

2. The reaction is explained, after the suggestion of Freundlich and Nathansohn, as one of a 2-stage photochemical oxidation of hydrogen sulfide to colloidal sulfur and a thionic acid, accompanied by reaction between hydrogen sulfide and the thionic acid which serve as stabilizing electrolytes for micelles of arsenic trisulfide and sulfur, respectively. Removal of the stabilizing electrolytes produces destabilization of the 2 colloids which are consequently precipitated. The increase in conductivity is explained as due to the building up of a concentration of the thionic acid sufficient to serve as the stabilizing electrolyte for the colloidal sulfur, the reaction between hydrogen sulfide and the thionic acid then proceeding at such a rate that the equilibrium is maintained between the several components of the system, further change in the conductance thus being prevented.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No 21]

THE CRYSTAL STRUCTURE OF HEXAMETHYLENE-TETRAMINE

BY ROSCOE G. DICKINSON¹ AND ALBERT L. RAYMOND

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Introduction

The successful determination of crystal structures by means of X-rays has for the most part been confined to elements and polar inorganic compounds. The structures found in these cases have been of such a character that it has been natural to regard the crystals as built up of atoms or ions rather than of molecules. It is to be expected, however, that the molecule retains its identity as such in crystals of organic compounds not possessing the character of salts.

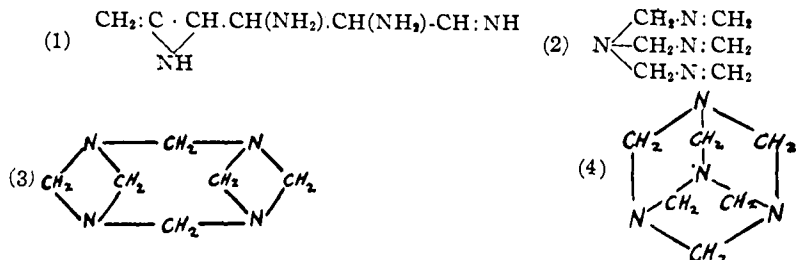
The investigation of such compounds presents difficulties which less frequently arise with inorganic compounds. Most organic substances which crystallize readily are relatively complicated in composition, and most of them crystallize in the triclinic, monoclinic, or rhombic system. The determination of the unit of structure is more difficult in these systems than in those possessing greater symmetry, and the positions of the atoms within the unit are much less fully fixed by symmetry alone. In order to avoid these difficulties as far as possible, hexamethylene-tetramine, $C_6H_{12}N_4$, was chosen for the investigation since it is one of the few known organic compounds without salt character which have cubic symmetry.

The commonest method of preparation of hexamethylene-tetramine is by the action of aqueous ammonia on aqueous formaldehyde according to the equation, $4 NH_3 + 6 CH_2O = C_6H_{12}N_4 + 6 H_2O$. The product, which is obtained by evaporation in a vacuum, is soluble in water and in

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alcohol, from which it crystallizes in colorless rhombic dodecahedra which are optically isotropic.²

The following structural formulas³ have been ascribed to this substance.



Although the last of these formulas apparently now finds most general acceptance, the chemical evidence in its favor as against (2) and (3) does not seem to be conclusive.

The Experimental Data

The hexamethylene-tetramine used was prepared by the method mentioned above. Crystals were formed by evaporation of both alcohol and chloroform solutions. The only observed form was $\{110\}$.

The X-ray data were obtained from spectral photographs and from Laue photographs made and treated substantially as previously described,⁴ except that the spectrum from (100) was obtained by transmission of the X-ray beam through a section of crystal cut parallel to (110). Several different Laue photographs were made with the incident beam at small inclinations from normal to (100), (111), and (110). One of these is diagrammatically reproduced in Fig. 1.

The angles of reflection of the rhodium $K\alpha_1$ radiation ($\lambda = 0.612 \text{ \AA.}$) are given in the second column of Table I. With the aid of the density (determined by us by the suspension method to be 1.341) the values of n^3/m given in the third column were calculated (m is the number of $\text{C}_6\text{H}_{12}\text{N}_4$ groups in the unit of structure and n is the order of reflection). From these it follows that either $m = 2$ and n has the values given in the fourth column, or $m = 16$ and n has twice the values given.

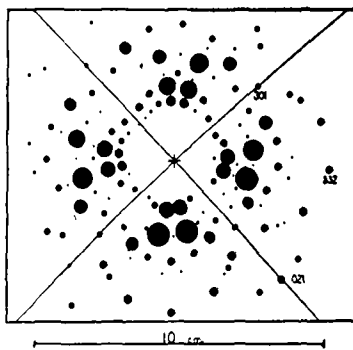


Fig. 1.—Diagrammatic reproduction of Laue photograph with incident beam slightly inclined from normal to (100) of $\text{C}_6\text{H}_{12}\text{N}_4$. Distance from crystal to plate, 5 cm.

² Sachs, *Z. Kryst. Mineralog.*, **34**, 160 (1901). Schwärzlin, *Ann.*, **331**, 105 (1904).

³ Beilstein, "Handbuch der Organischen Chemie," J. Springer, Berlin, **1**, 583 (1918).

⁴ Dickinson, *THIS JOURNAL*, **44**, 276, 1922.

TABLE I
 REFLECTION DATA FOR HEXAMETHYLENE-TETRAMINE

Plane	Observed angle of reflection	n^2/m	n for $m=2$	d_{100} for $m=2$	Relative intensities	$\sqrt{A^2 + B^2}$ $u = 0.235$ $v = 0.12$
(100)	4° 59'	3.95	2	7.04	medium	28
	[10 3]	..	4	..	absent	15
(110)	3° 32'	0.498	1	7.02	strong	58
	7 4	3.96	2	7.04	medium	23
	10 39½'	13.5	3	7.02	weak	33
	14 16½'	31.9	4	7.02	medium	124
	Calc. from density			7.01		

Taking $d_{100} = 7.02 \text{ \AA.}$, the smallest value of $n\lambda$ found for any spot on the Laue photographs was 0.30 \AA. , although wave lengths down to 0.23 \AA. were present in the X-rays used. Since the short wave lengths were comparatively ineffective in producing reflections from this crystal, spots having values of $n\lambda$ below 0.60 have been considered first-order reflections. The only planes giving first order reflections are those having 2 odd and 1 even indices; indeed, the great majority of all planes present were of this character. If the unit of structure containing 16 $C_6H_{12}N_4$ groups is assumed, no first-order reflections whatever are found; the smaller unit containing 2 molecules is therefore probable. A photograph taken with the incident beam perpendicular to (110) showed 2 symmetry planes.

Derivation of the Structure

We shall assume that the structure may be regarded as built up of some sort of like molecules of $C_6H_{12}N_4$ present as such, and investigate the consequences of this assumption in the light of the X-ray data. By *like* molecules it is implied that each atom in any one molecule has in every other molecule an atom equivalent to it under the operations of some cubic space group. In the application of the theory of space groups to the determination of crystal structure it is customary to consider immediately the various kinds of coördinate positions with which the *atoms* may be associated. In the present case, it is more convenient to consider first the equivalent positions with which the molecules as a whole are associated, and then the positions of the individual atoms. If the coördinates of the equivalent positions of the molecules are general, the molecules themselves need have no symmetry; but, if the number of equivalent positions in the unit becomes reduced as a result of locating them on one or more symmetry elements (and this is the only way in which the number can be reduced in a given space group), then the molecule must itself possess the symmetry of these elements.⁵

This point is discussed by Niggli, "Geometrische Krystallographie des Diskontinuums," Borntraeger, Leipzig, 1919, p. 135ff.

According to Niggli's tabulation,⁶ whenever the number of equivalent positions in any cubic space group is reduced to 2, the particle occupying these positions must have the symmetry of 1 of the 5 cubic point groups.

The minimum possible symmetry of the molecule being determined, the possible arrangements of the atoms within it may be investigated by considering the special cases of the coördinates of equivalent positions of the *point groups*. Whenever these reduce to less than 12 in number, they reduce to 1, 4, 6, or 8. As more than one 1-fold position never occurs, the only way of associating 4 nitrogen atoms and 6 carbon atoms with a point so as to give the aggregate any kind of cubic symmetry is by making all of the nitrogen atoms equivalent and likewise all of the carbon atoms. When this is done the nitrogen atoms will lie on trigonal axes and the carbon atoms on the digonal axes which are parallel to the cubic axes. Structural formula 4 is the only one that can have the necessary equivalence of the atoms.

We may now examine the space group arrangements of the atoms. In considering the X-ray data, the reflecting power of the hydrogen atoms will be assumed negligible as compared with those of the other atoms; the hydrogen atoms will be considered after the other atoms have been located. All of the arrangements of the carbon and nitrogen atoms consistent with the above conclusions are included in the following.

C at: (u00) (0u0) (00u) (\bar{u} 00) (0 \bar{u} 0) (00 \bar{u})
 $(\frac{1}{2}+u, \frac{1}{2}, \frac{1}{2}) (\frac{1}{2}, \frac{1}{2}+u, \frac{1}{2}) (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+u) (\frac{1}{2}-u, \frac{1}{2}, \frac{1}{2}) (\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}) (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u)$
 N at (1): (v \bar{v} v) (v \bar{v} \bar{v}) (\bar{v} v \bar{v}) (\bar{v} \bar{v} v)
 $(\frac{1}{2}-v, \frac{1}{2}-v, \frac{1}{2}-v) (\frac{1}{2}-v, \frac{1}{2}+v, \frac{1}{2}+v) (\frac{1}{2}+v, \frac{1}{2}-v, \frac{1}{2}+v) (\frac{1}{2}+v, \frac{1}{2}+v, \frac{1}{2}-v)$
 or (2): (v \bar{v} v) (v \bar{v} \bar{v}) (\bar{v} v \bar{v}) (\bar{v} \bar{v} v)
 $(\frac{1}{2}+v, \frac{1}{2}+v, \frac{1}{2}+v) (\frac{1}{2}+v, \frac{1}{2}-v, \frac{1}{2}-v) (\frac{1}{2}-v, \frac{1}{2}+v, \frac{1}{2}-v) (\frac{1}{2}-v, \frac{1}{2}-v, \frac{1}{2}+v)$

For first order reflections from planes having other than 2 odd and 1 even indices, the carbon atoms destructively interfere. But Arrangement 1 of the nitrogen atoms gives, $A = 0$. $B = 2\bar{N} \sum \sin 2\pi S_p v$, where $S_1 = h + k + l$, $S_2 = h - k - l$, $S_3 = -h + k - l$, $S_4 = -h - k + l$, and the summation is from $p = 1$ to $p = 4$. Since no reflections of this kind were found, the expression for B must become small. The term B does not in general become small except for values of v near 0 or $1/2$. These values would group 4 nitrogen atoms so closely as to be improbable.

With the nitrogen atoms in Arrangement 2, the values of A and B are, Class 1; h, k , and l all odd or only one odd.

$$n=1. \quad A=0; B=0.$$

$$n=2. \quad A=4\bar{C}(\cos 4\pi hu + \cos 4\pi kv + \cos 4\pi lw) + 2\bar{N} \sum \cos 4\pi S_p v;$$

$$B=2\bar{N} \sum \sin 4\pi S_p v;$$

Class 2; h, k , and l two odd and one even.

$$n=1. \quad A=4\bar{C}(\cos 2\pi hu + \cos 2\pi kv + \cos 2\pi lw) + 2\bar{N} \sum \cos 2\pi S_p v;$$

$$B=2\bar{N} \sum \sin 2\pi S_p v.$$

⁶ Ref. 5, p. 410.

Evidently, this arrangement accounts for the absence in the first order of any but planes of Class 2, whatever may be the values of the parameters u and v . In order to determine the best values to assign to these, it is apparently necessary to make some assumption concerning the relative reflecting powers of the carbon and nitrogen atoms. In the following calculations these have been taken proportional to the atomic numbers 6 and 7 respectively.

The X-ray data furnish numerous cases in which a plane reflected at the same wave length more strongly than other planes having the same or larger values of d/n . If the assumed values of the reflecting powers are approximately correct, it should be possible to find values of u and v which give calculated values of $A^2 + B^2$ in the proper order of inequality to account for these abnormal intensity relations. The locus of all the simultaneous values of u and v that satisfy a given inequality may be represented by a closed area (or areas) on a plot of u against v . Neglecting values of u that would bring the carbon atoms closer than 1 Å. to each other (their distance apart in the diamond is 1.54 Å.) the boundary of the region in which $A^2 + B^2$ for the fourth order from (110) is appreciably greater than the fourth from (100) was calculated and drawn. The

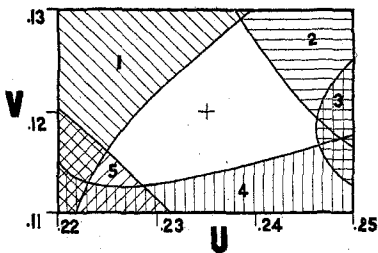


Fig. 2.—Possible values of u and v are shown by the unshaded area.

region thus enclosed was then examined for the values of u and v that make $A^2 + B^2$ for the fourth order from (110) greater than for the third from (110), and the region satisfying both conditions outlined. The successive application of a few such conditions rapidly limited the possible values to a small region around $u = 0.23$ and $v = 0.12$. In this region the values of $A^2 + B^2$ were calculated for about 30 planes for which data were available. The smallest region to which it was found possible to limit the values of the parameters is shown by the unshaded area in Fig. 2. In the numbered shaded areas the values of $A^2 + B^2$ fail to satisfy the following conditions: 1, $221 > 433$; 2, $721 > 710$; 3, $433 > 510$; 4, $721 > 320$; 5, $331 > 732$. The most probable values⁷ of the parameters are taken to be $u = 0.235$ and $v = 0.12$. The satisfactory character of the agreement obtained with these parameters is shown by Table II which was compiled from all of the photographs analyzed.⁸ The sign = or \geq is used to indicate that the intensities of the two spots were hardly safely distinguishable. When intensity comparisons were

⁷ The parameters $u = 0.765$, $v = 0.38$, 0.62 , or 0.88 lead to the same arrangement.

⁸ Any single comparison was, of course, made between spots on the same photographic plate.

made between planes of different classes, the values of $n\lambda$ for planes of Class 1 were divided by 2. The apparent precision of the determination of the parameters may be rendered somewhat fictitious through

TABLE II
SUMMARY OF LAUE PHOTOGRAPHIC DATA FOR HEXAMETHYLENE-TETRAMINE

Observed intensity relation	Corresponding values of d/n		Corresponding values of $\sqrt{A^2 + B^2}$ for $u = 0.235$, $v = 0.12$		Observed intensity relation	Corresponding values of d/n		Corresponding values of $\sqrt{A^2 + B^2}$ for $u = 0.235$, $v = 0.12$	
311>541	1.06	1.08	87	68	210>310	1.57	2.22	19	8
541>611	1.08	1.14	68	33	321>310	1.88	2.22	42	8
611 \geq 532	1.14	1.14	33	31	331 \geq 732	0.81	0.89	84	59
532>411	1.14	1.65	31	4	732>651	0.89	0.89	59	22
532>433	1.14	1.20	31	15	331 \geq 811	0.81	0.87	84	51
433>510	1.20	1.38	15	4	811>651	0.87	0.89	51	22
631 \geq 532	1.05	1.14	35	31	651>543	0.89	0.99	22	4
541>221	1.08	1.17	68	25	732>552	0.89	0.96	59	19
530>521	1.20	1.28	57	26	732>730	0.89	0.92	59	17
521>510	1.28	1.38	26	4	331>653	0.81	0.84	84	33
521>411	1.28	1.66	26	4	331>320	0.81	0.97	84	36
221 = 521	1.17	1.28	25	26	721>710	0.96	0.99	47	54
221>433	1.17	1.20	25	15	721>320	0.96	0.97	47	36
311 \geq 210	1.06	1.57	87	19	721>543	0.96	0.99	47	4
431>210	1.38	1.57	44	19	721>552	0.96	0.96	47	19
530>210	1.20	1.57	57	19	761>410	0.76	0.85	49	21
332>210	1.50	1.57	49	19

error in the assumed reflecting powers of the carbon and nitrogen atoms or through neglect of the hydrogen atoms, but it is very doubtful whether any considerably different arrangement could be made to account for the data.

Discussion of the Structure

The arrangement found for the carbon and nitrogen atoms is shown in Fig. 3; this arrangement is derivable from the space-groups T^3 , T^3_d , or T^4_d . The crystals should be assigned to the tetrahedral or to the tetrahedral class, probably the latter. The only previous information concerning the symmetry class has indicated holohedry; Groth⁹ states that the etch figures on (110) are rhombs parallel to the edges of the faces. Further crystallographic work including an attempt to detect pyro- or piezo-electric properties would be of interest.

It can readily be shown that if $v = \frac{1}{2}u$, lines drawn from the center of a carbon atom to the centers of 2 adjacent nitrogen atoms (such as the lines AB and AC in Fig. 3) will make with each other the angle between

⁹ Groth, "Elemente d. Phys. u. Chem. Krystallographie," Oldenbourg, Munich and Berlin, 1921, p. 266.

two lines drawn from the center of a regular tetrahedron to 2 vertices. The parameters found satisfy this condition well within the precision of

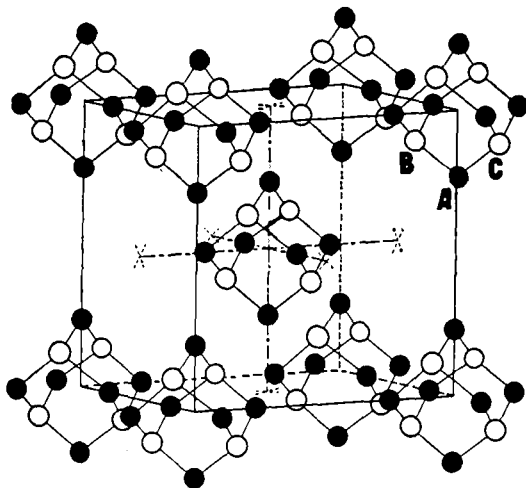


Fig. 3.—Arrangement of the carbon atoms (black circles) and nitrogen atoms (white circles) in $C_6H_{12}N_4$ crystals.

their measurement. Since the relative positions of these atoms are in accord with customary stereochemical views, the hydrogen atoms may be

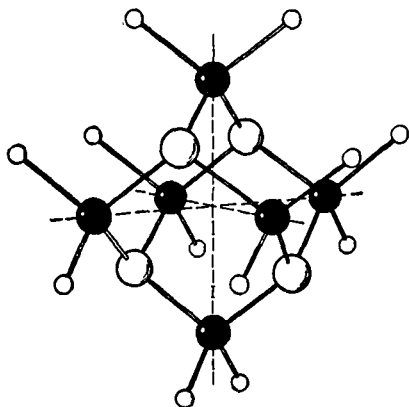


Fig. 4.—Single molecule of $C_6H_{12}N_4$, the small white circles represent hydrogen atoms. Perspective.

presumed to lie near the carbon atoms and in the direction of the other 2 tetrahedron vertices, so that the configuration of the molecule is that shown by Fig. 4. Such an arrangement is in fact compatible with the symmetry requirements.¹⁰ The hydrogen atoms will have approximately this arrangement if one of them is situated at $(\frac{3}{8}, \frac{3}{8}, \frac{1}{8})$ and in this case at least $\frac{5}{6}$ of them destructively interfere in all of the Laue photographic reflections considered except (311) and (331). This affords a possible reason why no inconsistencies were encountered when the intensity data were interpreted without considering the hydrogen atoms.

¹⁰ The space-group T_d^2 has as a special case the following 24 equivalent positions: $(rrs) (\bar{r}\bar{r}s) (\bar{r}\bar{r}s) (\bar{r}\bar{r}s) (srr) (\bar{s}\bar{r}\bar{r}) (\bar{s}\bar{r}\bar{r}) (\bar{s}\bar{r}\bar{r}) (rsr) (\bar{r}\bar{s}\bar{r}) (\bar{r}\bar{s}\bar{r}) (\bar{r}\bar{s}\bar{r})$

with 12 others differing from these only by the addition of $\frac{1}{2}$ to each coordinate. That the hydrogen atoms may be situated relative to the carbons in the manner indicated, it is necessary that $r - u = s$.

The parameters $u = 0.235$, $v = 0.12$ place the nearest carbon and nitrogen atoms 1.44 \AA . apart. The distance between the centers of molecules is much greater; each molecule is surrounded by 8 others at a distance of 6.08 \AA . and by 6 more at a distance of 7.02 \AA . The distance between the nearest atoms in two adjacent molecules presumably involves the position of the hydrogen atoms, and therefore cannot be stated with accuracy.

Summary

Hexamethylene-tetramine crystals have been investigated by X-ray methods using spectral photographs and Laue photographs. The data have been accounted for by a structure with tetrahedral symmetry that may be regarded as built up of like molecules of $C_6H_{12}N_4$ in parallel orientation and on a body-centered cubic lattice whose edge is 7.02 \AA . The carbon atoms are all equivalent, and likewise all the nitrogen atoms. This is in agreement with the structural formula numbered 4 in the introduction, but not with any other that has been suggested. Two nitrogen atoms are at a distance of about 1.44 \AA . from each carbon atom, and at least approximately in the directions of two vertices of a tetrahedron, in agreement with the prevailing view of the tetrahedral nature of the carbon atom.

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

THE REFRACTIVE INDICES OF SELENIC AND SELENIOS ACIDS¹

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The preparation of selenic acid has always required the formation of a dilute solution followed by concentration. For this reason a rapid and accurate method of determining the concentrations of selenic acid solutions seemed desirable. It was with this in view that the effort was made to determine the indices of refraction and the corresponding percentage compositions of the acid at frequent intervals over the whole range of possible dilutions. A similar study of selenious acid was also undertaken.

The preliminary investigation of the various methods of preparing selenic acid revealed that though it was a comparatively simple matter to make dil. selenic acid, its preparation in a pure and concentrated form was extremely difficult and in all probability had not yet been accomplished. Whether or not selenic acid was decomposed by hydrogen sulfide was uncertain, yet many of the methods for the preparation of the acid depended on the use of hydrogen sulfide, either as an important reagent in the preparation, or as a means of removing selenious acid from

¹ Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.