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## A Reinvestigation of Hexamethylenetetramine by Electron Diffraction

BY VERNER SCHOMAKER AND P. A. SHAFFER, JR.

An electron diffraction study of the structure of hexamethylenetetramine in the gas phase has been made by Hampson and Stosick,<sup>1</sup> who reported a C—N distance of  $1.47 \pm 0.02$  Å. on the assumption of a model, which satisfactorily reproduced their observations, with C—N—C and N—C—N angles of  $109^\circ 28'$ , the tetrahedral angle. Although these results agree with the bond distances and bond angles in related gas molecules, they stand in interesting disagreement<sup>2</sup> with the corresponding values for the crystal. Because this disagreement may have a bearing on other bond distance anomalies,<sup>2</sup> it seemed important to verify the work of Hampson and Stosick, which was based on photographs showing rings only out to  $s = 15.8$  (6 maxima and shelves), included no attempt to determine the best values of the C—N—C and N—C—N bond angles, failed to take into account the large amplitudes of vibration of the hydrogen atoms, and showed remarkably poor agreement between the observed calculated values of  $s$ , the average deviations from the mean of the ratios  $s/s_0$  for the various maxima and minima being 0.024 or about twice as great as the limit which may now be regarded as acceptable for a good determination.

Our expectation that hexamethylenetetramine should yield excellent photographs with rings extending to large angles of scattering was fulfilled, and an unusually precise interpretation was achieved. The new data include observations on fourteen maxima and shelves ( $s_{\max.} = 32.3$ ), one of which, A in Fig. 1, was not noticed by the earlier workers even though it appears on the part of the pattern which they observed on their photographs. The measurements agree well with

(1) G. C. Hampson and A. J. Stosick, *THIS JOURNAL*, **60**, 1814 (1938).

(2) P. A. Shaffer, Jr., *ibid.*, **69**, 1557 (1947).

the theoretical curve for our final model, showing an average deviation of only 0.008 both for the particular features considered by Hampson and Stosick and for all the features observed by us excepting the first minimum. However, the size determination exactly checks that of Hampson and Stosick, whose photographs were made in a different apparatus (at Oxford), and the angle determination precisely confirms their assumed value.

**Experimental.**—The electron diffraction photographs were made from crystalline hexamethylenetetramine, vaporized with the help of a high temperature nozzle,<sup>3</sup> in the apparatus described by Brockway.<sup>4</sup> Transmission photographs of gold foil ( $a_0 = 4.070$  Å.) were used for calibration of the electron wave length, which was approximately 0.06 Å. Corrections were made for film expansion.

**Radial Distribution Function.**—The characteristic features of the photographs are represented by the visual curve<sup>5</sup>  $I_{\text{vis}}(q)$  shown at the bottom of Fig. 1. From this curve an approximate radial distribution integral was obtained by punched-card summation<sup>5b,6</sup> of the formula<sup>5</sup>

$$rD(r) = \sum_{q=1,2,\dots}^{100} I_{\text{vis}}(q) \exp(-aq^2) \sin(\pi qr/10),$$

with  $a$  chosen to give  $\exp(-aq^2) = 0.075$  at  $q = 100$ . The variable  $q$  is defined as  $40/\lambda \sin \varphi/2 = 10s/\pi$ . The resulting curve (Fig. 1) has major peaks which correspond to the C—N bond dis-

(3) L. O. Brockway and K. J. Palmer, *ibid.*, **59**, 2181 (1937).

(4) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(5) (a) R. L. Spurr and V. Schomaker, *THIS JOURNAL*, **64**, 2694 (1942). (b) P. A. Shaffer, Jr., V. Schomaker, and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

(6) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *ibid.*, **14**, 648 (1946).

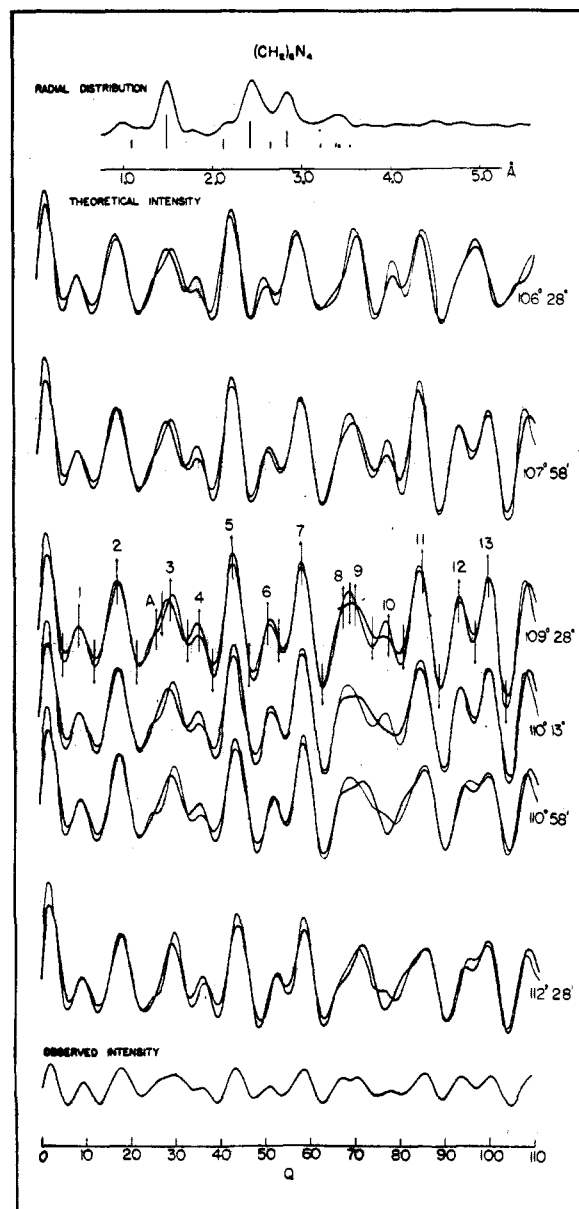


Fig. 1.—Electron diffraction curves for hexamethylenetetramine.

tance, the N···N and the shorter C···C distances, and the C···N distance in a model of the molecule having tetrahedral bond angles; the positions of these peaks and the corresponding distances for a model with exactly tetrahedral angles are 1.48 (1.480), 2.43 (2.417), and 2.83 (2.834 Å.), respectively.

The other significantly large features of the curve are generally in excellent agreement with our final model (as indicated by the vertical lines), although the resolution is not sufficient for the separate determination of any of the other interatomic distances. The peak at 0.99 Å. is exceptional, however, and stands greatly in error as a

representation of the C—H interaction expected at 1.09 Å. This error arises from a number of small errors in the drawing of the visual curve which, apparently accidentally, have concurrent effects on the radial distribution function at  $r \sim 1.0$  Å.

**Correlation of Observed and Calculated Intensity Functions.**—Theoretical intensity functions<sup>5</sup>

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

were calculated<sup>5b,6</sup> for various values of the C—N—C angle, with C—N = 1.48 Å., C—H = 1.09 Å., and  $\angle$ H—C—H = 109°28' throughout. An effective Z value of 1.20 was used for hydrogen to approximate its actual scattering power relative to carbon and nitrogen. In order to minimize the computational labor which would have been involved in a literal treatment of the temperature factors for the non-bonded N···H and C···H terms, for which the  $r_{ij}$  values varied from model to model, a procedure was adopted wherein two curves were plotted for each model. The heavy curve (Fig. 1) represents only the scattering due to non-hydrogen distances and the bonded C—H distances, with  $a_{ij}$  equal to 0.00018 for C—H<sup>7</sup> and zero otherwise; in addition to these terms, the light curve includes the non-bonded C···H and N···H terms with  $a_{C···H} = a_{N···H} = 0$ . The light curve is the significant one for small  $q$  and the heavy curve for large  $q$ , and an interpolated curve corresponding<sup>7</sup> to  $a_{C···H} = a_{N···H} \approx 0.00035$  is considered for the intermediate region.

The main items of the qualitative comparison are the following. The 106°28' model is unsatisfactory because of the complete lack of resolution of maxima 12 and 13. Neither curve 106°28' nor curve 107°58' adequately represents maximum 8–9, for which the observed weak doubling demands at least a broad maximum with a nearly flat top. The 109°28' curve is generally satisfactory.<sup>8</sup> Curve 110°13' is somewhat less satisfac-

(7) Approximate value which has been found satisfactory in other studies; see, for example, W. N. Lipscomb and V. Schomaker, *J. Chem. Phys.*, **14**, 475 (1946).

(8) The inner shoulder A is a little too far down the side of the principal maximum 8 but this is not serious since features of this type are difficult to interpret, in just this sense, and A in particular is rather weak. Furthermore, it can be seen that A depends entirely on the non-bonded C···H and N···H distances, which probably could be adjusted so as to relieve the apparent disagreement. In regard to the intensities of the main maxima and minima there are a number of rather small discrepancies with the visual curve that apply almost equally to all the theoretical curves; these discrepancies represent the errors in the visual curve that were mentioned in the discussion of the radial distribution function. Two of the discrepancies are obvious in Fig. 1, namely, those of the relative intensities of the second and third minima (where the light theoretical curves must be given greatest weight) and of the fifth and sixth minima (where the light and heavy theoretical curves have about equal weight).

The effect of the temperature factor of the C—H terms is not made obvious by the curves, but that for the C···H and N···H terms is seen to be important in the neighborhood of maxima 8–9 and 10, and perhaps even in the neighborhood of A, which otherwise would be stronger than is indicated by the photographs.

tory and curves  $110^{\circ}58'$  and  $112^{\circ}28'$  are poor, the tenth maximum, for example, having merged with its neighbor on the right. Our conclusion is that in the hexamethylenetetramine molecule in the gas phase the C-N bond angles are  $109.5^{\circ}$  with a limit of error of  $\pm 1^{\circ}$ .

The observed  $q_0$  values for maxima and minima are indicated by vertical arrows in Fig. 1 and are listed in Table I with the ratios  $q_{\text{calcd.}}/q_0$  for the finally accepted model with C-N = 1.48 Å. and tetrahedral angles. Consideration of Table I, and of similar comparisons for models with  $\angle$ C-N-C equal to  $107^{\circ}58'$  and  $110^{\circ}58'$ , leads to the result C-N = 1.48 Å. with a limit of error of  $\pm 0.01$  Å., if (see above)  $\angle$ C-N-C =  $109^{\circ}28' \pm 1^{\circ}$ . Hampson and Stosick<sup>1</sup> also found C-N = 1.48 Å. by the correlation method, but reported C-N = 1.47 Å. ( $\pm 0.02$  Å.) instead, perhaps on the basis of their imperfectly resolved radial distribution peak at 1.47 Å.

TABLE I  
ELECTRON DIFFRACTION DATA FOR HEXAMETHYLENETETRAMINE

Max.	Min.	$q_0^{\dagger a}$	$q_0$	$q_{\text{calcd.}}/q_0$
	1		5.7	(1.070)
1		9.4	9.3	0.989
	2	13.6	12.7	0.986
2		17.8	17.9	1.005*
	3	23.2	22.3	1.020
4			26.5	1.008
	4		27.8	0.993
3		27.9	29.7	1.000
	4	33.6	33.6	1.003
4		36.5	36.2	0.985
	5	39.8	39.1	0.998
5		43.0	43.5	1.000*
	6		47.3	1.013
6		50.3	51.4	1.012
	7		53.9	1.018

7		59.0	1.000*
	8	63.0	1.011*
8			
		69.6	1.006
9			
	10	74.7	1.009
10		78.3	0.990
	11	81.6	.983
11		86.0	.991*
	12	89.6	1.003*
12		94.0	1.000
	13	97.6	0.995
13		100.7	1.001
		Average <sup>b</sup>	1.001
		Average deviation	0.008

<sup>a</sup> Values of Hampson and Stosick.<sup>1</sup> For our best model,  $q_{\text{calcd.}}/q_0^{\dagger} = 0.996$ , a. d. = 0.029; if the first, second, fourth and fifth values are rejected (inner rings, rings adjacent to A),  $q_{\text{calcd.}}/q_0^{\dagger} = 1.003$ , a. d. = 0.016. <sup>b</sup> If only the six strongest, most symmetrical, and presumably most reliably measurable features represented by starred values are considered, the average is 1.001 and the average deviation is 0.005.

**Acknowledgment.**—We wish to express our gratitude to Professor Linus Pauling for suggesting this investigation, to Dr. R. A. Spurr and Mr. Kent Harmon for assistance in preparing the photographs and curves, and to the International Business Machines Corporation for the loan of the machines used in making the punched card calculations.

### Summary

A reinvestigation of hexamethylenetetramine vapor by electron diffraction has led to results (C-N =  $1.48 \pm 0.01$  Å. and  $\angle$ C-N-C =  $\angle$ N-C-N =  $109.5 \pm 1^{\circ}$ ; C-H = 1.09 Å. and  $\angle$ H-C-H =  $109^{\circ}28'$  assumed) in agreement with but more precise than those of the earlier investigation.<sup>1</sup>

PASADENA, CALIFORNIA

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## Anisotropic Oscillations in the Hexamethylenetetramine Crystal

BY P. A. SHAFFER, JR.

Whereas the carbon-nitrogen distance found for gas molecules of hexamethylenetetramine by the electron diffraction method,<sup>1</sup> 1.48 Å., agrees satisfactorily with the value predicted from the consideration of covalent radii,<sup>2</sup> previous investigations of the structure of hexamethylenetetramine crystals<sup>3</sup> have indicated a lower value, about

(1) G. C. Hampson and A. J. Stosick, *THIS JOURNAL*, **60**, 1814 (1938); V. Schomaker and P. A. Shaffer, Jr., *ibid.*, **69**, 1555 (1947).

(2) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, New York, 1940, p. 164.

(3) R. G. Dickinson and A. L. Raymond, *THIS JOURNAL*, **48**, 22 (1923); H. W. Gonell and H. Mark, *Z. physik. Chem.*, **107**, 181 (1923); R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934); R. Brill, H. G. Grimm, C. Hermann, and A. Peters, *Ann. Physik*, **84**, 393 (1939).

1.44 Å. The work reported in this paper was carried out in order to determine whether or not the reported difference in this interatomic distance for the crystal and the gas is real. If the carbon-nitrogen distance is indeed this short in the crystal, it may be of interest in connection with the anomalously short carbon-nitrogen bond distances found in the amino acids.<sup>4</sup>

In the first X-ray study of the crystal structure of hexamethylenetetramine Dickinson and Raymond found the space group of the crystal to be  $I43h$ , with the edge of the cubic unit equal to

(4) For a review of observed carbon-nitrogen bond distances see E. W. Hughes and W. N. Lipscomb, *THIS JOURNAL*, **68**, 1970 (1946).