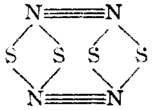
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 954]

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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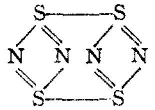
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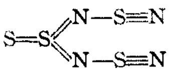
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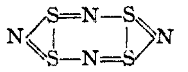
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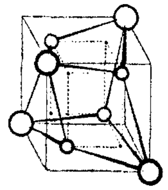
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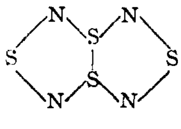
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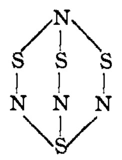
VII

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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(1) R. Schenck, *Ann.*, **290**, 171 (1896).

(2) W. Muthmann and A. Clever, quoted in ref. 8. Their paper in *Z. anorg. Chem.*, **13**, 200 (1896), however, does not mention the formula II.

(3) O. Ruff and E. Geisel, *Ber.*, **37**, 1573 (1904).

(4) A. Meuwsen, *ibid.*, **62**, 1959 (1929); **64**, 2301, 2811 (1931).

(5) F. M. Jaeger and J. E. Zanstra, *Proc. K. Acad. Wetensch. Amsterdam*, **34**, 782 (1931).

(6) E. Artini, *Z. Krist.*, **42**, 68 (1907); G. F. H. Smith, *Min. Mag.*, **16**, 97 (1911).

(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., β = 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., β = 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: $\text{As}-\text{O} = 1.78 \pm 0.02$ Å., $\text{As}-\text{As} = 3.20 \pm 0.02$ Å. and $\angle \text{As}-\text{O}-\text{As} = 128 \pm 2°$ ($\angle \text{O}-\text{As}-\text{O} = 99 \pm 2°$). These agree very well with the values of Hampson and Stosick:[20] namely, $\text{As}-\text{O} = 1.80 \pm 0.02$ Å., $\text{As}-\text{As} = 3.20 \pm 0.03$ Å. and $\angle \text{As}-\text{O}-\text{As} = 126 \pm 3°$. 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.

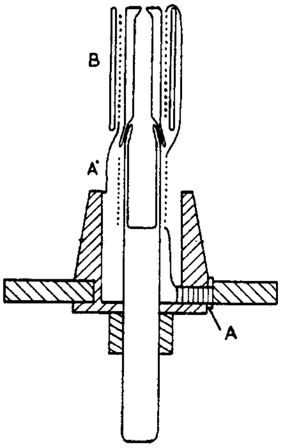

Fig. 1.—Diagram of the high temperature nozzle: A,A', leads for heating coil; B, glass shield for upper part of chimney. In actual practice the entire chimney was wrapped in asbestos.

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).

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

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

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

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.

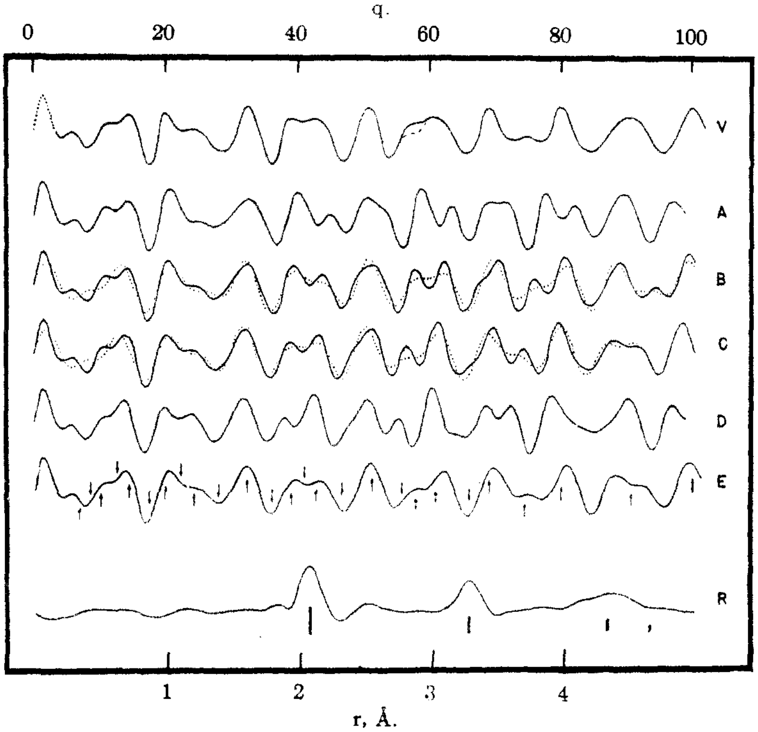

Fig. 2.—Electron diffraction curves for sulfur, S_8

	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

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.

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 intensity 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_F	$q_E/q_{obs.}$
	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

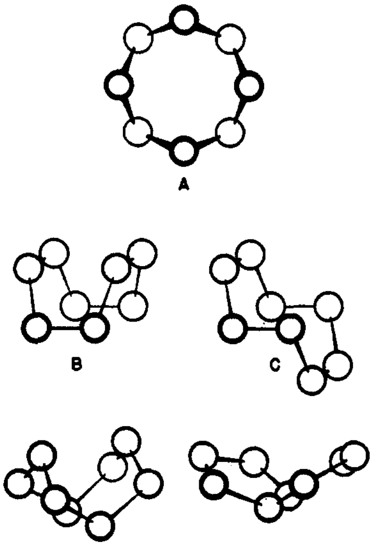

Fig. 3.—Some configurations of the eight ring: A, regular puckered ring (S_8 molecule); B, "tub" form; C, "chair" form; D, "cradle" form; E, "butterfly" form.

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

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

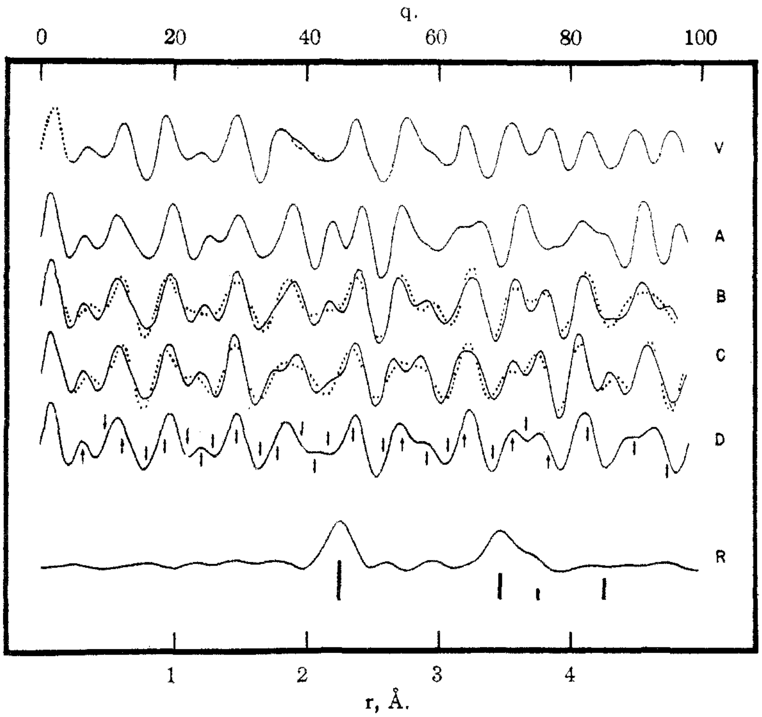

Fig. 4.—Electron diffraction curves for orpiment, As_4S_6:

	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., ∠ As–S–As = 100 ± 2° (∠ 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 ∠ 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).

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.

A regular 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 non-bonded 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 = 106° (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.

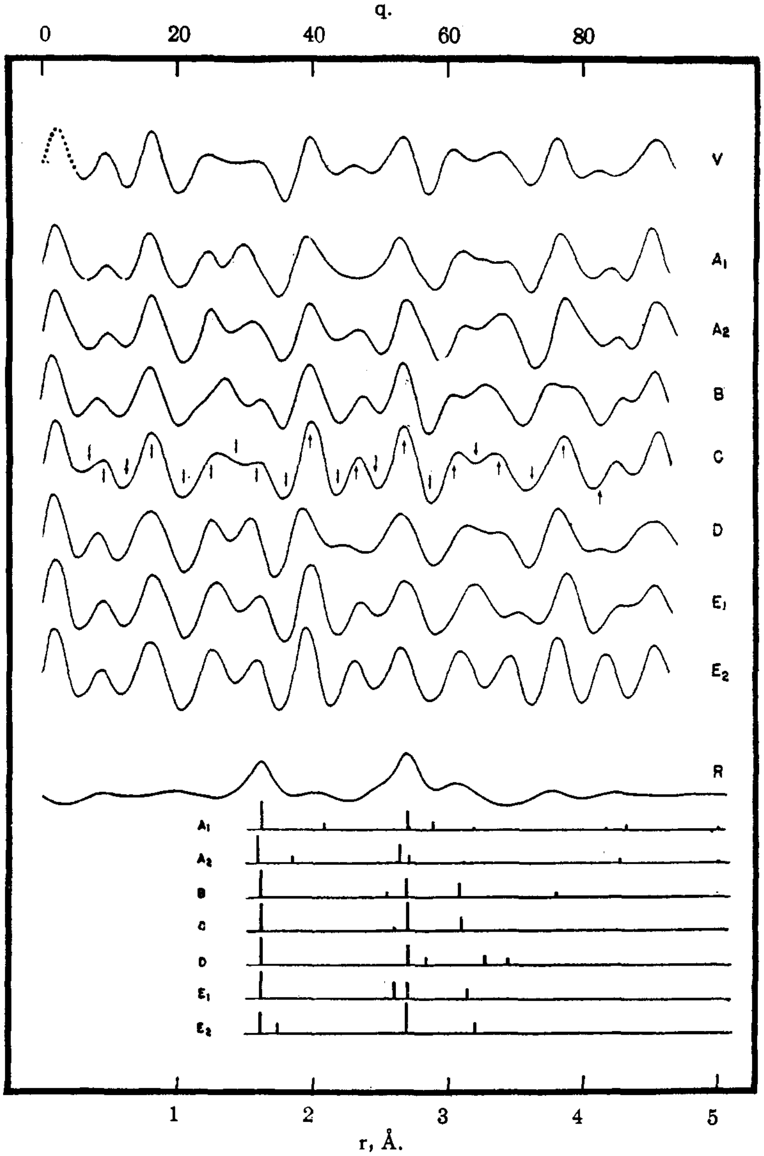

Fig. 5.—Electron diffraction curves for sulfur nitride, S_4N_4:

	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

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).

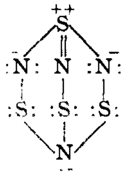
TABLE III

SULFUR NITRIDE

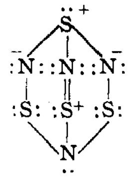
Min.	Max.	$q_{obs.}$	q_C	$q_C/q_{obs.}$
	1	8.90	9.0	(1.011)
2		12.24	11.7	(0.956)
	2	16.02	16.0	.999
3		20.60	20.6	1.000
	3	24.83	25.7	(1.035)
4		28.32	29.3	(1.034)
	4	31.53	31.8	1.009
5		35.95	35.6	0.990
	5	39.42	39.7	1.007
6		43.54	43.5	0.999
	6	46.23	46.8	1.012
7		49.14	49.6	1.009
	7	53.51	53.6	1.002
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.

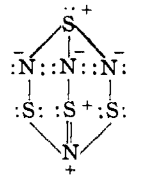
The "cage" structure represented by formula VII should consist of two interpenetrating but not concentric trigonal pyramids of nitrogen and sulfur atoms. Calculations were made for models with N—S = 1.62 Å., ∠ S—N—S = ∠ N—S—N = 112° for the two end groups NS_3 and SN_3 and the intervening N—S = 1.62 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 also to be noted that this structure could hardly account for most of the chemical properties of sulfur nitride.



A



B



C

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.

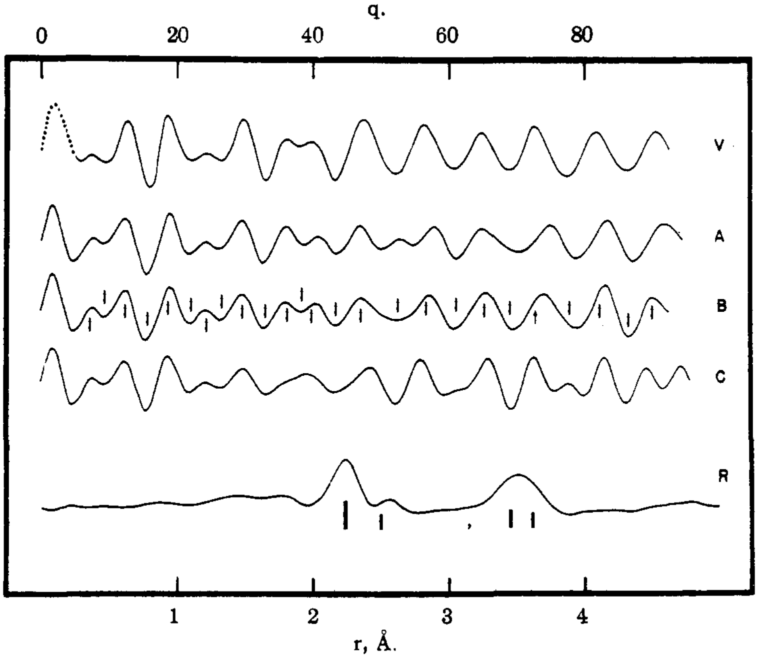


Fig. 6.—Electron diffraction curves for realgar, As_4S_4:

	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°.

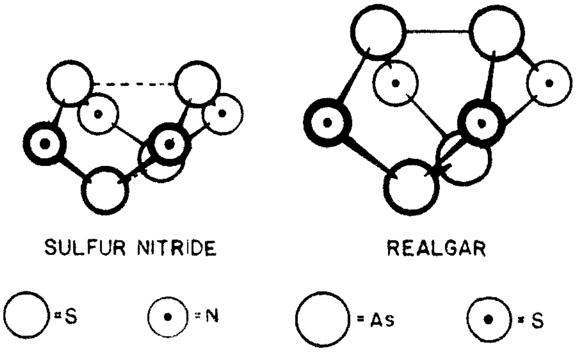
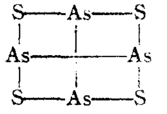


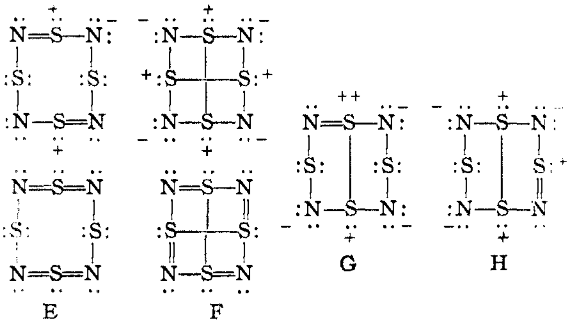
Fig. 7.—The molecular structures proposed for realgar and sulfur nitride.

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.



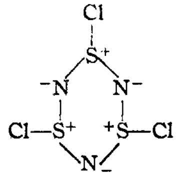
D.

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 ± 0.02 Å. and ∠ S−S−S = 105 ± 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 ± 0.02 Å., ∠ As−S−As = 100 ± 2° (∠ S−As−S = 114 ± 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 ± 0.02 Å., S−S = 2.69 Å., ∠ S−N−S = 112° and ∠ 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 ± 0.02 Å., As−As = 2.49 ± 0.04 Å., and ∠ As−S−As = 101 ± 4° (∠ S−As−S = 93°; ∠ 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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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Behavior of γ-Keto- and Aldehydo-Acid Derivatives at the Dropping Mercury Electrode. I. Esters and Anhydrides of 2-Benzoylbenzoic Acid

BY S. WAWZONEK,[1] H. A. LAITINEN AND S. J. KWIATKOWSKI

γ-Keto- and aldehydo-acids are of special interest since they and their derivatives can exist in two isomeric forms. Assignment of structure to these forms has been concerned mainly with the isomeric methyl and ethyl esters and has been accomplished both by chemical and physical means. Physical methods such as absorption spectra[2] and the use of refractive indices[3] have in general required both isomeric forms. Chemical methods used have been mainly generalizations. The most important of these is the rapid hydrolysis of the cyclic ester by means of concentrated sulfuric acid to give highly colored solutions in contrast to slow hydrolysis and a weaker color in the case of the normal esters.[4] Recent investigations have shown this test to be unsatisfactory in numerous cases.[5]

In this paper the use of the polarograph as a means of assigning structures to the esters of 2-benzoylbenzoic acid will be presented. The behavior of certain anhydrides at the dropping mercury electrode will likewise be mentioned. The study of certain amides of 2-benzoylbenzoic acid is described in the accompanying paper.[6] Work with other types of γ-keto- and aldehydo-acid derivatives is now in progress.

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(2) Hantzsch and Schwiete, *Ber.*, **49**, 215 (1916).

(3) (a) Egerer and Meyer, *Monatsh.*, **34**, 69 (1913); (b) von Auwer and Heinze, *Ber.*, **52**, 584 (1919).

(4) Meyer, *Monatsh.*, **25**, 477 (1904).

(5) (a) Blicke and Swisher, THIS JOURNAL, **56**, 904 (1934); (b) Newman and McCleary, *ibid.*, **63**, 1537 (1941).

(6) Wawzonek, Laitinen and Kwiatkowski, *ibid.*, **66**, 830 (1944).