

The Crystal Structure of Hydrazine Monohydrate

BY RUNE LIMINGA AND IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

(Received 13 December 1963)

The crystal structure of hydrazine monohydrate, $N_2H_4 \cdot H_2O$, has been determined from three-dimensional single-crystal X-ray data obtained at $-165^\circ C$. The crystals are trigonal (space group $P3_121$) with three molecules in a hexagonal unit cell with the dimensions: $a = 4.873 \pm 0.006$, $c = 10.94 \pm 0.01$ Å. Each water molecule is linked by six hydrogen bonds to hydrazine molecules (2.79, 2.79, 3.11, 3.11, 3.15 and 3.15 Å, respectively). The hydrazine molecules are not bonded to each other. A possible assignment of the hydrogen atoms to these bonds is given. This assignment is confirmed by the 'hydrogen peaks' appearing in the electron-density maps.

Introduction

The melting point diagram and other physical properties of the system hydrazine-water indicate only one intermediate compound, $N_2H_4 \cdot H_2O$. The melting point of this compound has been reported as $-51.7^\circ C$ (Mohr & Audrieth, 1949), and as $-51.5^\circ C$ (Hill & Summer, 1951). A higher value, $-46.8^\circ C$, was found by Semishin (1938). A list of references is given in the book by Audrieth & Ogg (1951).

An X-ray study of hydrazine hydrate at $-60^\circ C$ has been reported earlier (Zocchi, Busing, Ellison & Levy, 1962). According to this investigation the structure appears to be that of sodium chloride with disordered or rotating H_2O and N_2H_4 molecules. A powder sample of this material showed a transformation to a phase of lower symmetry on cooling to below $-80^\circ C$.

The present investigation involves the determination of the crystal structure of hydrazine hydrate from single-crystal X-ray diffraction data obtained at $-165^\circ C$. The relationship between the two different structures is discussed below. It should be noted, however, that the existence of the stated cubic form and the phase change at $-80^\circ C$ has not been observed in the present investigation as will be further demonstrated below.

Experimental

The crystals were grown from solutions of hydrazine and water sealed in glass capillaries (diameter about 0.3 mm, wall thickness 0.01–0.02 mm). The sample used was commercial hydrazine monohydrate (KEBO, *pro analysi*), with a composition of 50.2 mole% hydrazine (analysed by titration by the bromate method at the Central Analytical Laboratory, Institute of Chemistry, University of Uppsala). The single crystals were grown in the ordinary way in a modified Weissenberg camera (Olovsson, 1960). During crystal growth the melting point was found to be about $-52^\circ C$; this is in good agreement with two

of the earlier published values cited above. It was very difficult to obtain single crystals of this compound. Furthermore, the crystals were unstable. Initially capillaries of about 0.1 mm internal diameter were used, but the crystals always decomposed after some hours' exposure. When a larger crystal (capillary diameter about 0.3 mm) was used, it was possible to obtain enough data before the single crystal was destroyed.

The crystals were grown very slowly just below the melting point and then cooled gradually to about $-100^\circ C$ before examination by X-ray photography. If the crystal was found to be suitable it was adjusted and then cooled further to $-165^\circ C$. No phase transformation was observed between -100 and $-165^\circ C$. (These exposures were thus all done below the transformation temperature $-80^\circ C$ stated by Zocchi *et al.* and do not exclude a phase change).

In order to obtain more information about the possible phase transformation, a series of experiments was performed with powder samples. It turned out that all powder samples prepared in different ways (above and below $-80^\circ C$) gave the same photographs. Powders formed at $-60^\circ C$ and kept at $-65^\circ C$ during exposure were, for example, the same as those found at lower temperatures. Powders cooled from $-60^\circ C$ to $-110^\circ C$ indicated no phase change.

Furthermore all crystals prepared were optically anisotropic at all temperatures, and this excludes cubic symmetry for any of the crystals obtained in the present investigation.

Equi-inclination Weissenberg photographs, layers 0 to 2, were taken with Cu K radiation at $-165 \pm 5^\circ C$, the crystal rotating about the a axis. The relative intensities were estimated visually by a multiple-film technique (four films) and comparison with an intensity scale. The data were corrected for the Lorentz and polarization effects on the computer BESK. The number of independent reflexions recorded was 214, but the intensities of 40 of these were too weak

to be measured. About 95% of the reflexions within the Cu-reflexion sphere were thus recorded.

Unit cell and space group

The unit cell first chosen had orthogonal axes and the dimensions: $a' = 8.44 \pm 0.01$ Å, $b' = 4.92 \pm 0.05$ Å, $c' = 10.94 \pm 0.01$ Å. The a' and c' dimensions were determined from quartz-calibrated zero-layer Weissenberg photographs ($a = 4.913$ Å for α quartz at 25 °C; $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å, $\lambda(\text{Cu } K\alpha_2) = 1.54433$ Å). The dimension of b' (the rotation axis) was determined without calibration. With this choice of unit cell $I(hkl)$ was equal to $I(h\bar{k}l)$, indicating a plane of symmetry normal to b' or a twofold axis parallel to b' . The systematic absences required a C -centered cell; furthermore all reflexions $(00l)$ with $l \neq 3n$ were missing. The diffraction symmetry was later found to be $\bar{3}m$, indicating trigonal symmetry. A hexagonal unit cell was then chosen with $a = a'/\sqrt{3}$. The axis b' coincides with a . Accordingly, the dimensions of the new unit cell (at -165 °C) are:

$$a = 4.873 \pm 0.006, c = 10.94 \pm 0.01 \text{ Å}.$$

(The uncertainties are estimated maximum errors.)

The trigonal symmetry together with the systematic absences $(00l)$ for $l \neq 3n$ suggest the space groups $P3_121$ or $P3_221$, assuming that the absences are space group extinctions. The density of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was set equal to 1.03 g.cm^{-3} (linear interpolation between the density of ice, 0.92 g.cm^{-3} , and of solid hydrazine, 1.146 g.cm^{-3} at -5 °C). The density of liquid hydrazine hydrate at 0 °C is 1.048 g.cm^{-3} (Semishin, 1938). With three molecules per unit cell the calculated density is 1.11 g.cm^{-3} . As shown below, the structure is well described in terms of the space group $P3_121$ (D_3^4) with the nitrogen atoms in the general sixfold positions: (x, y, z) ; $(\bar{y}, x - y, \frac{1}{3} + z)$; $(y - x, \bar{x}, \frac{2}{3} + z)$; (y, x, \bar{z}) ; $(\bar{x}, y - x, \frac{1}{3} - z)$; $(x - y, \bar{y}, \frac{2}{3} - z)$ and the oxygen atoms in the threefold position (b) : $(x, 0, \frac{5}{6})$; $(0, x, \frac{1}{6})$; $(\bar{x}, \bar{x}, \frac{1}{2})$. (*International Tables for X-ray Crystallography*, 1952). It is of interest to notice that the central point of the N-N bond is in the threefold position (a) in $P3_121$.

Determination of the atomic coordinates

The atomic positions were determined from a three-dimensional Patterson synthesis. These preliminary atomic coordinates were improved in a series of three-dimensional electron density calculations and then further refined by least-squares methods. The program first used can handle only orthorhombic and lower symmetries (see below) and the refinements were therefore made with the use of the orthogonal cell originally chosen. Since the crystal slowly decomposed during the period of examination the inter-layer scale factor could not be based on the relative exposure times, but had to be determined by a series of least-

squares calculations. In these cycles the atomic coordinates were not varied. Mean values of F_o for the equivalent reflexions (*i.e.* those observed more than once) were taken at this stage and were used in the subsequent refinements of coordinates and isotropic temperature factors for nitrogen and oxygen and the over-all scale factor. The inter-layer scaling procedure described above was repeated three times in later stages of the refinements. The crystallographic calculations were performed on FACIT and IBM 7090 computers in Stockholm.

The least-squares program (SFLS) used for these calculations was written by Brändén & Åsbrink (to be published). Block-diagonal approximation is used in this program which minimizes the function $\sum w(|F_o| - |F_c|)^2$. The weighting factor w was taken as a constant $1/(4F_{\min})^2$ if $|F_o| \leq 4|F_{\min}|$ and otherwise as $1/F_o^2$. Reflexions too weak to be observed were given zero weight. Orthorhombic symmetry is the highest symmetry that this program can handle correctly. Structures of higher symmetry can be refined if they are treated as having lower symmetry, which necessitates the inclusion of more than the independent data. The standard deviations obtained are then incorrect. In the present case the least-squares refinements were performed for the structure described in terms of the monoclinic space group $C2$ with one oxygen and three nitrogen atoms in the general fourfold positions and one oxygen atom in the special twofold position (b) (*International Tables*, 1952). The dimensions assigned to the monoclinic cell were $a' = 8.44$, $b' = 4.87$, $c' = 10.94$ Å, $\beta = 90^\circ$, corresponding to those of the cell first chosen and to a volume twice that of the hexagonal unit cell.

After about 20 cycles of least-squares refinements the discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.122 (unobserved reflexions omitted in calculating all R values). The shifts of the atomic positions in the final cycles were less than about one tenth of the standard deviation for the coordinate in question. When the observed and calculated structure factors were compared at this stage it was found that several of the strong reflexions showed rather poor agreement. The Fourier difference maps were also unsatisfactory. The hydrogen atoms were now included, assigned to the hydrogen bonds as described below. Some cycles of least-squares refinements were then calculated, keeping the hydrogen parameters fixed (the temperature factor B for hydrogen was set equal to 6 Å^2). The R value decreased from 0.122 to 0.096. The total shifts in the oxygen and nitrogen positions were about 0.005 and 0.01 Å, respectively. The agreement between the above-mentioned structure factors was now good. The difference syntheses also showed improvement but still indicated some shifts. Some three-dimensional F_o and F_c syntheses were therefore calculated and back-shift corrections were applied. The R value decreased to 0.094.

The Fourier calculations were made on the com-

puter FACIT using programs designated STRIX and PROFFS, written by the present authors. The electron density maxima were located using a program designated LOKE, written by Lundberg & Olovsson. This program makes use of the method devised by Dawson (1961).

Finally, some cycles of least-squares calculations were performed with a full-matrix program, ORXLS, written by Busing & Levy (1959). This program was originally written for the IBM 704 computer but the present calculations were made on the IBM 7090 computer in Stockholm. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting factor w was taken as $1/F_o^2$ for F 's more than four times the minimum observable F in that region of the film, and as a constant $1/(16F_{\min}^2)$ for F 's smaller or equal to $4F_{\min}$ (Hughes, 1941). For reflexions too weak to be observed, F_o was set equal to $\frac{1}{2}F_{\min}$. The coordinates and individual temperature factors for nitrogen and oxygen and an overall scale factor were refined, keeping the hydrogen parameters fixed. These calculations started with the parameters given in Table 1(b). After five cycles the shifts in the atomic coordinates were less than about one tenth of the standard deviations and the R index (defined earlier) was 0.110 when the 40 unobserved reflexions were included. The R value without these reflexions was 0.095.

The atomic scattering factors used in these calculations were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for

neutral nitrogen and oxygen and those of McWeeny (1951) for neutral hydrogen.

The atomic parameters with standard deviations corresponding to different stages of the refinement are listed in Table 1; the observed and calculated structure factors are compared in Table 2. These are

Table 2. *Observed and calculated structure factors*

Asterisks indicate reflexions which were too weak to be measured. The $|F_o|$ values for these are given as $\frac{1}{2}F_{\min}$ and these values were used in the final least-squares refinement

h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $
0	0	12	3.3	2.9	2	0	-3	5.8	5.8
0	0	9	3.3	2.3	2	0	-4	3.9	3.3
0	0	6	24.0	22.2	2	0	-5	3.0	3.0
		3	13.1	12.1	2	0	-6	10.1	10.6
1	0	13	2.0	2.5	2	0	-7	8.8	8.6
1	0	12	2.4	2.7	2	0	-8	7.0	6.8
1	0	11	2.7	2.9	2	0	-9	3.9	3.0
1	0	10	1.1*	2.2	2	0	-10	2.0	1.7
1	0	8	2.5	2.0	2	0	-11	1.0*	0.9
1	0	7	9.6	9.6	2	0	-12	3.4	3.5
1	0	6	4.4	4.3	2	0	-13	2.0	2.7
1	0	5	6.5	6.3	3	0	11	2.2	2.4
1	0	5	0.8*	0.2	3	0	10	2.2	2.5
1	0	4	0.7*	0.6	3	0	9	2.9	2.5
1	0	4	2.7	2.2	3	0	8	5.2	5.6
1	0	3	45.5*	43.3	3	0	7	1.0*	0.2
1	0	1	1.7*	1.4	3	0	6	3.1	3.0
1	0	0	1.3	0.0*	3	0	5	1.0*	2.2
1	0	-2	5.9	5.8	3	0	4	2.5	2.5
1	0	-2	12.5	13.3	3	0	3	8.6	9.8
1	0	-2	31.0	28.6	3	0	2	3.4	3.0
1	0	-5	4.0	4.6	3	0	1	8.9	8.7
1	0	-6	3.8	3.1	3	0	0	0.9*	0.5
1	0	-6	2.6*	1.5	3	0	-1	1.5	2.1
1	0	-8	6.1	6.1	3	0	-2	1.0*	0.9
1	0	-10	4.5	4.5	3	0	-3	4.3	4.4
1	0	-10	5.1	5.6	3	0	-4	7.5	9.9
1	0	-11	2.2	2.2	3	0	-5	8.5	7.4
1	0	-12	1.4	1.4	3	0	-6	4.8	4.6
1	0	-13	2.0	2.4	3	0	-7	3.4	3.7
					3	0	-8	1.0*	0.2
2	0	13	1.6	2.7	3	0	-9	0.9*	0.6
2	0	12	2.0	2.1	3	0	-10	2.4	2.7
2	0	11	2.1*	1.0	3	0	-11	2.4	2.7
2	0	10	2.5	4.5	4	0	9	2.1	2.4
2	0	8	5.2	5.0	4	0	8	3.7	3.4
2	0	7	5.1	5.7	4	0	7	0.9*	1.3
2	0	6	1.0*	0.3	4	0	6	2.4	2.8
2	0	5	2.6	2.4	4	0	5	6.0	6.5
2	0	4	9.1	9.9	4	0	4	1.0*	0.5
2	0	3	0.8*	1.0	4	0	3	3.4	3.7
2	0	2	2.7	3.7	4	0	2	3.2	3.4
2	0	1	8.2	7.7	4	0	1	2.2	1.8
2	0	0	12.2	12.1	4	0	0	3.1	2.9
2	0	-1	14.0	14.8	4	0	-1	3.1	4.1
2	0	-2	10.9	12.1	4	0	-2	1.0*	1.2

Table 1. *Atomic parameters at different stages of the refinements*

After least-squares refinements (block-diagonal approximation)			
(a) Without hydrogen	(b) With hydrogen		
Oxygen		Oxygen	
$x = 0.7274$	$x = 0.7267$		
$y = 0$	$y = 0$		
$z = 5/6$	$z = 5/6$		
$B = 2.28 \text{ \AA}^2$	$B = 2.44 \text{ \AA}^2$		
Nitrogen:		Nitrogen:	
$x = 0.5924$	$x = 0.5943$		
$y = 0.8365$	$y = 0.8367$		
$z = 0.3137$	$z = 0.3131$		
$B = 2.10 \text{ \AA}^2$	$B = 2.14 \text{ \AA}^2$		
(c) After Fourier refinements with hydrogen		(d) After least-squares refinements (full-matrix) with hydrogen	
Oxygen		Oxygen	
$x = 0.7252$	$x = 0.7268 \pm 0.0010$		
$y = 0$	$y = 0$		
$z = 5/6$	$z = 5/6$		
$B = 2.44 \text{ \AA}^2$	$B = 2.55 \text{ \AA}^2$		
Nitrogen		Nitrogen	
$x = 0.5931$	$x = 0.5954 \pm 0.0010$		
$y = 0.8375$	$y = 0.8373 \pm 0.0010$		
$z = 0.3136$	$z = 0.3124 \pm 0.0003$		
$B = 2.14 \text{ \AA}^2$	$B = 2.40 \text{ \AA}^2$		

based on the parameters listed in Table 1(*d*), obtained at the final least-squares refinement with the full matrix program.

Discussion of the structure

The structure is shown in Fig. 1. The bond distances and angles (based on the final parameters, (*d*) in Table 1) with standard deviations are given in Table 3 and Fig. 2. The correlations between symmetry-related atoms and the uncertainty of the unit-cell dimensions were considered in the calculations of these standard deviations.

Each water molecule is hydrogen-bonded to six hydrazine molecules and each hydrazine molecule is hydrogen-bonded to six water molecules, thus forming a three-dimensional network. The oxygen–nitrogen distances are of two kinds; two short bonds equal to 2.79 Å and four longer bonds equal to 3.11, 3.11, 3.15 and 3.15 Å, respectively. The N···N distance in hydrazine, 1.45 ± 0.01 Å, is in agreement with the values reported earlier: 1.46 ± 0.02 Å in solid hydrazine (Collin & Lipscomb, 1951) and 1.45 ± 0.08 Å in the reported sodium chloride modification of solid hydrazine hydrate at -60 °C (Zocchi *et al.*, 1962).

The chemical arguments concerning the locations of the hydrogen atoms are based on the generally accepted ideas that (*a*) the angles H–O–H and H–N–H are about 109°, (*b*) the hydrogen atom is close to the axis of the bond, (*c*) only one hydrogen atom is

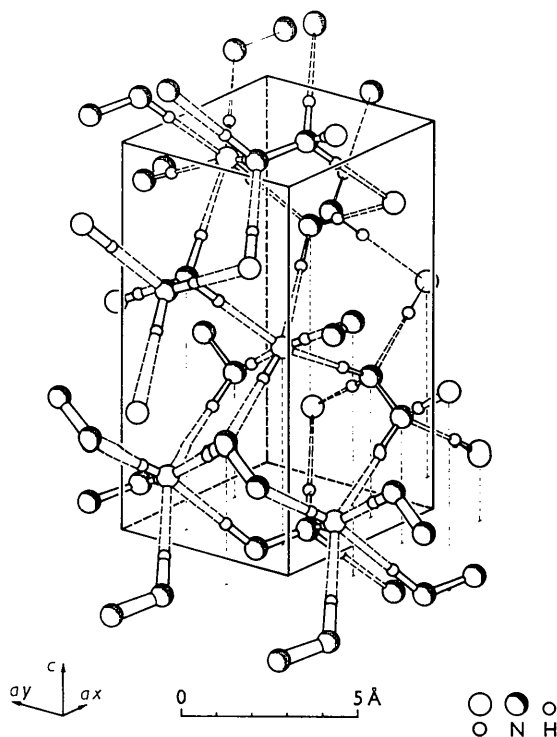


Fig. 1. The crystal structure of hydrazine monohydrate.

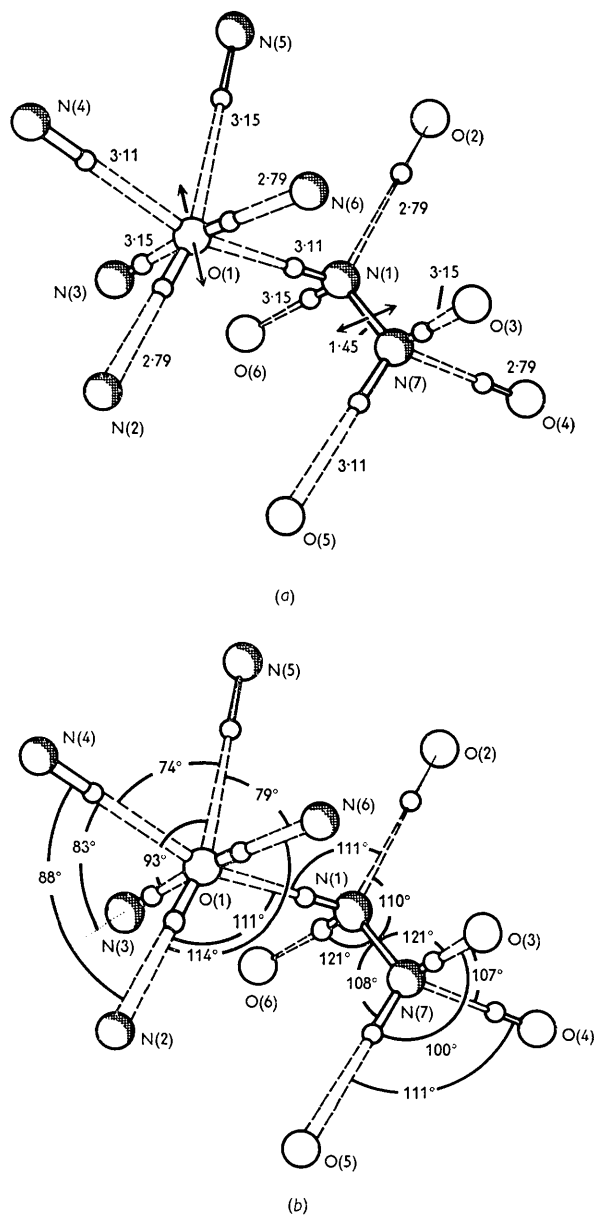


Fig. 2. Bond distances and angles to the neighbours of a water molecule and a hydrazine molecule. The orientation is the same as in Fig. 1. The twofold axes passing through O(1) and through the centre of the N–N bond, respectively, are indicated.

present in each bond and (*d*) an electron pair is available reasonably close to each hydrogen bond. When these concepts are applied, the only possible assignment of hydrogen atoms to the different atoms appears to be that shown in Fig. 1. Thus, the two hydrogen atoms of the water molecule form short hydrogen bonds (2.79 Å) each of which involves the electron pair of one nitrogen atom in different hydrazine molecules. This O–H···N distance is consistent with a mean value of 2.80 Å, obtained for this type

of bond from the bond lengths in some different compounds (Pimentel & McClellan, 1960). On the other hand such values are not directly comparable, as was pointed out by Olovsson (1960). Each electron pair of the water molecule is used for two weak hydrogen bonds (3.11 and 3.15 Å) to nitrogen atoms in different hydrazine molecules. Roughly speaking, oxygen contributes one-half of an electron pair to each N-H...O bond. Similar cases have been found earlier, for example in the crystal structure of ammonia monohydrate (Olovsson & Templeton, 1959), where the oxygen atom contributed one-third of an electron pair to each of three bonds (3.21, 3.26 and 3.29 Å). For a number of different amine compounds, the average N-H...O distance is 3.04 Å (Pimentel & McClellan, 1960) but this value is not directly comparable with the present case.

Table 3. Bond distances and angles with standard deviations (cf. Fig. 2)

Around the oxygen atom		
Bond	Distance	
O(1)-N(2) = O(1)-N(6)	2.790 ± 0.006 Å	
O(1)-N(1) = O(1)-N(4)	3.113 ± 0.006	
O(1)-N(3) = O(1)-N(5)	3.149 ± 0.006	
Around the nitrogen atoms		
Bond	Distance	
N(1)-N(7)	1.447 ± 0.009 Å	
N(1)-O(2) = N(7)-O(4)	2.790 ± 0.006	
N(1)-O(1) = N(7)-O(5)	3.113 ± 0.006	
N(1)-O(6) = N(7)-O(3)	3.149 ± 0.006	
Bonds	Angle	
N(1)-O(1)-N(2) = N(4)-O(1)-N(6)	111.2 ± 0.2°	
N(1)-O(1)-N(3) = N(4)-O(1)-N(5)	74.2 ± 0.2	
N(1)-O(1)-N(4)	145.9 ± 0.3	
N(1)-O(1)-N(5) = N(3)-O(1)-N(4)	82.6 ± 0.1	
N(1)-O(1)-N(6) = N(2)-O(1)-N(4)	87.6 ± 0.1	
N(2)-O(1)-N(3) = N(5)-O(1)-N(6)	78.7 ± 0.1	
N(2)-O(1)-N(5) = N(3)-O(1)-N(6)	161.0 ± 0.2	
N(2)-O(1)-N(6)	113.8 ± 0.3	
N(3)-O(1)-N(5)	93.4 ± 0.2	
O(3)-N(7)-O(4) = O(2)-N(1)-O(6)	107.2 ± 0.2	
O(3)-N(7)-O(5) = O(6)-N(1)-O(1)	99.7 ± 0.1	
O(3)-N(7)-N(1) = O(6)-N(1)-N(7)	120.8 ± 0.4	
O(4)-N(7)-O(5) = O(2)-N(1)-O(1)	111.2 ± 0.2	
O(4)-N(7)-N(1) = O(2)-N(1)-N(7)	109.8 ± 0.2	
O(5)-N(7)-N(1) = O(1)-N(1)-N(7)	107.7 ± 0.2	

The hydrogen atoms were assigned to positions on straight lines joining the hydrogen-bonded atoms, 0.97 Å from oxygen (coordinates: 0.141, 0.906, 0.116) and 1.03 Å from nitrogen (coordinates: 0.398, 0.802, 0.264 and 0.490, 0.653, 0.374), respectively. These hydrogen atoms are in the general sixfold positions of the space group $P3_121$. In a three-dimensional F_o-F_{ch} synthesis well resolved 'hydrogen peaks' appeared close to the positions where the hydrogen atoms had been placed. No other peaks as large as these appeared in the whole three-dimensional synthesis. F_o was based on all atoms; F_{ch} was the con-

tribution to F_c from the heavy atoms, in this case oxygen and nitrogen.

The dihedral angles (based on the final parameters, d) in Table 1) between planes defined by the nitrogen atoms of the hydrazine group and the nearest oxygen neighbours are shown in Fig. 3. The angle φ of internal rotation from the *cis* position of the NH₂ groups in a hydrazine molecule is 58.5°, assuming that the hydrogen atoms lie on the lines connecting nitrogen to oxygen (Fig. 4). Penney & Sutherland (1934) in their valence-bond treatment of hydrazine concluded that a value of about 100° for this angle φ should give the most stable configuration. In a far-infrared spectrum study of hydrazine (Yamaguchi, Ichishima, Shimanouchi & Mizushima, 1959) this angle was found to be 90–95°. Collin & Lipscomb (1950, 1951) assume that the hydrazine molecule in solid hydrazine has the eclipsed configuration, *i.e.* φ is equal to 0° or 120°.

It is of interest to notice that there is one twofold axis passing through O(1) and one through the centre of the N-N bond (Fig. 2).

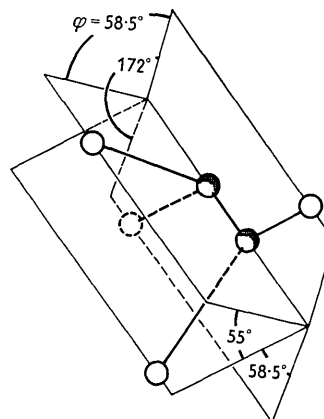


Fig. 3. Dihedral angles between planes defined by the nitrogen atoms of the hydrazine group and the nearest oxygen neighbours. φ is the angle of internal rotation of the NH₂ groups from the *cis* position.

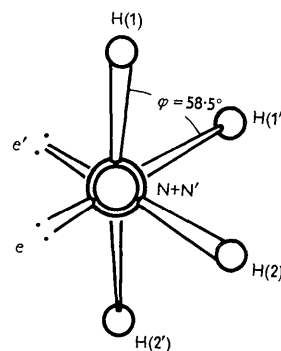


Fig. 4. View of the hydrazine molecule along the direction of the N-N bond (hydrogen assumed to be on the line connecting nitrogen to oxygen).

Comparison between the structures at -60 and -165 °C

In an X-ray study of hydrazine hydrate at -60 °C Zocchi *et al.* (1962) found that the structure was of the sodium chloride type ($a_0 = 6.76 \pm 0.02$ Å) with disordered or rotating H₂O and N₂H₄ molecules replacing Na⁺ and Cl⁻ respectively. A transformation to a phase with lower symmetry was observed by these authors at about -80 °C. The present structure is based on data obtained at -165 °C and should therefore correspond to the low-temperature modification. However, as pointed out earlier a cubic modification has not been observed in the present investigation.

In the present structure the arrangement around the hydrazine and water molecules is roughly octahedral if the molecules are regarded as spherical. The distances from a water molecule to the centres of the surrounding hydrazine molecules are: 3.11, 3.11, 3.40, 3.40, 3.57 and 3.57 Å, respectively. If the water molecules are given the same *x* and *y* coordinates as the spherical hydrazine molecules, keeping the *z* coordinates fixed (total shift about 0.2 Å), a much more regular octahedral arrangement is obtained around the (spherical) water and hydrazine molecules. The distances from H₂O to the centres of N₂H₄ are now: 3.28, 3.28, 3.39, 3.39, 3.39 and 3.39 Å, respectively. The *c* axis would then correspond to the body diagonal *d* in a cube with a unit length of $d/\sqrt{3} = 6.32$ Å. This value indicates a contraction in the direction of the *c* axis as compared with the value for the unit length ($a_0 = 6.76 \pm 0.02$ Å) of the high temperature phase at -60 °C described by Zocchi *et al.* (1962). A contraction in this direction seems quite reasonable from a consideration of the structure. The unit length of the distorted cube based on other distances (in planes parallel to the *xy* plane) is about 6.9 Å, and is thus in agreement with the value reported by Zocchi *et al.* (1962). From the discussion above, it follows that the displacements of the atoms at the reported phase transformation are of the order of 0.2 Å.

We wish to express our gratitude to the head of the Institute, Prof. G. Hägg for his great personal interest

in this work. Many thanks are due to Drs W. R. Busing, H. A. Levy, S. Åsbrink, C.-I. Brändén and Mr B. Lundberg for the use of their computer codes and to Dr L. Gustafsson for the analysis of hydrazine hydrate.

This work has been supported by grants from the Swedish National Science Research Council which are here gratefully acknowledged. The authors are also indebted to the Computer Division of the National Swedish Office for Administrative Rationalization and Economy for putting computer time at their disposal.

References

- AUDRIETH, L. F. & OGG, B. A. (1951). *The Chemistry of Hydrazine*. New York: John Wiley, London: Chapman and Hall.
- BERGHUIS, J., HAANAPPEL, I. J. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BUSING, W. R. & LEVY, H. A. (1959). *CF Memo 59-4-37*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, April 1959.
- COLLIN, R. L. & LIPSCOMB, W. N. (1950). *J. Chem. Phys.* **18**, 566.
- COLLIN, R. L. & LIPSCOMB, W. N. (1951). *Acta Cryst.* **4**, 10.
- DAWSON, B. (1961). *Acta Cryst.* **14**, 999.
- HILL, T. C. H. & SUMMER, J. F. (1951). *J. Chem. Soc.* p. 838.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
- International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.
- MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
- MOHR, P. H. & AUDRIETH, L. F. (1949). *J. Phys. Chem.* **53**, 901.
- OLOVSSON, I. (1960). *Ark. Kemi*, **16**, 437.
- OLOVSSON, I. & TEMPLETON, D. H. (1959). *Acta Cryst.* **12**, 827.
- PENNEY, W. G. & SUTHERLAND, G. B. B. M. (1934). *J. Chem. Phys.* **2**, 492.
- PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*, p. 289. San Francisco and London: Freeman and Co.
- SEMISHIN, V. J. (1938). *J. Gen. Chem. (USSR)*, **8**, 654.
- YAMAGUCHI, A., ICHISHIMA, I., SHIMANOCHI, T. & MIZUSHIMA, S.-I. (1959). *J. Chem. Phys.* **31**, 843.
- ZOCCHI, M., BUSING, W. R., ELLISON, R. D. & LEVY, H. A. (1962). *Acta Cryst.* **15**, 803.