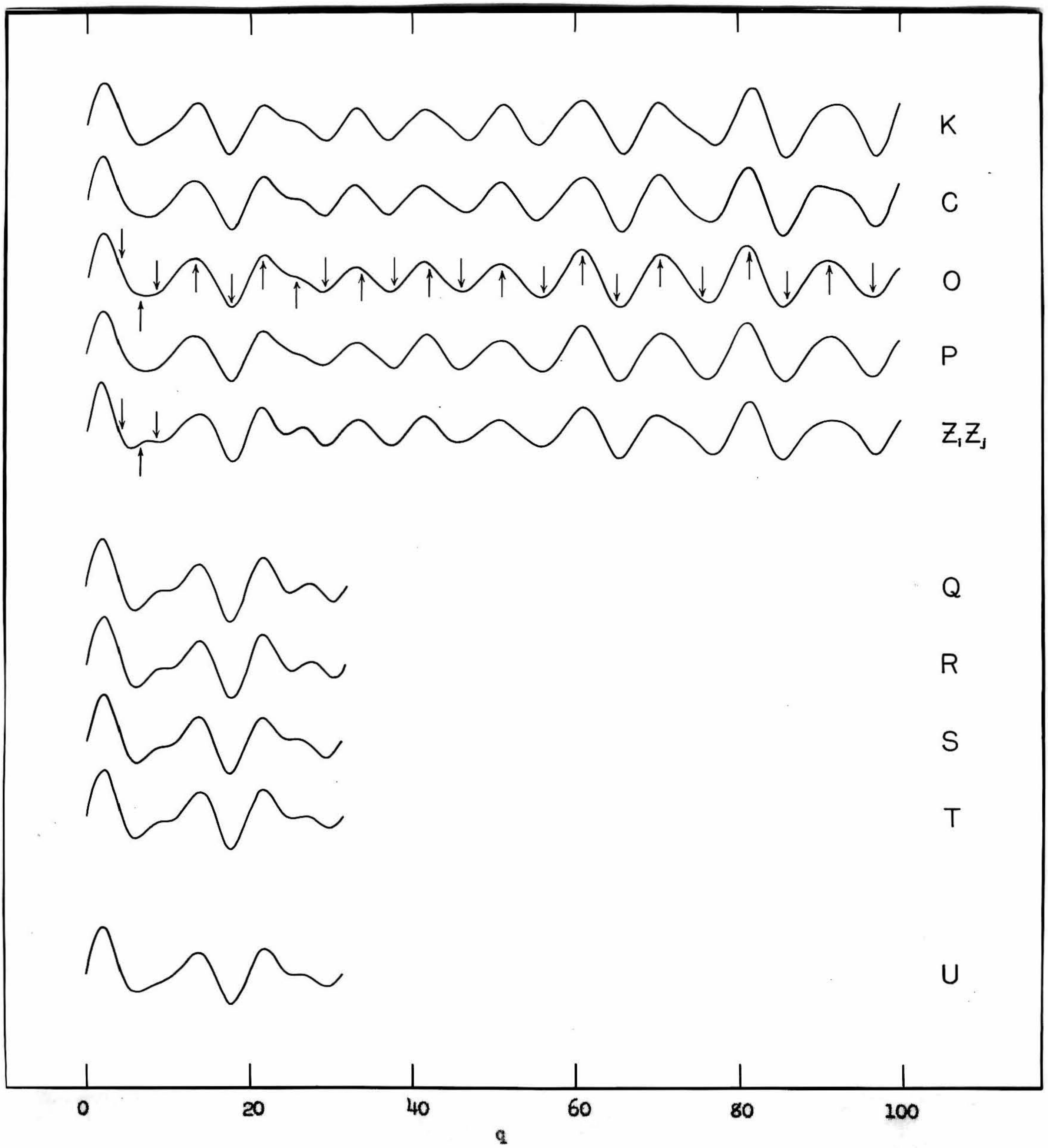

Fig. 3. Electron diffraction curves for dimethyltrisulfide. Legend on the following page.

Fig. 3 (Continued)

Molecular parameters for the various models are:
C-H = 109 Å; C-S = 1.78 Å; S-S = 2.04 Å; S...H = 2.45 Å;
long C...S = 4.00 A; $b_{C...H}$ = 0.00016; other parameters varied as follows:

chain models I

	$b_{S...H}$	$b_{S...S}$	$b_{\text{long } C...S}$
K	0	0	term omitted
C	0.0003	0	0.0009
O	0.0003	0.0003	0.0009
P	0.0003	0.0009	0.0009
Z_iZ_j	0.0003	0.0003	0.0009

C...S = 3.02 Å and S...S = 3.22 Å for all chain models

dithiosulfone models III

	S...S	C...S	(∠ C-S-C)
Q	3.02	3.12	119°30'
R	3.12	3.02	134°
S	3.02	3.22	102°
T	3.22	3.02	132°30'

thiodisulfide models II

U	3.22	3.02

Table I

min	max	q_{obs}	q_0	q_0/q_{obs}
1		4.42		
	1	6.61		
2		8.52		
	2	13.35	13.2	0.989
3		17.73	17.7	.998
	3	21.59	21.6	1.000
	3'	25.70		
4		29.37	29.0	0.988
	4	33.85	33.0	.975
5		37.86	37.3	.985
	5	42.03	41.5	.987
6		45.93	46.2	1.006
	6	50.93	50.9	0.999
7		56.19	55.9	.995
	7	60.92	60.8	.998
8		65.17	65.7	1.008
	8	70.51	70.6	1.001
9		75.78	76.3	1.007
	9	81.50	81.2	0.996
10		86.12	85.8	.996
	10	91.33	91.2	.999
11		96.74	96.6	.999
			average	0.996
			average deviation	0.006

only slightly less satisfactory than curve O. This indication of a relatively large value required for $b_{S\ldots S}$ is rather surprising. We know of no other molecules in which the temperature effect is so large for a distance between heavy atoms bonded to the same atom. The large temperature factor required for the long C...S distance, on the other hand, is quite reasonable, and indicates that only a small potential restricts internal rotation at the temperature at which the photographs were made.

Scattering curves for several of the models of types II and III which were calculated are shown in Fig. 3. The only important essential differences between these models and chain structure models are differences of amplitude of the short C...S term and the long C...S term, of which the latter is most important for our argument, the essential long C...S term having only half strength in type II models and being absent in type III models. It is seen that these curves are quite unsatisfactory with respect to the first ring. (At large scattering angles these curves and curve O are closely similar, none having an appreciable 4.0 Å contribution.) Since no variation in molecular parameters whatever makes the initial portions of these curves correspond to the appearance of the photographs, we conclude that, to the accuracy of our observations of the inner rings, neither II nor III is the structure of dimethyltrisulfide.

Our final values for the parameters of the satisfactory straight chain structure are: C–H = 1.09 Å (assumed), C–S, 1.78 ± 0.04 Å, S–S = 2.04 ± 0.02 Å, ∠ H–C–S = 112° (assumed), ∠ S–S–S = 104° ± 5°, ∠ C–S–S = 104° ± 5°. (C...S = 3.02 ± 0.04 Å and S...S = 3.22 ± 0.04 Å).

The terminal CH_3-S bonds are rotated about 106° from the plane of the sulfur chain.

Discussion.- The chain structure found for dimethyltrisulfide is in agreement with the chain structures proposed for the three disulfides which have been previously investigated by the electron diffraction method, H_2S_2[6], S_2Cl_2[5,7], and $(CH_3)_2S_2$[6]. In all four molecules, the bonded S-S distance is 0.02-0.03 Å shorter than the S-S distance 2.07 Å in S_8[14]. The C-S distances in $(CH_3)_2S_2$ and $(CH_3)_2S_3$ are the same, and are 0.04 Å shorter than the distance in $(CH_3)_2S$[15]. These shortenings are probably significant although they are within the limits of experimental error in each case. When sulfur forms single covalent bonds with two other atoms, the existing data indicate the angle decreases as the electronegativity of the bonded atoms increases: the observed values are 107° in $(CH_3)_2S_2$, 105° in S_8, 104° in $(CH_3)_2S_3$, 103° in S_2Cl_2, and 101° in SCl_2.

In addition to the direct experimental evidence of the electron diffraction data, the sulfur-sulfur distance also suggests that the molecule has the straight chain structure I, inasmuch as it is approximately equal to the S-S distance in the singly bonded molecules just mentioned and is indeed just equal to the distance in $(CH_3)_2S_2$ which is agreed to have the singly bonded structure; it is about 0.15 Å greater than would be expected for an S-S bond of the type to be found in structure III and about 0.08 Å greater than the average to be expected for structure II, on the basis of the Pauling-Huggins covalent radii[16]. Although no test of these covalent-radius predictions of sulfur-sulfur multiple bonds is available, a rather close analogy can be drawn with the phosphorus-sulfur bonds in P_4S_3, in which the bonds are presumed to be single bonds, as contrasted to the phosphorus-sulfur bonds in phosphorus sulfoxide, thiophosphoryl fluoride, and thiophosphoryl chloride. The P-S distances in $P_4O_6S_4$, PSF_3, and $PSCl_3$ are 1.85 Å[17], 1.85 Å[18], and 1.94 Å[19], respectively (the covalent radius sum for a double bond is 1.94 Å[16]), while in P_4S_3 the P-S single bond distance is about 2.12 Å[20]. (radius sum 2.14 Å). Here the 0.2 Å difference between the lengths of the single and double bonds between phosphorus and sulfur is found to be valid, even though there might be some question, as there is for the special sulfur-sulfur bonds in structures II and III, as to whether the phosphorus-sulfur bond in the thiophosphoryl compounds should have the same length as that predicted in a conventional double bond.

The same conclusion is suggested by the bond angles of 104°. These bond angle values are reasonable for the singly bonded atoms in the chain structure I but they do not seem reasonable for the angles involving the doubly bonded sulfur atoms in structures II and III. For structure III, moreover, the S-S-S and C-S-S bond angles of 104° correspond to a C-S-C bond angle of greater than 130°, an unreasonably high value by a wide margin.

Summary.- Dimethyltrisulfide $(CH_3)_2S_3$ has been investigated by the electron diffraction method. The molecule was found to have the chain configuration, with the following interatomic distances and angles: C-H = 1.09 Å (assumed), C-S = 1.78 ± 0.04 Å, S-S = 2.04 ± 0.02 Å, $\angle$H-C-S = 112° (assumed), $\angle$S-S-S = 104° ± 5°, $\angle$C-S-S = 104° ± 5°. The results also suggest that the C-S bonds oscillate with rather large amplitude about a mean position approximately 106° out of the plane of the three sulfur atoms.

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The Electron Diffraction Investigation of Isomeric Lewisites

This investigation of the two isomers of β-chlorovinyldichloroarsine, Lewisite I (b.p. 190° at 760 mm.) and Lewisite II (b.p. 150.2° at 760 mm.), was undertaken in order to determine which is the <u>cis</u> form and which is the <u>trans</u> form. MacDowell and Emblem[1] found the dipole moments of Lewisite I and Lewisite II to be 2.21×10^{-18} e.s.u. and 2.61×10^{-18} e.s.u. respectively*, and on this basis assigned the <u>trans</u> structure to Lewisite I and the <u>cis</u> structure to Lewisite II. Confirmation of this assignment seemed desirable because of the small difference between the observed moments and because of the uncertainty which we believe would necessarily arise from the presence of two polar groups ($\diagdown AsCl_2$ and $\overset{Cl}{\diagdown}C{=}C\diagdown$ or $\underset{Cl}{/}C{=}C\diagdown$) joined by a single bond with more or less unpredictable freedom of internal rotation in the neighborhood of an unknown preferred orientation. In addition, it was hoped that information could be obtained concerning the influence of the carbon-carbon double bond on the arsenic-carbon single bond distance and of the organic group on the arsenic-chlorine distance.

<u>Experimental.</u>- The sample of the higher boiling isomer I was obtained from Dr. C. E. Redemann of the University of Chicago, and that of isomer II was provided by Edgewood Arsenal through the courtesy

*These values are not consistent with the value 1.77×10^{-18} e.s.u. found by C. T. Zahn and H. Mohler, Helv. Chim. Acta <u>21</u>, 1292 (1938) for a preparation of β-chlorovinyldichloroarsine which, on the basis of this value, they concluded was a mixture of the <u>cis</u> and <u>trans</u> isomers.

of Gen. W. C. Kabrich and Col. M. F. Peake. The constants given by Redemann for the sample of isomer I are: b.p., 72-73° C. at 10 mm.; $d^{25°} = 1.8799$; and $n_D^{25°} = 1.6068$; in fairly close agreement with the accepted values. According to Edgewood Arsenal the sample of isomer II had a refractive index corresponding to a composition of 4% of isomer I and 96% of isomer II, while chemical analysis showed 4.68% of isomer I, 95.04% of isomer II, and 0.22% of arsenic trichloride. This degree of purity is sufficient for electron diffraction investigation.

Diffraction photographs were made in the usual way[2]. For both substances photographs were obtained which show the main rings extending nearly to the limit of the camera.

Interpretation.- Both the radial distribution method[3] and the correlation method[2,4] were used in interpreting the pictures. The photographs of the two isomers were found to be rather similar, but upon careful examination they showed definite, significant differences. Curves 3 and 4 of Fig. 1 were drawn in accordance with previous experience in this laboratory to represent the visual appearance of the photographs and the measurements made on them. These curves were used for the calculation of the radial distribution integrals as well as in the subsequent correlation procedure.

The radial distribution curves, 1 and 2 of Fig. 1, for the two isomers are very similar except for two significant differences. For isomer I there is a distinct, although broad, peak at 4.45 Å, while

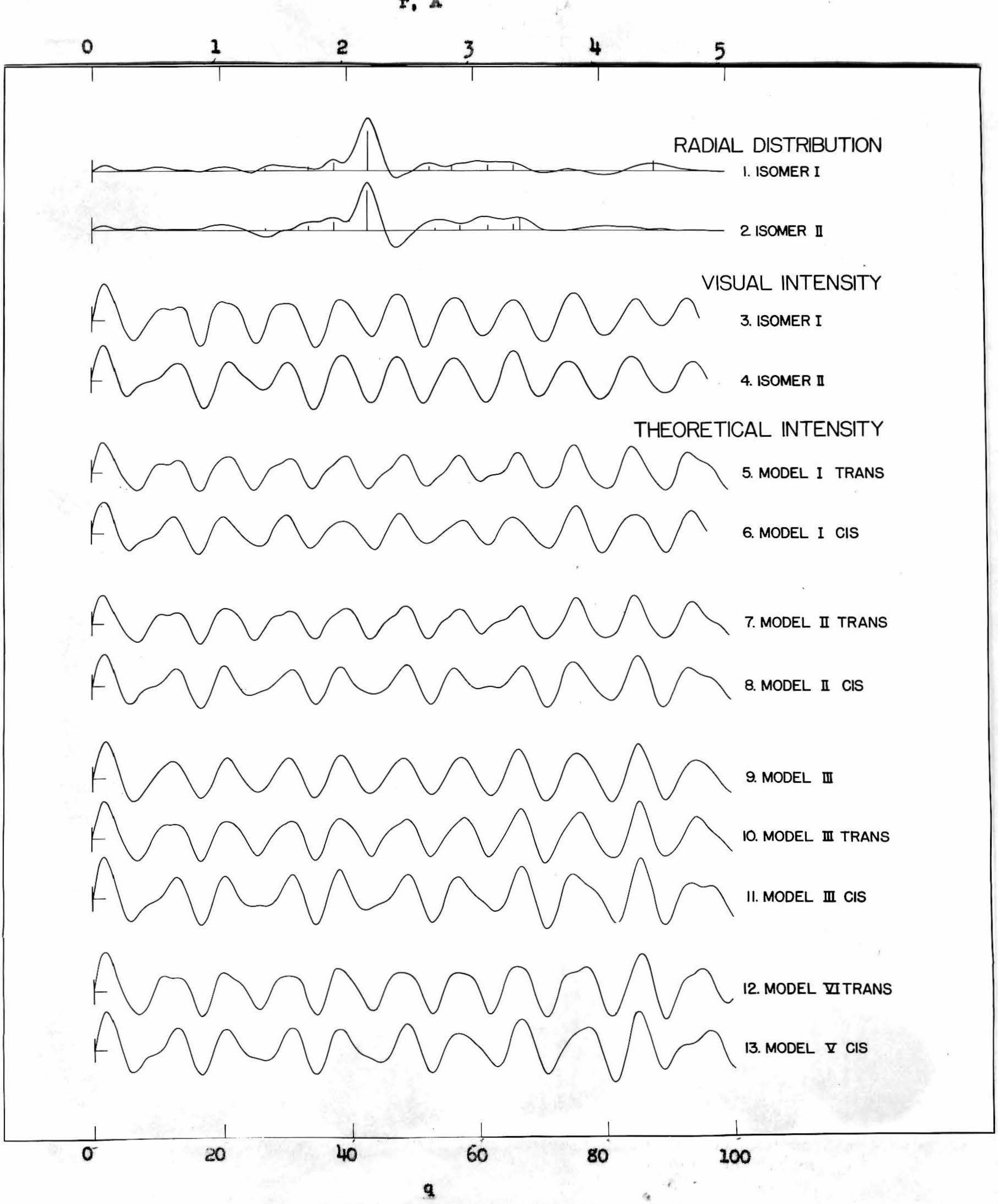


Fig. 1. Electron diffraction curves for Lewisite. Models described in text. Curve No. 9 was calculated for Model III with the omission of the non-bonded As...Cl term. $q = \frac{40}{\lambda} \sin \frac{\theta}{2}$.

no such peak occurs on the curve for isomer II. On the other hand, the curve for isomer II lies much higher than the other at 3.3 Å. These are the non-bonded As...Cl distances which would be expected respectively for the _trans_ and _cis_ isomers; hence it is very probable that isomer I is the _trans_ compound, and isomer II is the _cis_. The remaining significant features of both curves are interpreted as follows in terms of specific interatomic distances: 1.7 Å, C-Cl; 1.90 Å, C-As; 2.17 Å, As-Cl; 2.75 Å, C...Cl and C...As (unresolved); 3.1 Å, C...Cl; 3.3 Å, Cl...Cl (in the case of the _cis_ compound, this distance is nearly coincident in the As...Cl). The various distances between 2.7 Å and 3.3 Å contribute about equally with a total of about 25% to the whole scattering. It is not surprising, therefore, that the corresponding regions of the radial distribution curves are not well resolved. A reasonable interpretation may be made, however, using the bond distances indicated by the first parts of the curves, and the bond angle values found for related molecules. The vertical lines under curves 1 and 2 represent, for our best molecular models described below, the interatomic distances and scattering coefficients which are independent of the angle of internal rotation about the C-As bond.

Since nine parameters are required to fix the configuration and dimensions of each molecule, the number of curves which would have to be calculated in a thorough correlation treatment would be prohibitive, and, furthermore, it is certain that a complete structure determination could not be achieved. Theoretical scattering curves were calculated, nevertheless, for the models listed in Table 1 in order to verify the conclusions from the radial distribution functions. A curve for which the As...Cl term was omitted was also calculated for model III. The *cis* and *trans* models differ only by this one term if we make the reasonable assumption that the terms which are dependent on the rotation of the $AsCl_2$ group have very large temperature factors and may therefore be neglected. General agreement is satisfactory, being best for model V *cis* and for model VI *trans*. The quantitative comparison of $q_{calc.}/q_{obs.}$ for measurements of fifteen features, excluding those of the first and last main rings and the eighth maximum, gives 0.999 and 0.997 for the models V *cis* and VI *trans* respectively, with average deviations of 0.010 in both cases. At large q values, particularly at the eighth and last main rings, the agreement is improved by omitting the As...Cl term. This corresponds to an appreciable temperature factor for this term; it is indicated that this temperature factor is larger for the *cis* molecule as is to be expected from the greater contribution to variation of the As...Cl distance made in this molecule by bending vibrations.

Evidence for the correctness of the identification of the two isomers is also given by consideration of the differences between certain features of the respective curves, in particular the shoulder preceding the first maximum, the asymmetry of the second maximum, and the asymmetry of the third minimum.

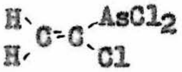
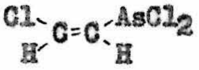
Discussion.- This work confirms the identification of

Table 1

Models for Lewisite

Model	As-C	∠Cl-As-Cl	∠Cl-C=C	∠Cl-As-C	∠As-C C
I (both)	1.94 Å	98°	125°	98°	125°
II (both)	1.94 Å	98°	120°	98°	125°
III (both)	1.90 Å	100°	124°	100°	120°
V (*cis*)	1.90 Å	100°	124°	100°	124°
VI (*trans*)	1.90 Å	100°	120°	100°	120°

In all models C=C = 1.36 Å, C-Cl = 1.69 Å, As-Cl = 2.17 Å.

MacDowell and Emblem[1] that isomer I, the higher boiling isomer, has the trans structure and that isomer II has the cis structure. It should be pointed out that the possibility that isomer II has the structure  $\mathrm{H_2C{=}C(Cl)AsCl_2}$ is not excluded by our data, since the As...Cl and other important distances in a model for this structure could reasonably be made to be nearly the same as those found here under the assumption of the structure  $\mathrm{ClHC{=}CHAsCl_2}$. MacDowell and Emblem concluded from their consideration of the dipole moment values that neither Lewisite I nor II can have this formula. Presumably there is chemical evidence also.

The bond distances in these molecules are in accord with previous work. The As-Cl distance, 2.17 Å, is to be compared with that in $AsCl_3$, 2.17 ± 0.02 Å[5]. The As-C distance, 1.90 Å, is considerably less that 1.98 Å the distance found[6] in trimethylarsine and the sum of the covalent radii, as might be expected for an As-C bond adjacent to a double bond. A shortening of the C-Cl bond from 1.76 Å to 1.70 Å seems to be suggested by the radial distribution integrals, and actually this latter value is about what would be expected from the known values[7] in the chloroethylenes.

The bond angles cannot be said to have been determined with accuracy, but it is probable that both ∠Cl-C=C and ∠As-C=C are between 120° and 125°, and that ∠Cl-As-Cl and ∠Cl-As-C are near 100°, the value found for $AsCl_3$[5].

Summary.- An electron diffraction investigation of two isomers of β-chlorovinyldichloroarsine (Lewisite) shows that isomer I (b.p. 190° at 760 mm.) has the *trans* structure, and that isomer II (b.p. 150.2° at 760 mm.) has the *cis* structure. The interatomic distances found are in accord with those in related substances.

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An Electron Diffraction Investigation of Methylal and Ethylene Glycol

Although the electron diffraction method for determining molecular structures has been most often applied in cases where the configuration or bond structure of the molecule in question are in doubt, information of value may likewise be obtained by the investigation of simple compounds the structures of which are well known from other considerations. In these latter instances it is desirable to determine the interatomic distances as precisely as possible in order that small deviations from the expected or normal distances may be detected, since it seems certain that significant changes in chemical reactivity or other properties imply only small changes in molecular structure such as often lie within the accuracy of the electron diffraction method. The present study is a part of a more extended program under way in this Laboratory in which a large series of simple substances are being investigated by electron diffraction with the improved techniques now available. Since work on neither methylal (dimethoxymethane) nor ethylene glycol has been previously reported, it seemed desirable to report our results at this time.

Experimental.- The diffraction photographs were prepared with the apparatus described by Brockway[1]. Each substance was redistilled before use, generous first and last portions being discarded. Fifteen or more photographs were prepared of each substance. The values of $q_o = 40/\lambda \sin \vartheta/2$ in the tables are averages of measurements of two observers of ten or more photographs. By the use of the measured values q_o and the appearance of the photograph, the visual curves V of Figures 1 and 2 were drawn in accordance with previous experience to correspond with the general character of the theoretical intensity curves calculated with the formula $I(q) = \sum_{ij} \frac{Z_iZ_j}{r_{ij}} \exp(-a_{ij}q^2) \sin(\frac{\pi}{10} r_{ij}\, q)$. The temperature factors a_{ij} were given the values 0.00016 for bonded hydrogen terms, 0.0004 for non bonded hydrogen terms, the longest carbon-carbon term in methylal and the oxygen-oxygen term in ethylene glycol and zero for all other terms, except the hydrogen-hydrogen terms, which were neglected. Radial distribution functions were calculated[2] from the visual intensity curve by means of the equation $r\, D(r) = \sum_{q_i} I(q_i) \exp(-bq_i^2) \sin(\frac{\pi}{10} q_i r)$ where $\exp(-aq_{max}^2) = 0.1$.

Methylal.- Photographs of methylal were taken with the sample at 0° C and at room temperature. The scattering pattern is represented by the curve V of Fig. 1. The radial distribution integral, RD of Fig. 1, shows the following maxima: 1.10 Å, 1.43 Å, 2.07 Å, 2.36 Å, and two broad maxima at 2.8 Å and 3.6-3.7 Å respectively. The first two peaks are the bonded C-H and C-O distances respectively. The maximum at 2.36 Å, which arises from non-bonded C...O and O...O terms, indicates C-O-C and O-C-O angles close to 112°. It was not deemed feasible to attempt independent evaluation of these angles, nor to test models in which the C-O-C-O-C chain was not coplanar. The peak at 3.6-3.7 Å, corresponding to non-bonded C...O distances in models of this type, suggests coplanarity, and since rotation dependent terms are necessarily of relatively low weight, variations of this nature would have very little effect on the theoretical

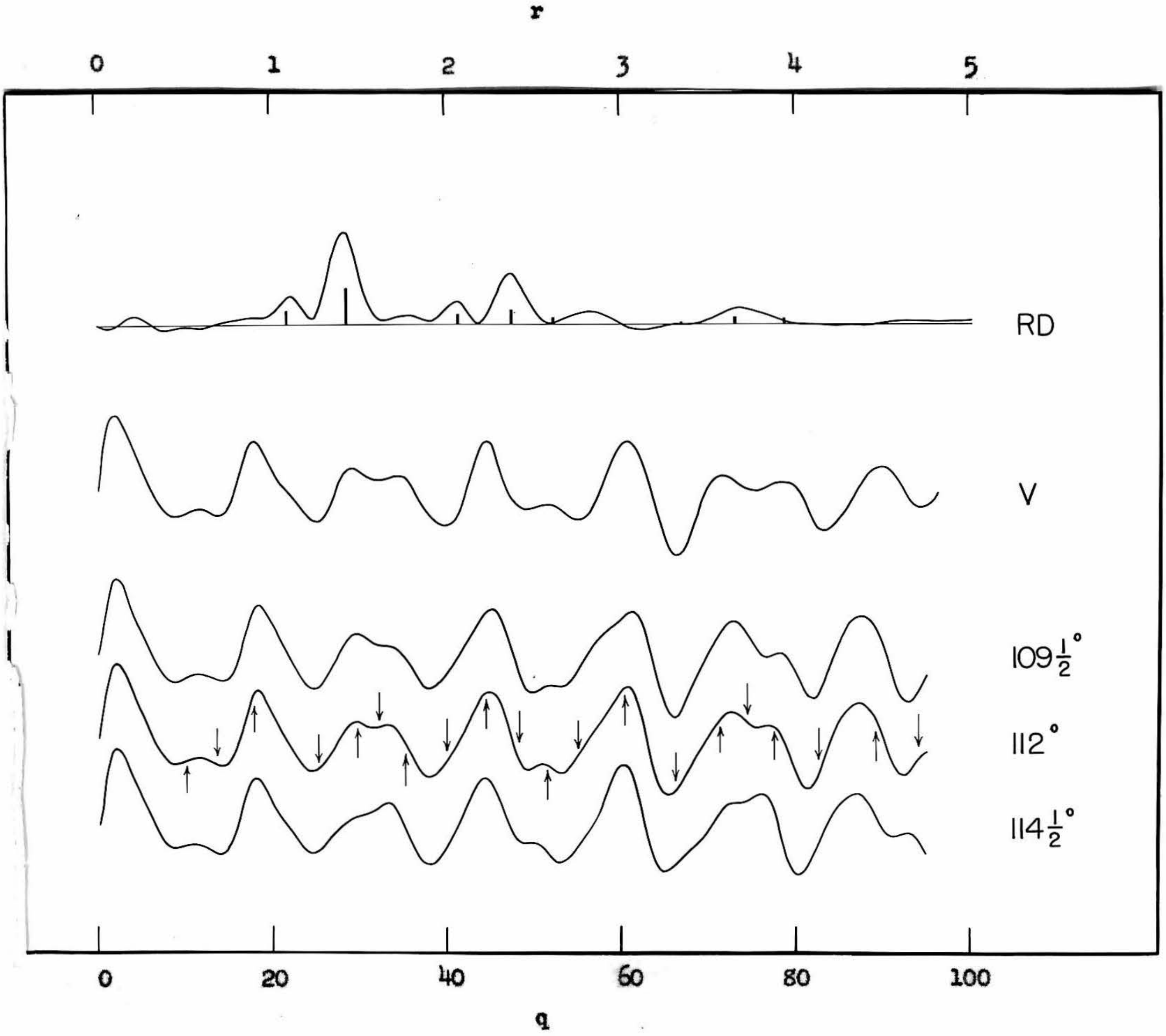

Fig. 1. Electron diffraction curves for methylal

intensity curves.

Theoretical intensity curves shown in Fig. 1 were calculated for three models, each with C-H = 1.09 Å, C-O = 1.43 Å, and ∠ C-O-C = ∠ O-C-O = 109½°, 112° and 114½° respectively. All H-C-O angles were assumed to be tetrahedral. The curves for the 109½° and 114½° models show unsatisfactory relations between the intensities of the 3rd and 4th maxima, the 6th and 7th minima, and the 8th and 9th maxima. Quantitative comparisons for the 112° model are given in Table I. We accept the following structural parameters for the methylal molecule: C-H = 1.09 ± 0.04 Å, C-O = 1.42 ± 0.02 Å, average of ∠C-O-C and ∠O-C-O = 112° ± 2°.

Ethylene glycol.- Photographs of ethylene glycol were obtained using the high temperature nozzles[3,4]. Considerable difficulty was encountered in obtaining good photographs, perhaps because of the high heat of vaporization of the substance. The scattering pattern is very similar to that of methylal, as shown by the curve V of Fig. 2. The radial distribution function, RD of Fig. 2, shows maxima which may be interpreted as follows: the broad first maximum includes the bonded O-H (0.97 Å) and C-H (1.09 Å) distances, the second at 1.44 Å is the unresolved average of the C-O and C-C distances. The broad maximum at 2.08 Å includes three different non-bonded O...H and C...H terms, and the maximum at 2.39 Å is the non-bonded C...O distance. The weak maximum at 3.65 Å, corresponding to the O...O distance, suggests that the molecule has the trans configuration.

Theoretical intensity curves were calculated for the models indicated in Fig. 3. In all models O-H = 0.97 Å, C-H = 1.09 Å, and bond angles involving hydrogen atoms were assumed to be tetrahedral. Curves for the molecule in the trans configuration were calculated for all models;

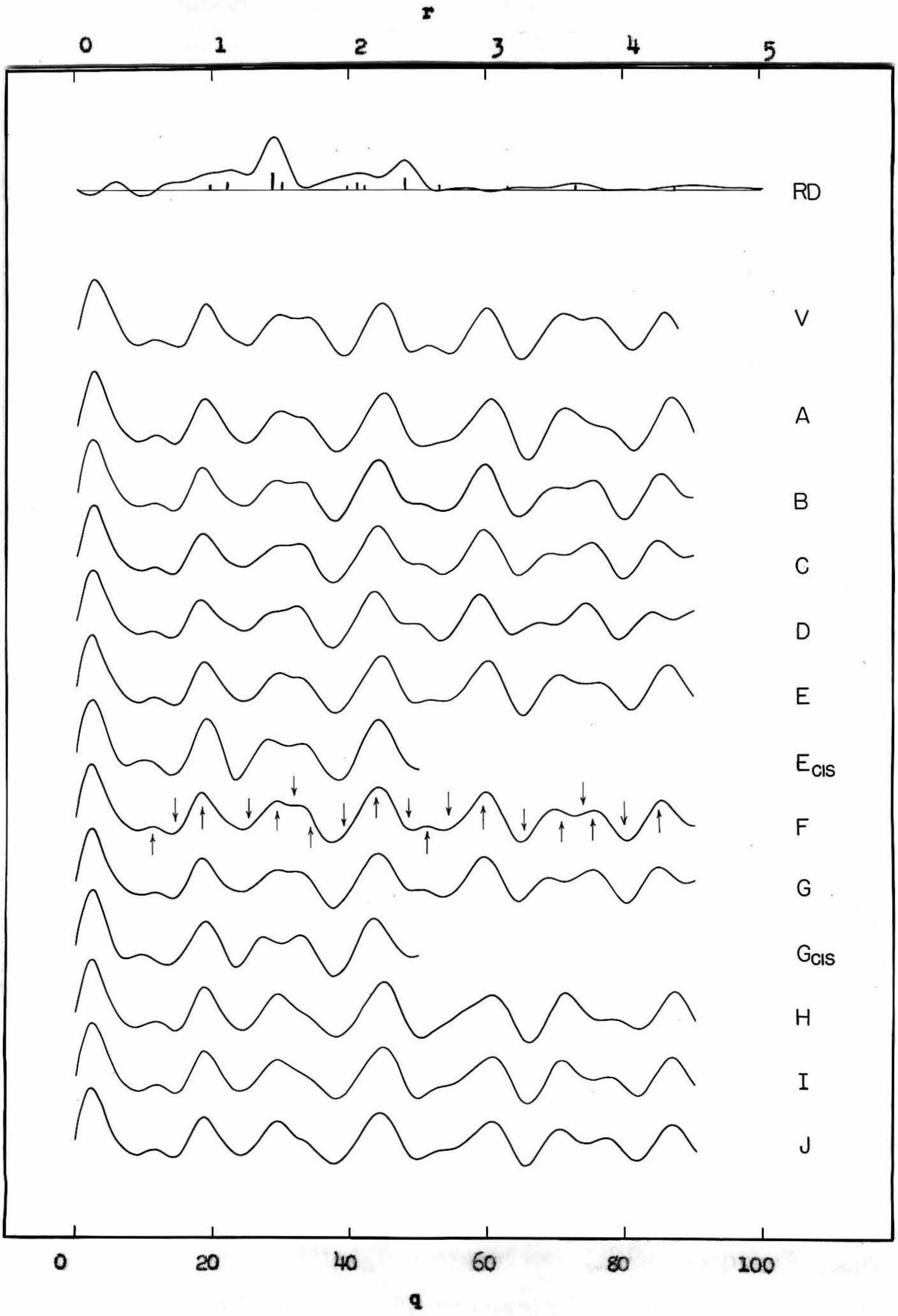

Fig. 2. Electron diffraction curves for ethylene glycol

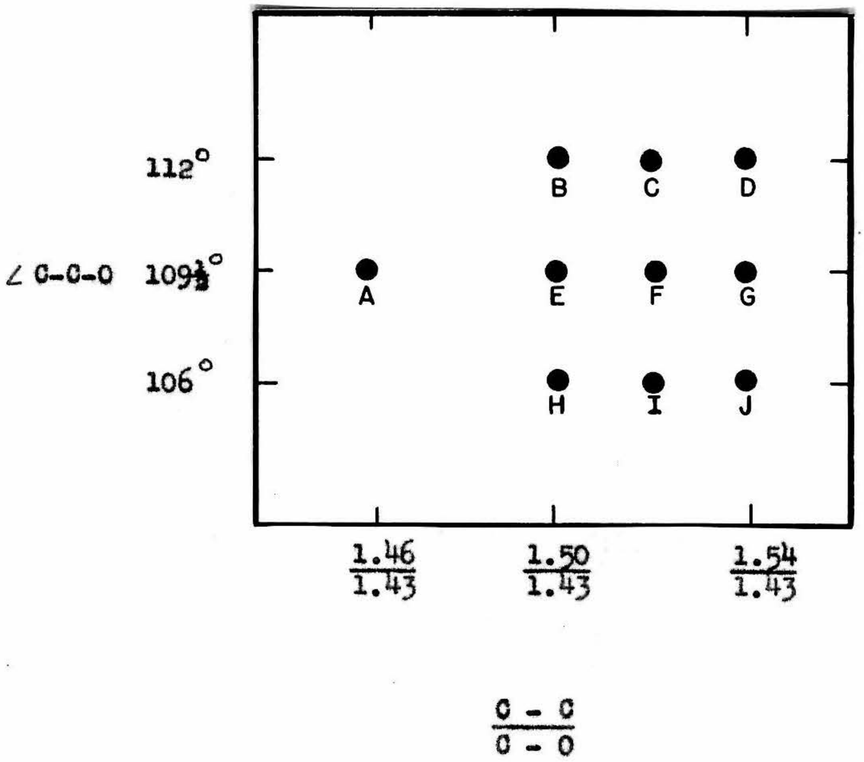

Fig. 3. Plot showing the molecular parameters for the various models of ethylene glycol

Table I

Methylal

Min	Max	q_{obs}	q_{112°	$\frac{q_{112^\circ}}{q_{obs}}$
	1	10.05	11.5	(1.143)
2		13.54	14.3	(1.056)
	2	17.85	18.1	1.014
3		25.13	24.8	.987
	3	29.83	29.8	.999
4		32.20	31.9	.991
	4	35.31	33.5	(.949)
5		39.97	38.4	.961
	5	44.44	44.7	1.006
6		48.06	49.5	(1.030)
	6	51.48	51.1	.993
7		55.06	53.2	(.966)
	7	60.35	60.7	1.006
8		66.20	65.7	.992
	8	71.21	72.4	(1.015)
9		74.35	75.6	(1.017)
	9	77.50	77.2	(.996)
10		87.64	81.3	.984
	10	88.97	87.4	.982
11		93.98	92.3	.982
			average	.991
			average deviation	.010

curves for the molecule in the cis configuration were calculated for models E and G only. The cis models are rendered unsatisfactory with regard to the position of the 1st maximum and the lack of asymmetry of the 3rd minimum. Since the terms by which the cis and trans models differ are subject to the temperature effect, the cis curves are not shown beyond $q = 50$. The appearance of the photographs is best represented by the curve F. The relative intensities of the components of the two doublet maxima, 3 and 4, and 8 and 9 and the relative depths of minima 6 and 7, are rather sensitive to changes in the structural parameters, and consideration of these combined with the quantitative comparison in Table 2, lead to the following parameters for the ethylene glycol molecule: O-H = 0.97 Å (assumed), C-H = 1.09 Å (assumed), C-O = 1.43 ± 0.02 Å, C-C = 1.52 ± 0.02 Å, $\angle$ C-C-O = $109\frac{1}{2}^\circ \pm 2^\circ$, probably trans configuration.

Discussion.- The carbon-carbon distance in the glycol molecule is suggested by the electron diffraction data to be 0.02 Å shorter than the sum of the covalent radii. The explanation of this effect, if it is real, is not apparent to us, although it seems possible that some type of hyper-conjugation may be present. Unpublished work in this laboratory has indicated that the carbon-carbon distance in several other simple oxygen-containing molecules may also be slightly short, viz., 1.51 ± 0.02 Å in diethyl ether, and 1.51 ± 0.03 Å in dioxane.

The bond angles and carbon-oxygen distances are normal in both molecules.

Summary.- An electron diffraction investigation of methylal and ethylene glycol gave the following structural parameters for these molecules:

Table II

Ethylene Glycol

Min	Max	q_{obs}	q_F	q_F q_{obs}
	1	11.20	11.2	(1.000)
2		14.59	14.4	(.987)
	2	18.49	18.4	.995
3		25.22	24.8	.983
	3	29.25	29.3	1.002
4		31.74	32.0	1.008
	4	34.24	33.3	(.973)
5		39.17	37.9	.968
	5	43.85	44.0	1.003
6		48.41	49.3	(1.018)
	6	51.20	51.1	.998
7		54.38	53.8	(.989)
	7	59.31	59.7	1.007
8		65.27	64.8	.993
	8	70.86	69.8	(.985)
9		73.68	72.5	(.984)
	9	75.22	75.8	(1.009)
10		79.8	80.3	1.006
	10	84.8	85.3	1.006
			average	.997
			average deviation	.010

Methylal: C-H = 1.09 ± 0.04 Å, C-O = 1.42 ± 0.02 Å, average of ∠C-O-C and ∠O-C-O = 112° ± 2°; ethylene glycol: O-H = 0.97 Å (assumed), C-H = 1.09 Å (assumed), C-O = 1.43 ± 0.02 Å, C-C = 1.52 ± 0.02 Å, C-C-O = 109½° ± 2°, probably trans configuration.

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The Determination of the Interatomic Distances in Silver Molybdate, Ag_2MoO_4

Silver molybdate was first examined by the X-ray method in 1922 by Wyckoff,[1] who found that crystals of the substance had what is now called the spinel structure. With the methods available at that time, Wyckoff was unable to determine accurately the value of the oxygen parameter; an approximate value of $x = 3/8$ was given by him.

Since a precise value of the parameter would yield accurate values for both the molybdenum-oxygen and the silver-oxygen distance, we have reinvestigated this crystal by the X-ray method. The size of the molybdate group does not appear to have been hitherto determined and the length of the silver-oxygen bond is of interest in connection with the problem of correlating color and bond character.[2-4]

Experimental.- Silver molybdate was prepared by adding aqueous silver nitrate to aqueous sodium molybdate. The resulting precipitate was washed with water and dissolved in dilute ammonium hydroxide. Slow evaporation of the solution yielded small bright yellow octahedral crystals. A tiny crystal, about 0.1 mm. in its greatest dimension, was chosen for X-ray examination. Measurement and indexing of symmetric and asymmetric Laue photographs taken with the general radiation from a tungsten target, and of a series of oscillation photographs taken with MoK_α radiation ($\lambda = 0.711$ Å.) confirmed the size of the unit cell, $a_o = 9.26$ Å., and the space group, O_h^7 - Fd3m, found by Wyckoff.[1] The intensities of the reflections on the oscillation photographs were estimated visually by means of the multiple film technique; the three films used in each set were interleaved by 0.001 inch copper foil in order to decrease the intensity on the successive films sufficiently.

In all calculations of F values the atomic f curves in "Internationale Tabellen zur Bestimmung von Kristallstrukturen" were used; dispersion corrections of 1.5 and 4.0 were subtracted from the values for silver and molybdenum, respectively. The corrected f curves were then multiplied by the temperature factor, $e^{-\beta(\sin \vartheta/\lambda)^2}$; the value $\beta = 1.5$ was determined from the observed F values of the reflections (hkl) for which h = 4n, k = 4n, l = 4n; these F values are not very structure sensitive. The effect of absorption was ignored since it is believed to have been unimportant because of the favorable size and shape of the crystal used.

Determination of the Parameter.- Although the scattering power of oxygen is small compared to those of silver and molybdenum, the calculated F values of many of the reflections to which the contributions of the silver atoms and the molybdenum atoms are of opposite sign were found to vary sufficiently with x to allow a precise determination of the parameter.

Preliminary consideration of the ratio $F_{(333)}/F_{(111)}$ fixed the limits $0.36 < x < 0.38$. The F values of the ten available reflections of the type mentioned above were then calculated for values of x between these limits, in intervals of 0.002 in x. These F values were then used to calculate the dependence on x of the ratio of F values of any two reflections, the restriction being made however that all ratios between F values whose plots of F vs. x were of nearly the same slope were not calculated. By comparing the ratio curves so obtained with the observed ratios, twenty-one values of x were obtained. Some of these data are illustrated in Fig 1. These values were weighted by multiplying each by the difference in slope of the two F curves involved. The weighted mean value of the parameter x obtained in this way is 0.3639, the average deviation is 0.0018, and the most probably deviation is 0.0004. On the other hand, if the observed and calculated F values of these ten reflections are treated by the method of least squares,[5] a simple procedure if the calculated F curves are used to evaluate the values of $\partial F_{hkl}/\partial x$, the value $x = 0.3634$ is obtained. We adopt 0.364 ± 0.002 as the best value of x, taking all sources of error into account.

A comparison of calculated and observed F values for some representative reflections is presented in Table I. The agreement between observed and calculated F values of the strongest reflections could probably be improved by correcting for extinction.

Discussion.- The $MoO_4^{=}$ group has the configuration of a regular tetrahedron, with Mo-O = 1.83 ± 0.03 Å. Each silver atom is surrounded by a nearly regular octahedron of oxygen atoms, each at 2.42 ± 0.02 Å.

A plausible single bond tetrahedral radius for molybdenum can be derived from the apparent radius of 1.38 Å. for molybdenum in MoS_2[6] and $K_4Mo(CN)_8\ 2H_2O$[7] by applying a correction factor of 0.97 for change in coordination.[8] The value obtained, 1.34 Å., may be slightly large

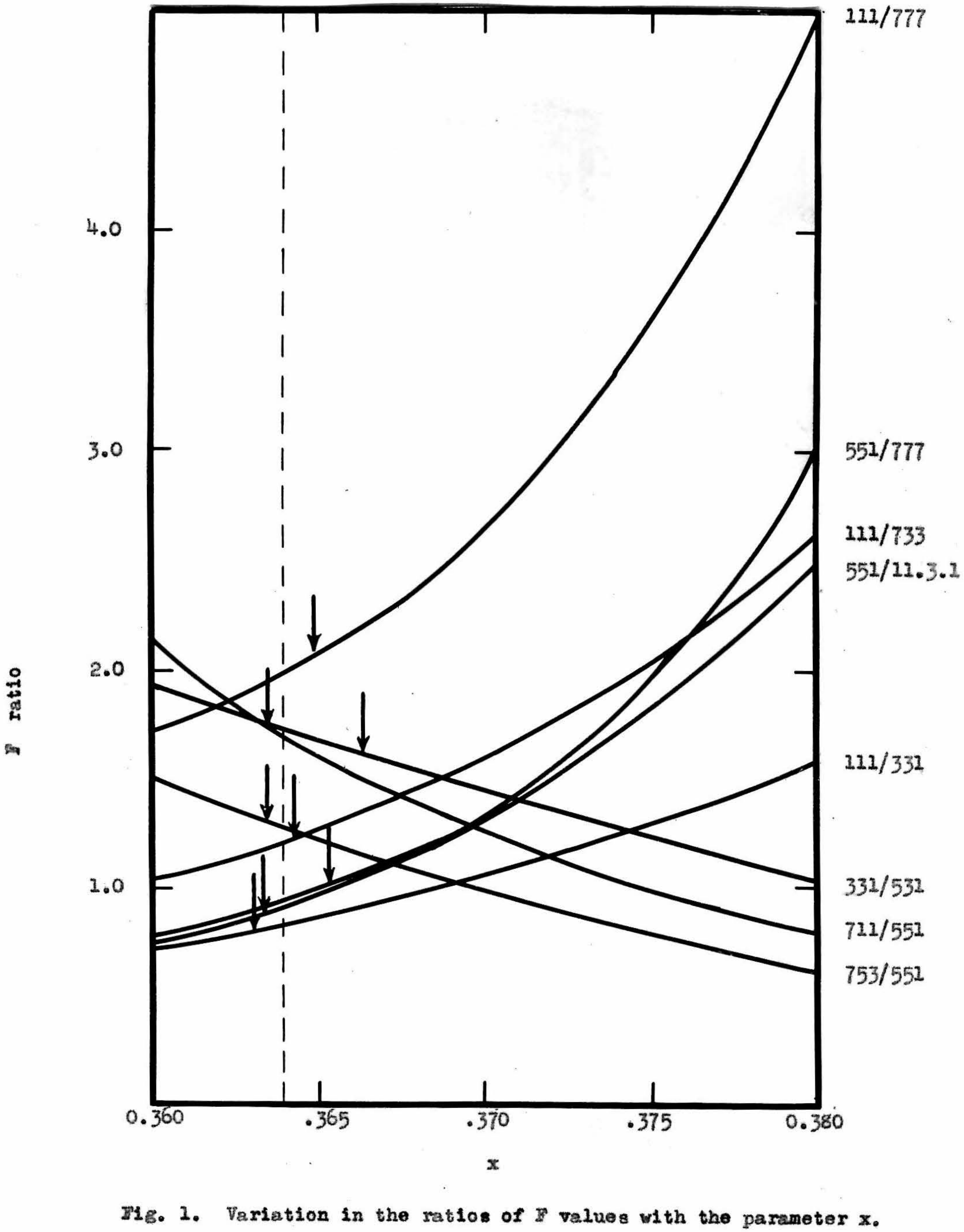

Fig. 1. Variation in the ratios of F values with the parameter x. Arrows indicate the observed values of the ratios.

Table I

Values of F_{hkl}

(hkl)	$F_{obs.}$	$F_{calcd.}$	(hkl)	$F_{obs.}$	$F_{calcd.}$
111*	118	109	862	112	78
220	264	248	951	167	139
311	405	456	10.2.2	179	178
222	306	396	953	< 40	34
400	398	447	10.4.2	73	67
331*	145	130	11.3.1*	50	53
333	383	376	882	< 40	3
511	282	303	10.6.0	59	54
440	450	659	866	80	67
531*	72	75	10.6.2	156	141
442	< 35	2	777*	57	54
620	160	140	10.6.4	92	61
622	249	279	12.4.0	197	215
444	231	339	12.4.2	< 40	2
551*	51	50	10.8.2	57	52
711*	89	85	10.6.6	135	114
642	127	127	12.6.2	60	45
731	227	258	10.10.0	60	48
800	376	356	10.8.6	45	34
733*	96	90	11.9.1	76	63
822	99	105	10.10.2	102	94
555	182	181	12.8.2	< 40	2
662	226	222	12.6.6	33	33
840	176	197	13.7.1	64	68
911	39	42	14.6.0	59	38
753*	67	64	10.10.6	66	76
842	< 40	2	12.10.2	25	28
664	108	83	13.9.1	53	57
931	167	171	16.0.0	145	111
844	304	341	12.10.6	35	24
933	< 40	43	12.12.0	86	80
771*	73	73	14.10.2	44	46
10.2.0	97	83			

* These reflections were used in the parameter determination.

because of the difference expected between the radii of quadrivalent and sexavalent molybdenum.[9]

The observed molybdenum-oxygen distance is thus 0.17 Å. shorter than the sum of the radii. This shortening is of the same order of magnitude as the following shortenings in other tetrahedral XO_4^{m-} ions which have been observed previously: 0.23 Å. in $SiO_4^{\equiv}$,[10] 0.21 Å. in $PO_4^{\equiv}$,[10] 0.10 Å. in $AsO_4^{\equiv}$,[4] 0.22 Å. in $VO_4^{\equiv}$,[11] 0.19 Å. in $SO_4^{=}$,[10] 0.17 Å. in ClO_4^{-},[10] and 0.15 Å. in IO_4^{-}.[12]

The Ag-O distance of 2.42 Å. is somewhat shorter than the ionic radius sum of 2.46 Å.[3] Ag-O distances of 2.51, 2.50 and 2.42 Å. have been found in the colorless salts $AgClO_3$, Ag_2SO_4 and $KAgCO_3$, respectively.[4] In the yellow salts Ag_3PO_4 and Ag_2CO_3 the distances are 2.34 and 2.3 Å., respectively, and in Ag_3AsO_4, which is red, the distance is also 2.34 Å.[4] These distances are in only rough accord with Pitzer-Hildebrand rule, which states that the color of a salt formed from colorless ions is a measure of the covalent character of the bonds between the ions.[2] Considerable work on the absorption spectra of various compounds is needed before the relation of color to covalence can be fully discussed.

<u>Summary</u>.- A redetermination of the parameter in silver molybdate has been carried out using data obtained from oscillation photographs. The value obtained, $x = 0.364 \pm 0.002$, leads to the distances Mo-O = 1.83 ± 0.03 Å. and Ag-O = 2.42 ± 0.02 Å. The significance of these distances is briefly discussed.

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The Crystal Structure of Hydrazinium Dichloride, $N_2H_6Cl_2$

The crystal structure of hydrazinium dichloride was first investigated by Wyckoff,[1] who found that crystals of the substance belong to the space group T_h^6-Pa3, and that four molecules of $N_2H_6Cl_2$ are situated in the unit cube, with a_o=7.89Å. Wyckoff, with the methods then available, was able to arrive at only approximate values of the two parameters necessary to determine the structure completely (excluding the hydrogen atoms). He described the structure as "a CaF_2 grouping in which the chlorine ions are displaced from the symmetrical $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ positions by the dumb-bell shaped N_2H_6 groups."[2]

We have investigated this crystal by the x-ray diffraction method in order to determine the interatomic distances accurately. The N-N distance is of interest in connection with the as yet unsettled question of the effect of formal charge on interatomic distance. The N-H...Cl distance affords further information on hydrogen bonding between nitrogen and chlorine. The structure also provides interesting comparisons with those of hydrazinium difluoride[3] and methylammonium chloride.[4]

Experimental.- Eastman White Label hydrazinium dichloride was dissolved in dilute hydrochloric acid. Slow evaporation of the solution yielded tiny octahedra suitable for x-ray examination. Crystals not over 0.2 mm in greatest dimension were mounted on the x-ray goniometer heads in the usual way. Laue photographs showed that the symmetry class of the crystals was either T or T_h. Oscillation photographs were taken with CuK_α radiation (λ=1.542Å) over the range required to give complete data for the zero, first, and second layer lines. In order to facilitate the visual estimation of intensities the multiple film technique was used.[5] The effect of absorbtion was ignored, since the size and shape of the crystals were favorable for doing so.

Measurement of the equatorial reflections on the oscillation photographs gave the value $a_0=7.87\pm0.01\text{Å}$, in satisfactory agreement with Wyckoff's value of 7.89Å. A very heavily exposed oscillation photograph showed no intermediate layer lines which would require the choice of a larger unit cell. The regular vanishing of (hk0) when $h=2n$, observed on the oscillation photographs, confirms Wyckoff's choice of the space group T_h^6-Pa3. The observed density,[6] 1.4226, requires four (calculated 3.98) molecules of $N_2H_6Cl_2$ per unit cell. The eight nitrogen atoms lie in the positions[7] $\pm(uuu)$, $(\frac{1}{2}+u, \frac{1}{2}-u, \bar{u})$, $(\bar{u}, \frac{1}{2}+u, \frac{1}{2}-u)$, $(\frac{1}{2}-u, \bar{u}, \frac{1}{2}+u)$; and the eight chlorine atoms in a set of similar positions $\pm(vvv)$, etc.

For the calculation of F values, the atomic scattering factors of James and Brindley[8] were used. The f values for N were increased by 2f of H as an approximation to include the effect of the hydrogen atoms. All atomic f values were multiplied by the temperature factor $\exp-\beta(\sin\vartheta/\lambda)^2$, and the value $\beta=1.5$ was found to give satisfactory agreement between observed and calculated structure factors.

Determination of The Parameters.- The approximate parameter values of Wyckoff, $u=0.04$, $v=0.27$, enable the assignment of signs to the F values of all of the observed (hk0) reflections. A Fourier projection on (001) made with the twenty-three available (hk0) reflections is shown in Fig. 1. The smaller resolved peaks represent the nitrogen atoms; the larger peaks represent pairs of chlorine atoms which are too close together

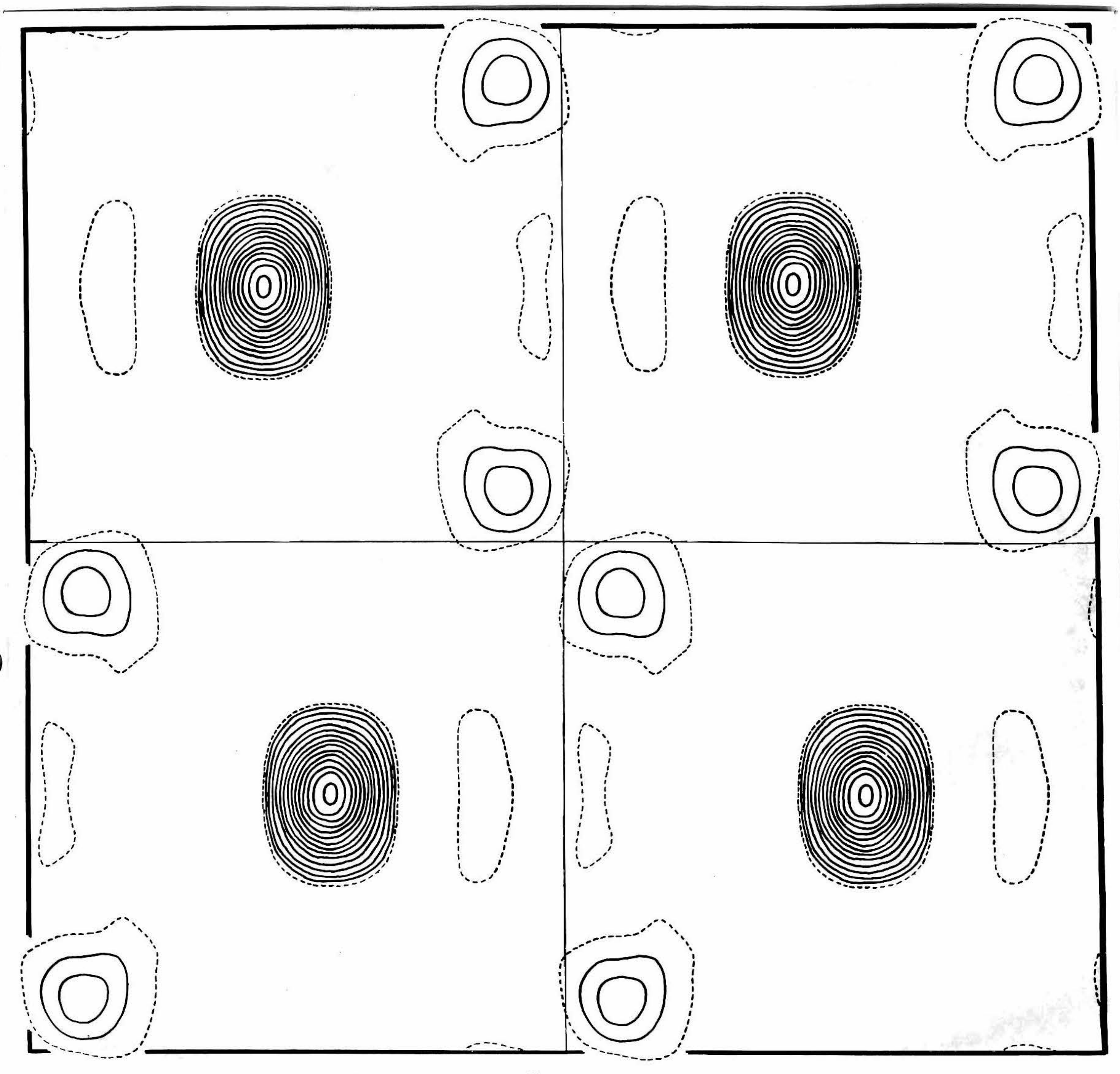

Fig. 1. Fourier projection of one unit cell on (001).

in this projection to be resolved. The symmetry of the cell, however, allows an accurate estimation of the chlorine parameter as well as the nitrogen parameter. The values $u = 0.052$ and $v = 0.278$ are indicated by this projection. It may be pointed out that the heights of the two kinds of peaks are in the ratio 3.9 : 1, whereas the ratio expected, $2Cl^-$: NH_3^+, is 36:9 = 4:1. The two small peaks and the asymmetry of the nitrogen peak (dotted in Fig. 1) undoubtedly arise from the omission of reflections which lie outside the limit of copper K_α radiation.

Since both nitrogen atoms and chlorine atoms lie on a body diagonal of the unit cube, this crystal is well suited to the application of the Fourier method of calculating the electron density along a line. The general expression for the electron density as a function of the coordinates x, y, and z simplifies for the case $x = y = z = d$ to

$$\rho(d) = K \sum_H A_H \cos 2\pi Hd, \text{ where } A_H = \sum_{h+k+l=H} F_{hkl}.$$

In making this summation, all available (hk0), (hk1), and (hk2) data were used, the signs of all F values being determined from the parameters obtained with the projection on (001). The use of equalities of the type $F_{hkl} = -F_{\bar{h}kl}$ for $h = 2n$ or $k = 2n$, etc., increased the number of known F values to nearly 300. The reflections were classified according to $h+k+l$, and the series was summed over $h+k+l=0$ to 15 from $d=0$ to $d=\frac{1}{2}$ in intervals of 0.004 in d. Both this summation and the projection on (001) were made with the use of punched cards and International Business Machines.[9] The density function $\rho(d)$, the curve labelled OBS in Fig. 2, gives the values $u=0.052$ and $v=0.279$, which are in excellent agreement with the values given

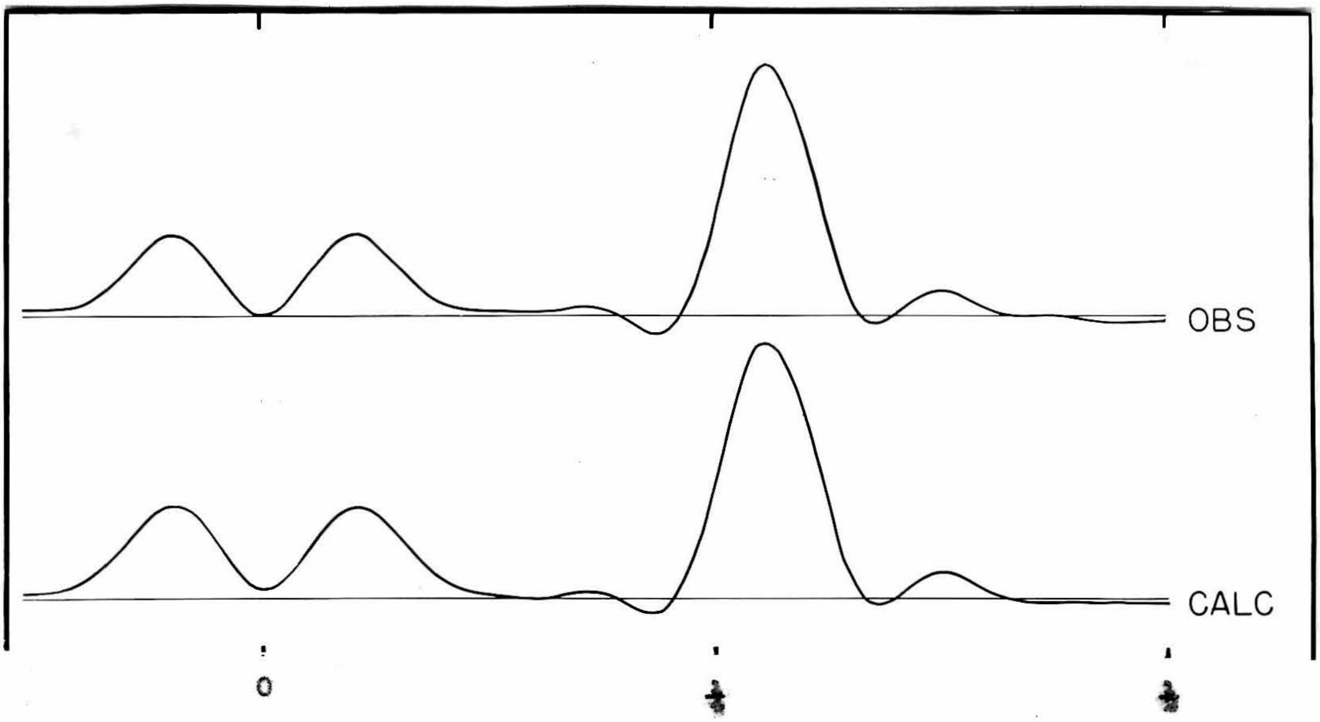

Fig. 2. Electron density along the line x = y = z = d

by the (001) projection.

Since data obtained only from the zero, first, and second layer lines were used, no reflections for which h, k, and l were each > 3 were included in the calculation of the function (d). Although this function apparently was satisfactorily convergent, the effect of the missing spectra on the positions of the maxima was not known. For this reason, we calculated a second density function, using, in place of the observed F values, a set of F values calculated for a structure in which $u=0.052$ and $v=0.278$. The same terms were omitted in the calculation of this second density function as were omitted in the calculation of the first. The resulting curve, labelled CALC in Fig. 2, shows maxima at $u=0.052$ and $v=0.278$. The omission of terms of high order in h, k, and l did not lead to parameters which were significantly different from those which were assumed, and we may, therefore, infer that the parameters obtained with the observed data are a correspondingly accurate representation of the atomic positions in the crystal.

Since there have been cases in which the inclusion of the scattering of the hydrogen atoms led to a significant improvement in the agreement between observed and calculated values of F_{hkl},[10] we recalculated all F_{hkl} with $\sin \vartheta/\lambda < 0.30$, placing the twenty-four hydrogen atoms in the general positions[9] of Pa3 with $x=0.108$, $y=0.039$, and $z=0.126$. These values place groups of three hydrogen atoms 1.03Å from each nitrogen atom, on lines between the nitrogen atoms and its closest chlorine neighbors. The over-all effect was a very small improvement of doubtful significance.

The above results lead us to the parameter values $u=0.052$ and v=0.279. We believe it very unlikely that either of these parameters is in error by more than ± 0.0015.

The agreement between observed and calculated values of F is shown in Tables I and II. It is probable that the very strongest reflections, viz., (200), (220), (400), (410), (111), and (222), which are all observed to be too weak, are subject to extinction.

Discussion. The values of the parameters lead to the following interatomic distances: the N-N distance within the hydrazinium group is 1.42Å, and from the limits of error given for this parameter it is very unlikely that this distance can be in error by more than ± 0.04Å. A drawing of the structure showing the environment of one $N_2H_6^{++}$ group is shown in Fig. 3. Each nitrogen atom has four closest chloride neighbors, one (type I) lies at 3.10Å±0.04Å on an extension of the line through the two nitrogen atoms, the other three (type II), also at 3.10±0.02Å, form a triangular pyramid with the nitrogen atom, the angles N-N···Cl being 100° ± 2°. Each chloride ion has four nitrogen neighbors, one of type I and three of type II, and in addition six chloride neighbors which form the equilateral triangle are connected to the nitrogen atom by hydrogen bonds; the configuration of the $N_2H_6^{++}$ is staggered or trans.

It is of interest to compare in detail the structure of $N_2H_6Cl_2$ with that of $N_2H_6F_2$.[3] In both crystals the halide ions form hydrogen bonds leading to N-H···X distances which are shorter than the sums of the respective ionic radii*, 0.11Å shorter in the chloride and 0.14Å shorter in the

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* An ionic radius one of $-NH_3$ group of the hydrazinium ion may be taken equal to the ionic radius of 1.54Å for NH_4^+, observed in NH_4Br and NH_4Cl. This value leads to an ionic radius of 1.41Å when corrected to coordination number 4.

Table I. Values of F_{hk0}.

(hk0)	F_{obs}	F_{calc}
200	4.1	-7.8
210	3.4	+3.5
220	7.3	+13.4
230	4.9	-5.2
400	5.9	+7.9
410	5.5	-6.9
420	5.4	-5.3
430	2.8	+2.1
250	< 0.4	0.0
440	4.3	+4.1
600	3.8	-3.8
610	4.9	+5.1
620	2.3	+2.1
450	4.7	-4.3
630	5.5	-5.9
640	2.4	-2.1
270	1.0	-1.2
650	1.3	+1.3
800	< 0.4	-0.7
810	4.8	-4.9
470	< 0.4	-0.1
820	1.1	-1.5
660	1.2	+1.1
830	3.3	+3.2
840	< 0.4	0.0
670	1.7	-1.8
850	3.1	-2.9

Table II. Value of F_{hkl}.

(hkl)	F_{obs}	F_{calc}	(hkl)	F_{obs}	F_{calc}	(hkl)	F_{obs}	F_{calc}
111	4.3	+6.0	261	5.3	-5.4	812	3.9	+3.9
211	2.4	-1.8	541	1.3	-1.4	182	0.4	+0.4
221	4.3	-4.5	451	3.5	+3.2	742	< 0.4	+0.6
311	2.1	+2.6	622	2.8	-3.0	472	1.3	-1.5
222	5.1	-6.3	542	0.6	+0.6	822	< 0.4	-0.3
321	1.4	-1.3	452	0.7	+0.9	661	1.6	-1.7
231	1.5	+1.3	631	2.5	+2.3	831	2.5	-2.3
322	1.2	+1.1	361	< 0.4	-0.5	381	1.0	-1.1
411	< 0.4	0.0	632	3.1	+2.9	751	0.6	+0.7
331	0.4	+0.7	362	1.1	+1.1	662	0.7	-0.7
412	4.4	+4.4	711	0.6	-0.8	832	3.9	-3.7
142	2.0	+2.0	551	0.7	-0.6	382	< 0.4	+0.4
332	2.6	-2.1	641	2.0	+1.8	752	1.4	+1.4
422	5.1	+5.8	461	3.7	+3.4	572	< 0.4	+0.3
431	3.0	-3.1	721	0.6	-0.6	841	< 0.4	0.0
341	3.2	-2.9	271	2.0	+2.0	481	3.1	-3.1
511	0.6	-0.3	552	0.7	-0.8	911	1.0	-1.2
432	4.6	-5.6	642	1.7	+1.6	842	0.5	-0.5
342	2.6	-2.0	722	< 0.4	0.0	921	< 0.4	-0.1
512	2.4	-2.0	731	1.0	-1.0	291	1.2	-1.2
152	1.5	-1.8	651	3.8	-3.4	761	0.4	-0.5
441	3.9	-3.5	561	1.8	-1.7	671	3.6	+3.4
552	2.5	-2.5	732	1.3	-0.9	762	0.4	-0.4
531	0.6	+0.4	372	0.6	-0.6	672	< 0.4	+0.3
442	3.4	-3.4	652	3.4	-3.4	922	< 0.4	0.0
532	1.5	+1.7	562	< 0.4	-0.2	851	3.3	+2.9
352	< 0.4	0.0	811	0.6	+0.6	581	< 0.4	-0.1
611	1.7	-1.6	741	1.0	-1.1			
621	0.8	-0.8	471	2.5	-2.6			

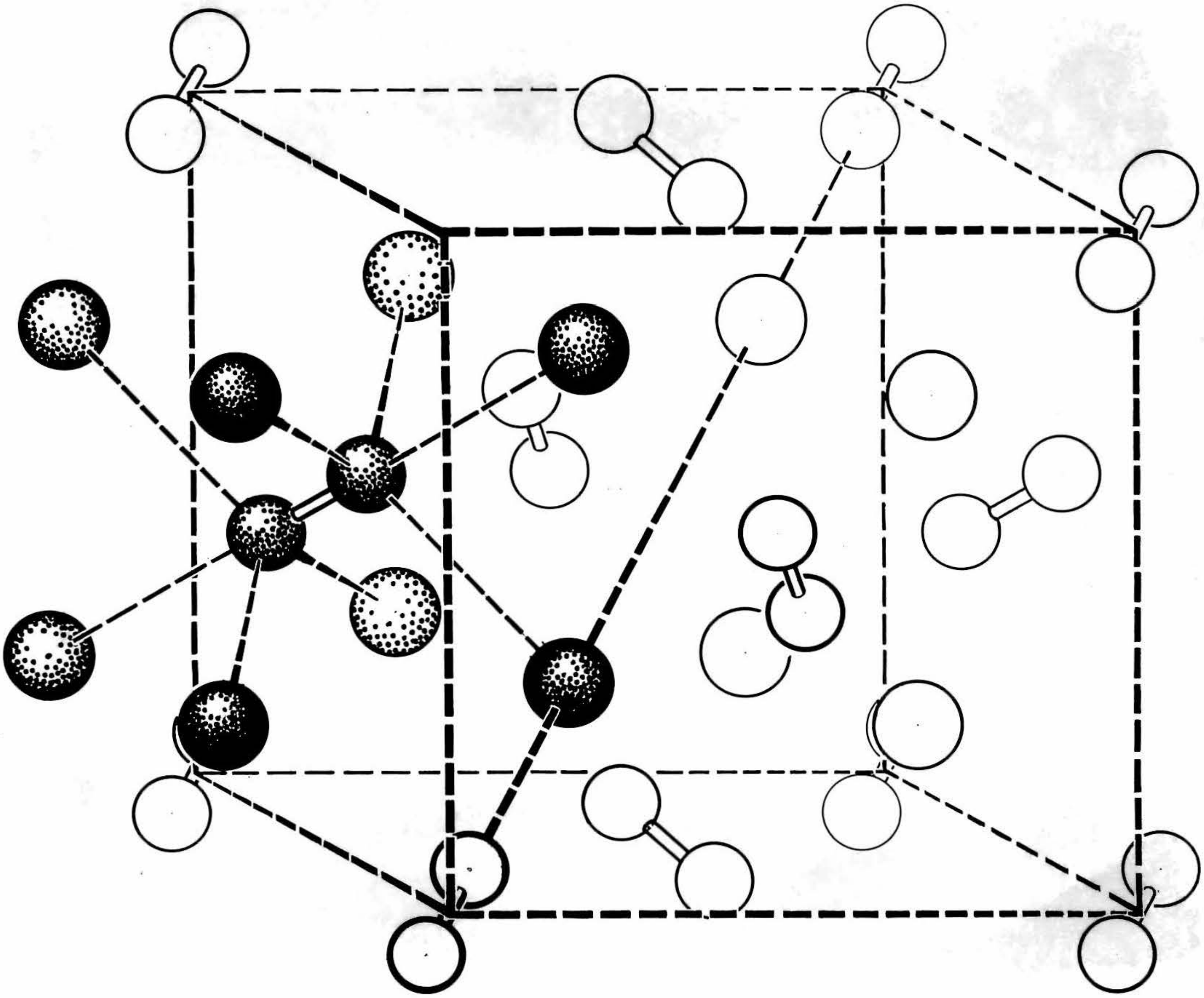

Fig. 3. One unit cell of the crystal, showing the environment of one $N_2H_6^{++}$ group, and the body diagonal along which p(d) was determined. The large balls represent chloride ions, the small balls, nitrogen atoms .

fluoride. In both crystals a nitrogen atom has four closest halide neighbors, three of which are hydrogen bonded, and one of which lies on the extension of the N-N axis. In $N_2H_6Cl_2$, this fourth chloride ion lies the same distance from the nitrogen atom as do the other three chloride ions, whereas in $N_2H_6F_2$ the fourth fluoride ion lies at a distance 0.18Å greater than do the other three. This N···F distance is approximately the sum of the ionic radii. The angle N-N···X is 100° in $N_2H_6Cl_2$ and 110° in $N_2H_6F_2$. The smaller angle and the equality of the four N-H···X distances in the chloride suggest that the fourth chloride ion is subject to significant attraction by the three hydrogen atoms, a situation not unlikely if the actual value of the angle N-N-H is closer to the tetrahedral value 109°28'. In both crystals a halide ion has four nitrogen neighbors. In $N_2H_6F_2$, a fluoride ion has, in addition, three closest fluoride neighbors, at distances 0.68Å greater than the sum of the ionic radii, so that the structure essentially does not depend on any F···F contacts. In $N_2H_6Cl_2$, on the other hand, a chloride ion has six closest chloride neighbors, at distances only 0.36Å greater than the radius sum. It is possible that Cl···Cl contacts are of some importance in determining this structure. The major difference between the two structures then arises from the greater coordinating ability of chloride ion as compared to that of fluoride ion. The configuration of the $N_2H_6^{++}$ ion is trans in both crystals.

The N-H···Cl distance of 3.10Å may be compared with the N-H···Cl distance of 3.18Å found in NH_3CH_3Cl.[4] In the latter crystal, the CH_3-NH_3 groups are probably rotating, and furthermore only three hydrogen bonds are formed, on the average, between a nitrogen atom and four chloride ions. These differences lead to much weaker and consequently longer N-H···Cl bonds in methylammonium chloride.

The N-N distance in both hydrazinium dichloride and hydrazinium difluoride is the same, 1.42Å. This distance is 0.05Å shorter than the N-N distance in gaseous hydrazine.[11] This shortening has been attributed to the formal charges on the nitrogen atoms.[3] However, since the structure of the $N_2H_6^{++}$ ion for which there are adjacent charges on each nitrogen atom contributes but 25 percent to the normal state of the ion,[3] it seems essentially illogical to attribute a shortening of this magnitude to the formal charges. The formal charge effect, as originally conceived,[12,13] was intended to correct the covalent radius of an atom which had a formal charge of +1 by about -0.03Å. Some molecules in which this effect might be expected, together with the available experimental data, are presented in Table III. Because of the uncertainty involved in predicting distances which are involved in single-bond double-bond resonance, only single covalent bonds are included in the table. The predicted distances are those in the table of revised covalent radii of Schomaker and Stevenson.[14]

It is apparent that the correction for formal charge is not generally applicable. There do not seem to be sufficient experimental data concerning this point so that a satisfactory revision of the original correction can be made. X-ray investigations of a hydroxylammonium salt such as NH_3OHCl and of a metallic peroxide would provide additional information of interest.

<u>Summary</u>.- Accurate values of the two parameters in the structure

Table III

Bond	Compound	Observed distance	Predicted distance*
$O-N^+$	HNO_3	1.41 ± 0.02Å[a]	1.43Å
$C-N^+$	$C(NO_2)_4$	1.47 ± 0.02Å[b]	1.46Å
	CH_3NH_3Cl	1.46 ± 0.01Å[c]	
	$(CH_3)_3NO$	1.49 ± 0.02Å[d]	
N^+-N^+	$N_2H_6F_2$	1.42 ± 0.02Å[e]	1.47Å
	$N_2H_6Cl_2$	1.42 ± 0.04Å[f]	
$C-S^+$	$(CH_3)_2SO$	1.84 ± 0.02Å[d]	1.81Å
$C-S^{++}$	$(CH_3)_2SO_2$	1.81 ± 0.02Å[d]	1.81Å

* Reference 15 in text.

a - L. R. Maxwell and V. M. Mosley, Phys. Rev. 57, 1079A (1940).
b - A. J. Stosick, J. Am. Chem. Soc. 61, 1127 (1939).
c - Reference 4 in text.
d - R. E. Rundle, Dissertation, California Institute of Technology (1941).
e - Reference 3 in text.
f - This determination.

of crystalline hydrazinium dichloride have been determined by the x-ray diffraction method, with the use of one and two dimensional Fourier syntheses. The N-N separation in this crystal is 1.42A, and is equal to that in hydrazinium difluoride. This N-N distance is 0.05A shorter than in gaseous hydrazine. Each chloride ion forms hydrogen bonds with three nitrogen atoms, the structure consisting of a three dimensional network of N-H•••Cl bonds. The angle N-N-H•••Cl is 100°. The configuration of the $N_2H_6^{++}$ ions is trans. The differences between this structure and that of hydrazinium difluoride probably arise from the greater coordinating ability of the chloride ion as compared with that of the fluoride ion. The shortening of the N-N distance may be caused in part by the formal charges on the nitrogen atoms, although it seems certain that this formal charge effect is not of general validity.

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10 -- For example, H. A. Levy and R. B. Corey, J. Am. Chem. Soc. 63, 2095 (1941). Cf. also reference 6.

11 -- P. A. Giguere and V. Schomaker, J. Am. Chem. Soc. 65, 2025 (1943).

12 -- N. Elliott, J. Am. Chem. Soc. 59, 1380 (1937).

13 -- L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1940), second edition, p. 171.

14 -- V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).

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I wish to express my thanks to Professor Verner Schomaker for introducing me to the technique of the electron diffraction method, and for valuable aid and illuminating discussions of all of the electron diffraction investigations. The advice of Professor J. H. Sturdivant during the course of the x-ray investigations was most helpful. The assistance of Dr. Chia-Si Lu, Dr. William N. Lipscomb, Dr. William Shand, and Mr. George Humphrey in some of the investigations is gratefully acknowledged. I am also indebted to Professor Linus Pauling for helpful suggestions and encouragement throughout the course of the work.

PROPOSITIONS SUBMITTED BY JERRY DONOHUE

Ph.D. Oral Examination, May 28, 1947, 9:00 A.M., Crellin Conference Room
Committee: Professors Schomaker (Chairman), Badger, Niemann, Pauling
Sturdivant, Swift, Ward, and Dr. Davidson

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1. The single bond radii of boron, silicon, phosphorus, germanium, arsenic, tin, and antimony, and the double bond radii of oxygen, nitrogen, and carbon should be revised (Thesis, Part I).

2. Better agreement with observed data is obtained if one calculates the interatomic distances in covalent molecules with the equation of Schomaker and Stevenson and the revised atomic radii, rather than with the Pauling-Huggins radii and additivity.

3. The Schomaker-Stevenson equation may also be successfully applied to the prediction and interpretation of the lengths of double bonds.

4. Double bond character occurs very infrequently in bonds between atoms of other than the first row elements.

5. (a) The structure of cycloöctatetraene with symmetry D_4-42 which was recently proposed by E. R. Lippincott and R. C. Lord (J.A.C.S. 68, 1868 (1946)) is much less probable than one with symmetry $D_{2d} - \bar{4}2m$.

(b) An electron diffraction investigation of cycloöctatetraene is very desirable.

6. Since in the application of the Pauling theory of directed valence the obvious approach may not be the correct approach, assertions that an observed configuration is not predicted by the theory should not be taken too seriously.

7. Contrary to the statements of G. L. Clark and C. O. Werner (Z. Krist. 88, 162 (1934)) their determination of the space group and unit cell of the silver nitrate-urea addition compound does not establish the value of n in $(AgNO_3 \cdot urea)_n$ as 2 or 4. Consequently their proposed structure for the complex is without significance.

8. Sufficient experimental data are now available to demonstrate that the formal charge effect proposed by N. Elliott (J.A.C.S. 59, 1380 (1937)) is not valid. Conversely, there *is* an effect in the case of bonds between two atoms of opposite formal charge.

9. The discussion of W. Shand and R. Spurr (J.A.C.S. 65, 179 (1943)) to explain the abnormally large bond angle they found in ozone is not in accord with previously determined properties of bonded atoms.

10. (a) K. J. Palmer's electron diffraction data on sulfur monochloride (J.A.C.S. 60, 2360 (1938)) yield more information than was obtained by Palmer.

(b) Contrary to rather prevalent current opinion, the electron diffraction method for determining molecular structures is not at the end of its rope.

11. The system of using kX units in addition to Å is unnecessarily confusing except in cases unrelated to chemistry. I propose that the kX unit be banished from the Crellin Laboratory.