

## The Crystal Structure of *N:N'*-Diacetylhexamethylenediamine

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The crystal structure of *N:N'*-diacetylhexamethylenediamine has been determined. The symmetry is triclinic, space group  $P\bar{1}$ , and the cell dimensions are:  $a = 12.35$ ,  $b = 5.44$ ,  $c = 4.93$  Å;  $\alpha = 116^\circ 37'$ ,  $\beta = 99^\circ 04'$ ,  $\gamma = 94^\circ 18'$ . There is one molecule in the unit cell. The preliminary structure has been deduced from a molecular transform of the molecule, and refined by projections on (010) and (001). The molecule lies approximately in the (210) plane. The hexamethylene chain and the acetylamine groups are planar, the angle between the normals to these planes being  $11\frac{1}{2}^\circ$ . The molecules are linked by hydrogen bonds into chains parallel to the  $c$  axis.

### Introduction

The various types of hydrogen-bonding schemes possible in crystal structures of molecules containing two  $-\text{CO.NH}-$  groups have been listed by Wells (1954). Diacetylhexamethylenediamine is one of a series of compounds of this type which it is proposed to examine structurally in order to determine the system of intermolecular hydrogen bonding. In addition, the data from the accurate analysis of this structure have proved of value in the determination by Sandeman (1955) of the directions of the transition moments of infra-red bands by the use of polarized radiation. The compound was particularly suitable for polarized infra-red study since, in a triclinic cell containing only one molecule, each bond has only one orientation in the crystal, and so for each type of vibration the direction of dipole-moment change is unique.

### Experimental

*N:N'*-Diacetylhexamethylenediamine ( $\text{C}_{10}\text{H}_{20}\text{O}_2\text{N}_2$ ) forms colourless triclinic crystals, platy on (100) and elongated along [001]. It is extremely fibrous in directions parallel to [001]. The cell constants  $a$ ,  $b$  and  $c$  were measured from rotation photographs about each axis, and  $\alpha^*$ ,  $\beta^*$  and  $\gamma^*$  were obtained directly from goniometric measurements. The remaining constants  $a^*$ ,  $b^*$  and  $c^*$ , and  $\alpha$ ,  $\beta$  and  $\gamma$ , were obtained by calculation.

$$\begin{aligned} a &= 12.35, \quad b = 5.44, \quad c = 4.93 \text{ \AA}; \\ \alpha &= 116^\circ 37', \quad \beta = 99^\circ 04', \quad \gamma = 94^\circ 18'; \\ a^* &= 0.0832, \quad b^* = 0.2084, \quad c^* = 0.2324 \text{ \AA}^{-1}; \\ \alpha^* &= 62^\circ 10', \quad \beta^* = 77^\circ 37', \quad \gamma^* = 80^\circ 31'. \end{aligned}$$

Space group:  $P\bar{1}$ .

Experimental density:  $1.14 \text{ g.cm.}^{-3}$ ; theoretical density:  $1.154 \text{ g.cm.}^{-3}$  calculated for one molecule in the unit cell.

The intensity data were recorded on [b] and [c] zero-layer Weissenberg photographs using  $\text{Cu K}\alpha$  ra-

diation. Three superposed films were used for a long and short exposure about each axis, and the intensities were estimated visually by comparison with a calibrated scale of time exposure from the same crystal. No absorption corrections were applied since the crystal was small and had been dissolved away until it was approximately equidimensional. The ( $h0l$ ) and ( $hk0$ ) structure amplitudes were deduced after correcting for the appropriate geometrical factors.

The scattering-factor curves applied to the carbon, nitrogen and oxygen structure factors were those deduced by McWeeny (1951). In the preliminary stages of the structure determination the temperature factor was approximated to the value  $\exp(-4.0 \sin^2 \theta / \lambda^2)$ . A more accurate value was later obtained, together with the scale factor, by plotting  $\log(F_o/F_c)$  against  $(2 \sin \theta)^2$ . This gave values  $\exp(-3.81 \sin^2 \theta / \lambda^2)$  and  $\exp(-3.64 \sin^2 \theta / \lambda^2)$  for the ( $h0l$ ) and ( $hk0$ ) reflexions respectively.

### Structure determination

Since there is only one molecule in the unit cell and its configuration can be assumed to be known with sufficient accuracy, it was considered that the molecular-transform method (Knott, 1940) could be used to obtain a direct solution of the crystal structure. The molecule was assumed to be planar, the bond lengths and inter-bond angles in the chain to be  $1.54$  Å and  $109^\circ 28'$  respectively, and the C=O bond length to be  $1.20$  Å. The transforms of the C, N and O atoms were weighted in the ratio 6:7:8. Then the molecular transform of the centrosymmetrical molecule is given by:

$$\begin{aligned} T &= 2[6 \cos 2\pi(1x'a^* + y'b^*) \\ &\quad + 6 \cos 2\pi(3x'a^* - y'b^*) \\ &\quad + 6 \cos 2\pi(5x'a^* + y'b^*) \\ &\quad + 6 \cos 2\pi(9x'a^* + y'b^*) \\ &\quad + 6 \cos 2\pi(11x'a^* - y'b^*) \\ &\quad + 7 \cos 2\pi(7x'a^* - y'b^*) \\ &\quad + 8 \cos 2\pi(9x'a^* + (1.64/0.44)y'b^*)], \end{aligned}$$

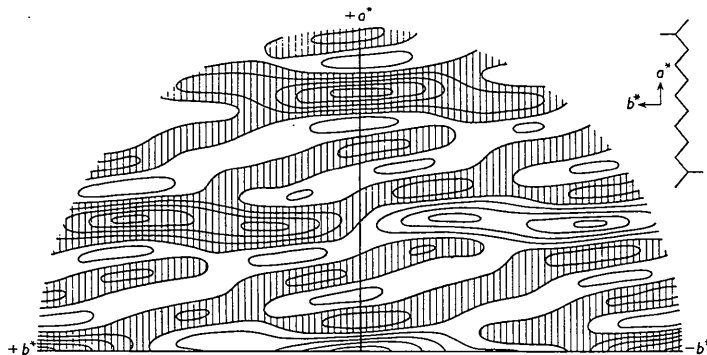


Fig. 1. Molecular transform of the molecule (shaded areas negative).

where  $x' = 0.63 \text{ \AA}$ ,  $y' = 0.44 \text{ \AA}$ , and  $a^*$  and  $b^*$  are rectangular axes in the plane of the molecule,  $a^*$  being along its length.

The transform was evaluated at intervals of  $1/37.8$  and  $1/26.4$  reciprocal units along  $a^*$  and  $b^*$  respectively, using Bevers-Lipson strips for all atoms except the oxygen, which had to be summed individually since its  $y$  coordinate was not a simple multiple of that of the other atoms.

The transform showed the series of ridges and troughs characteristic of long-chain hydrocarbons, only slightly modified by the nitrogen and oxygen atoms (Fig. 1). The  $(h0l)$  and  $(hk0)$  reciprocal lattices were drawn out on the same scale as the transform, and each reciprocal point was weighted with the value  $F_o/f_{\text{carbon}}$  for that plane. The carbon scattering curve was introduced so that the amplitude scale of the weighted reciprocal lattice correspond more directly to that of the transform.

Correlation of the large  $(h0l)$  reflexions was readily obtained, and the signs of 70 out of the 99 observed reflexions in this zone were determined directly. In the  $(hk0)$  zone the fit obtained was not so extensive, probably owing to the molecule being more inclined from the  $(001)$  plane than from the  $(010)$  plane, and the signs of 44 out of the 119 observed reflexions were determined directly.

Fourier projections on  $(010)$  and  $(001)$  were calculated incorporating all the terms whose signs had been determined from the transform. Refinement was effected by successive projections. The final projection on  $(010)$  (Fig. 2(a)), showed excellent resolution of all the atoms, and enabled accurate estimation of the  $x$  and  $z$  coordinates to be made. In the  $(001)$  projection (Fig. 2(b)) there was considerable overlap and the  $-\text{NH}_2$  group occurred as a composite peak. In this case the  $y$  coordinates were taken as those which best fitted the peak when combined with the  $x$  coordinates from the  $(010)$  projection. The resolution of the remaining four carbon atoms was sufficient for their centres to be determined accurately.

Difference syntheses were plotted for both the  $(010)$  and  $(001)$  projections. The positive peaks corresponded

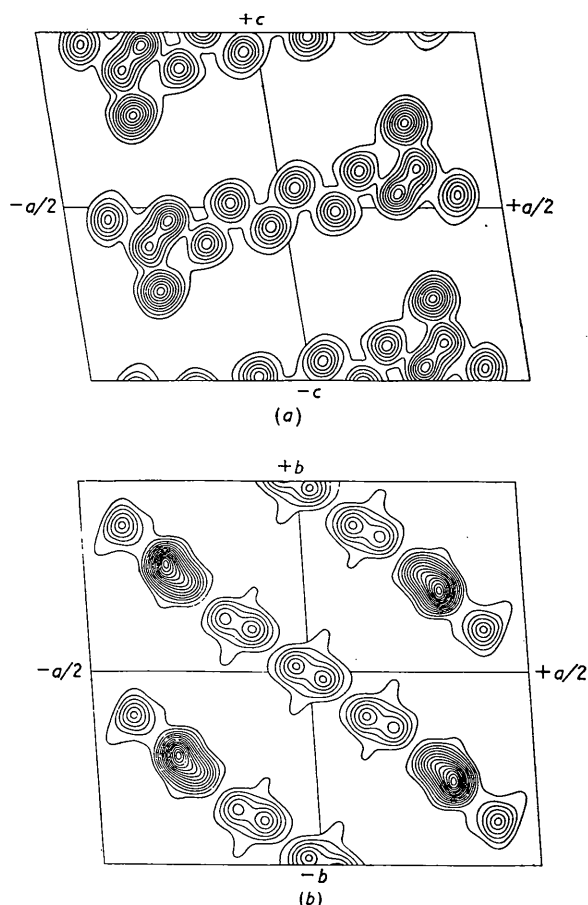


Fig. 2. Projection of the electron density on (a)  $(010)$ , (b)  $(001)$ .

to the hydrogen positions, (theoretical positions for the hydrogen atoms of the hexamethylene group (Table 1) were calculated assuming a C-H bond length of  $1.08 \text{ \AA}$  and tetrahedral angles) but were not sufficiently resolved to give accurate hydrogen coordinates.

The structure amplitudes calculated from the final coordinates (Table 2) are compared with the observed values in Table 3 for the  $(h0l)$  and  $(hk0)$  reflexions. The observed values of the extremely strong  $(210)$

Table 1. *Theoretical hydrogen coordinates (excluding the methyl group)*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	
C <sub>1</sub>	H'	0.079	0.152	0.303
	H''	0.980	0.855	0.190
C <sub>2</sub>	H'	0.171	0.897	0.822
	H''	0.072	0.600	0.709
C <sub>3</sub>	H'	0.234	0.901	0.401
	H''	0.134	0.604	0.288
N <sub>6</sub> —H	0.282	0.506	0.866	

Table 2. *Fractional atomic coordinates*

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C <sub>1</sub>	0.0338	0.033	0.114
C <sub>2</sub>	0.1178	0.220	0.024
C <sub>3</sub>	0.1872	0.283	0.210
C <sub>4</sub>	0.3208	0.583	0.230
C <sub>5</sub>	0.4032	0.763	0.073
N <sub>6</sub>	0.2654	0.463	0.075
O <sub>7</sub>	0.3097	0.550	0.485

reflexion and the next strongest reflexion, (10 $\bar{1}$ ), are considerably weaker than the calculated values owing to extinction. Excluding these two reflexions, the agreement factor  $R = \sum(|F_o| - |F_c|) \div \sum|F_o|$  has values 0.097 and 0.124 for the (*h*0*l*) and (*hk*0) zones.

An evaluation of Cruickshank's formula (1949) for the standard deviation of a peak position in terms of the central curvature of the peak and the structure-factor agreement was made from the final (*h*0*l*) projection. The values obtained were:

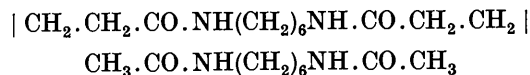
$$\begin{aligned} \text{Carbon: } \sigma(x) &= 0.005 \text{ \AA}, \quad \sigma(z) = 0.007 \text{ \AA}. \\ \text{Oxygen: } \sigma(x) &= 0.004 \text{ \AA}, \quad \sigma(z) = 0.004 \text{ \AA}. \end{aligned}$$

The formula was not applicable to the (*hk*0) projection because of the peak overlap.

### Description of the structure

The structure consists of chains of molecules lying approximately in the (210) plane, and linked in the

[*c*] direction by hydrogen bonds of length 2.88 Å between the nitrogen and oxygen atoms of adjacent molecules (Fig. 3(a)). It is closely related to the structure of polyhexamethylene adipamide, (Bunn & Garner, 1947), one repeat unit of which is compared with the *N*:*N'*-diacetylhexamethylenediamine molecule below:



The *a*, *b* and *c* axes of polyhexamethylene adipamide are equivalent to the *c*, *b* and [2 $\bar{1}$ 0] axes of *N*:*N'*-diacetylhexamethylenediamine respectively, and the cell dimensions relative to these axes are:

Polyhexamethylene adipamide

$$\begin{aligned} a &= 4.9, \quad b = 5.4, \quad c = 17.2 \text{ \AA}; \\ \alpha &= 48\frac{1}{2}^\circ, \quad \beta = 77^\circ, \quad \gamma = 63^\circ. \end{aligned}$$

*N*:*N'*-Diacetylhexamethylenediamine

$$\begin{aligned} c &= 4.93, \quad b = 5.44, \quad [2\bar{1}0] = 17.06 \text{ \AA}; \\ [b] : [2\bar{1}0] &= 46^\circ 12', \quad [c] : [2\bar{1}0] = 80^\circ 11', \quad [b] : [c] = 63^\circ 23'. \end{aligned}$$

In addition to the hydrogen bonds of 2.88 Å there are 27 interatomic distances of less than 4.2 Å between the seven atoms in the asymmetric half-molecule and the adjacent molecules. These are listed in Table 4 for the molecule with centre at (0, 0, 0) and the adjacent molecules whose centres are given in brackets.

The shape of the molecule may be described in terms of three planes. The six carbons of the central hexamethylene group (C<sub>1</sub>C<sub>2</sub>C<sub>3</sub>C<sub>1</sub>'C<sub>2</sub>'C<sub>3</sub>') lie accurately on the mean plane

$$0.6762x + 0.7076y - 0.2052z = 0. \quad (i)$$

The terminal acetylamine groups lie on two parallel planes 0.84 Å apart on each side of the origin, whose normals are inclined at an angle of 11° 28' to the normal of the hexamethylene plane. The equation to

Table 3. *Comparison of observed and calculated F(h0l)'s and F(hk0)'s*

<i>h</i>	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	1.0	1.5	1.5	1.0	1.5											
5	-1.0	-1.0	-1.5	-1.0	-1.5											
4	3.0 < 1.0	1.5 < 1.0	3.0	5.0	1.0	2.0	2.5									
3	6.5 < 1.0	6.0	5.0	4.0	5.5	5.0	3.0 < 1.0	1.0 < 1.0	0.5							
2	9.0	9.5	1.0	5.0	2.0	10.0	8.0	3.5 < 1.0	1.0 < 1.0	1.0	1.5	1.0				
1	22.5	14.5	11.5	2.5	5.0	6.0	11.5	3.5	5.0	1.0	1.5	1.0 < 1.0	4.5	1.0		
0	5.5	22.0	18.5	2.0	9.0	3.0	8.5	5.0	1.5	4.5	3.5 < 1.0	2.5	4.0	1.0		
1	25.0	4.0	10.5 < 1.0	11.0	9.5	12.0	12.5	6.5 < 1.0	1.5 < 1.0	1.5	3.0 < 1.0					
2	5.0	6.5	6.0 < 1.0	1.0	2.5	8.0	11.0 < 1.0	1.0 < 1.0	1.0	1.5	1.5 < 0.5					
3	3.0 < 1.0	6.0	1.5	8.5	4.5	4.0	12.5	4.5	2.0 < 1.0	1.0 < 1.0	1.0	1.5				
4	2.0	6.5 < 1.0	3.5 < 1.0	4.0	3.0 < 1.0	4.5	1.5	2.0 < 1.0	1.5							
5	2.5	2.5	5.0	2.0 < 1.0	1.0	1.0 < 1.0	0.5 < 0.5									

<i>h</i>	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
5	1.5	1.0	4.0	1.0	1.0 < 0.5	0.5 < 0.5										
4	7.5	4.0	3.0 < 1.0	1.5 < 1.0	1.0	4.5	1.0	2.0	1.0							
3	5.0	2.0	4.0 < 1.0	2.5	11.5	6.5	5.5	2.0	1.5	2.0 < 0.5	0.5					
2	7.0	4.5	12.0	17.5	19.5	12.0 < 1.0	6.0	4.0	1.0 < 1.0	1.0	1.0	1.0				
1	16.5	19.5	36.0	15.5	9.5	15.0	4.5	4.5	2.5	2.0	2.5	1.0	1.5	2.5 < 0.5		
0	5.5	22.0	18.5	2.0	9.0	3.0	8.5	5.0	1.5	4.5	3.5 < 1.0	2.5	4.0	1.0		
1	12.0	1.5	7.0	1.5	20.5	1.5	7.0	8.5	4.0 < 1.0	2.0	8.5 < 1.0	2.0 < 0.5				
2	5.5	4.5	20.0	10.0	10.0	8.0	4.0	1.5 < 1.0	10.5	2.5	2.5 < 1.0	1.0 < 0.5				
3	9.5	9.5	6.0	4.5	2.0	2.5	3.0	9.5	5.5	2.0	1.5	1.5	1.0 < 0.5			
4	1.5	2.0 < 1.0	3.0	3.5	5.5	5.5	1.0	2.0	1.0	1.5	1.0	4.5				
5	< 1.0	2.0	2.0	2.0	4.0	1.0	1.0 < 0.5	1.5	1.0	3.5						

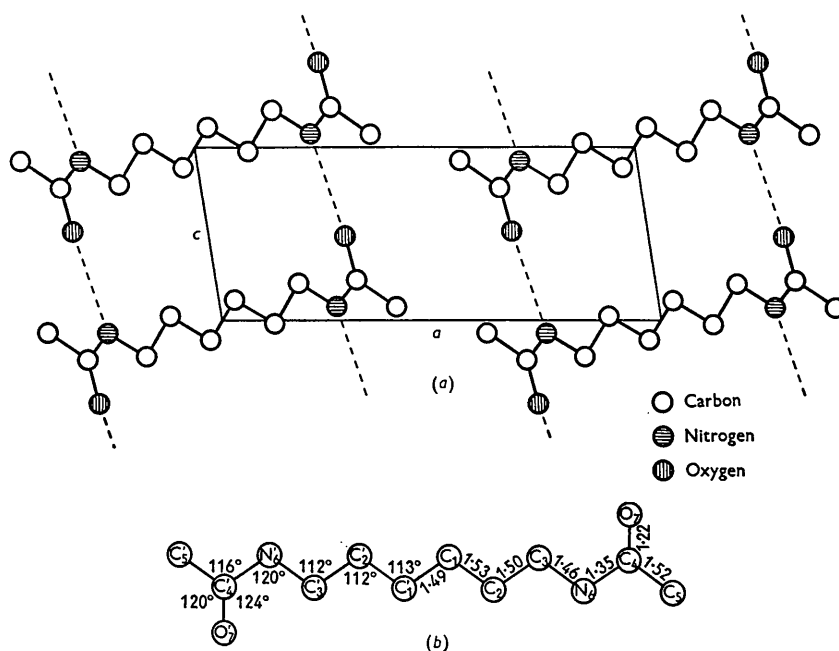


Fig. 3. (a) Projection of the structure on (010), showing the arrangement of hydrogen bonds. (b) Dimensions of the molecule.

Table 4. *Interatomic distances less than 4.2 Å*

All distances are in Ångström units

C <sub>1</sub>	-C <sub>1</sub> '(0, 0, 1)=3.89	-C <sub>3</sub> (0, 1, 0)=4.18	-N <sub>6</sub> (0, 1, 0)=4.15
C <sub>2</sub>	-C <sub>3</sub> (0, 0, 1)=3.92	-C <sub>6</sub> (0, 1, 0)=4.16	-C <sub>4</sub> (0, 1, 0)=3.70
	-O <sub>7</sub> (0, 1, 0)=3.72		
C <sub>3</sub>	-C <sub>2</sub> (0, 0, 1)=3.92	-C <sub>4</sub> (0, 1, 0)=3.99	-O <sub>7</sub> (0, 1, 0)=3.70
	-C <sub>5</sub> (0, 1, 0)=4.09		
C <sub>4</sub>	-C <sub>2</sub> (0, 1, 0)=3.70	-C <sub>3</sub> (0, 1, 0)=3.70	-C <sub>5</sub> (1, 1, 1)=4.07
C <sub>5</sub>	-C <sub>3</sub> (0, 1, 0)=4.09	-N <sub>6</sub> (0, 1, 0)=4.05	-C <sub>4</sub> (1, 1, 1)=4.07
	-O <sub>7</sub> (1, 1, 1)=3.68	-C <sub>5</sub> '(1, 1, 0)=3.98	-C <sub>5</sub> '(1, 1, 1)=4.08
	-C <sub>5</sub> '(1, 2, 0)=3.57		
N <sub>6</sub>	-C <sub>5</sub> (0, 1, 0)=4.05	-C <sub>1</sub> (0, 1, 0)=4.15	-C <sub>2</sub> (0, 1, 0)=4.16
O <sub>7</sub>	-C <sub>2</sub> (0, 1, 0)=3.72	-C <sub>3</sub> (0, 1, 0)=3.70	-C <sub>5</sub> (1, 1, 1)=3.68

the mean plane containing the -CH<sub>2</sub>.NH.CO.CH<sub>3</sub> group is

$$0.7297x + 0.6836y - 0.0143z = 0.4199 \quad (\text{ii})$$

for atoms C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, N<sub>6</sub>, O<sub>7</sub>, and

$$0.7297x + 0.6836y - 0.0143z = -0.4199 \quad (\text{iii})$$

for atoms C<sub>3</sub>', C<sub>4</sub>', C<sub>5</sub>', N<sub>6</sub>', O<sub>7</sub>'.

The perpendicular displacements (in Ångström units) of the atoms from the respective planes are:

	Plane (i)	Plane (ii)
C <sub>1</sub>	-0.004	—
C <sub>2</sub>	-0.002	—
C <sub>3</sub>	+0.002	+0.004
C <sub>4</sub>	—	-0.010
C <sub>5</sub>	—	+0.006
N <sub>6</sub>	—	-0.004
O <sub>7</sub>	—	+0.003

It is of interest that the normals to the planes containing the acetylamine groups make an angle of

89° 11' with the *c* axis and 88° 29' with the direction of the N<sub>6</sub>-O<sub>7</sub> hydrogen bond. This means that the adjacent hydrogen-bonded molecules are almost exactly coplanar, the perpendicular distance between their acetylamine planes being 0.07 Å.

The bond lengths and inter-bond angles of the *N*:*N'*-diacetylhexamethylenediamine molecule are shown in Fig. 3(b). They agree closely with the values adopted for a model polypeptide chain by Pauling, Corey & Branson (1951) from the averages of values found in DL-alanine, L-threonine, *N*-acetyl-glycine, and β-glycyl-glycine:

	<i>N</i> : <i>N'</i> -Diacetyl-hexamethylenediamine	Polypeptide chain
C <sub>3</sub> -N <sub>6</sub>	1.46 Å	1.47 Å
N <sub>6</sub> -C <sub>4</sub>	1.35	1.32
C <sub>4</sub> -O <sub>7</sub>	1.22	1.23
C <sub>4</sub> -C <sub>5</sub>	1.52	1.53
C <sub>2</sub> -C <sub>3</sub> -N <sub>6</sub>	112°	110°
C <sub>3</sub> -N <sub>6</sub> -C <sub>4</sub>	120	120
N <sub>6</sub> -C <sub>4</sub> -C <sub>5</sub>	116	117
N <sub>6</sub> -C <sub>4</sub> -O <sub>7</sub>	124	122
C <sub>5</sub> -C <sub>4</sub> -O <sub>7</sub>	120	121

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