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Hydrogen Bond Studies

22.* The Crystal Structure of Hydrazine Tetramethanol, $N_2H_4 \cdot 4CH_3OH$

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The crystal structure of $N_2H_4 \cdot 4CH_3OH$ has been determined from three-dimensional X-ray data collected at −188°C. Two formula units crystallize in a tetragonal unit cell with the dimensions: $a = 10.418$ and $c = 4.779$ Å. The space group is $P4_2$. The CH_3OH molecules are hydrogen bonded to each other and to the N_2H_4 molecules, thus forming a three-dimensional network. The hydrogen bond lengths are: N—H···O = 2.959, 3.025 Å, O—H···N = 2.682 Å, and O—H···O = 2.737 Å.

The present investigation is part of a systematic study of the crystal structures formed by some simple hydrogen-bonded compounds in the systems N_2H_4—H_2O, N_2H_4—C_2H_5OH, and N_2H_4—CH_3OH. The structures of $N_2H_4 \cdot H_2O$ and $N_2H_4 \cdot 2C_2H_5OH$ have been reported earlier.[1,2]

The melting point diagram [3] of the system N_2H_4—CH_3OH indicates three intermediate compounds, $N_2H_4 \cdot nCH_3OH$ with $n = 1$, 2, and 4. The compound $N_2H_4 \cdot CH_3OH$ has an incongruent melting point at −47.3°C, while the other two, $N_2H_4 \cdot 2CH_3OH$ and $N_2H_4 \cdot 4CH_3OH$, melt congruently at −57.8° and −69.5°C, respectively. Attempts have been made by one of the authors (R.L.) to collect single-crystal X-ray data for all these compounds. However, single-crystals of $N_2H_4 \cdot CH_3OH$ could not be prepared. Three-dimensional data for the other two have been collected. The structure of $N_2H_4 \cdot 4CH_3OH$ will be reported in the following, and that of $N_2H_4 \cdot 2CH_3OH$ in a later paper.

* The preceding paper in this series: *Hydrogen Bond Studies 21. The Crystal Structure of Sulfuric Acid Monohydrate* by I. Taesler and I. Olovsson appeared in *Acta Cryst. (In press.)*.

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EXPERIMENTAL

A sample containing 3.98 moles methanol per mole hydrazine was prepared by mixing suitable amounts of anhydrous N_2H_4 and CH_3OH, respectively. The methanol used was commercial methanol (KEBO, *puriss*, max. 0.03 % H_2O), and the anhydrous hydrazine was prepared and analyzed as described earlier.[2] Capillaries (diameter about 0.3 mm, wall thickness 0.01 – 0.02 mm) were filled with the solution and sealed in a flame. All operations with the pure materials were carried out in a dry box in an atmosphere of dry nitrogen.

Single crystals were grown in a Weissenberg camera with low-temperature equipment.[4] The observed melting point was about −70°C, which agrees with the value reported earlier. Equi-inclination photographs were taken at −188°C, with Ni-filtered CuK radiation using the multiple-film method (five films). The layers $0 \leq l \leq 4$ were recorded with the crystal rotating about the [001] axis. The number of independent reflexions recorded was 597 but 40 of these were too weak to be measured. About 82 % of the reflexions within the copper reflexion sphere were thus recorded.

The relative intensities were obtained by visual comparison with a calibrated scale. The intensity range was 1 to 5000. The intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. The linear absorption coefficient for Cu$K\alpha$ radiation is 7.5 cm^{-1}.

UNIT CELL AND SPACE GROUP

The diffraction symmetry $4/m$ indicated a tetragonal space group. No systematic absence of reflexions was observed. Since the $00l$ reflexions were not recorded, no information about the type of fourfold axis could be obtained. Several of the space groups having the diffraction symmetry $4/m$ were thus possible. However, those with eightfold general positions could be ruled out, as the nitrogen atoms must be located in special positions in these space groups and these positions were not compatible with the dimension of the hydrazine molecule. In the three-dimensional Patterson function $P(u,v,w)$ there was a concentration of peaks in the section $P(u,v,\frac{1}{2})$, indicating a translation by 0.5 along the fourfold axis. Of the remaining possible space groups only two can have such translations, namely $P4_2$ and $P\bar{4}$; in the latter case with the z coordinates of the atoms near or equal to 0.25. The space group $P4_2$ was chosen as the most probable, and the subsequent refinement of the structure confirmed this choice. Attempts to solve the structure in $P\bar{4}$ were without success.

The atoms are located in the general fourfold positions in $P4_2$:[5] (x,y,z); $(\bar{x},\bar{y},z)$; $(\bar{y},x,\frac{1}{2}+z)$; $(y,\bar{x},\frac{1}{2}+z)$.

There are five independent non-hydrogen atoms, namely one nitrogen, two oxygens and two carbons. In addition there are ten independent hydrogen atoms.

The a dimension of the unit cell was obtained from zero layer oscillation photographs and the c dimension from a rotation photograph. Each of these was calibrated with a quartz single crystal as was described in an earlier paper; the numerical values used for the CuK wavelengths and for the dimensions of α quartz were the same.[2] The a dimension, based on 44 observations, was fitted to the measured θ values by the method of least squares. The unit cell dimensions at −187°C are as follows:

$$a = 10.418 \pm 0.001,\ c = 4.779 \pm 0.007\ \text{Å}$$

With two units of $N_2H_4 \cdot 4CH_3OH$ in the unit cell the calculated density is 1.03 g.cm^{-3}. No experimental determination of the density was made.

DETERMINATION OF THE ATOMIC COORDINATES

The position of the nitrogen atom could be determined from the Harker vectors in a three-dimensional Patterson synthesis. The fact that the centre of the N—N bond lies on a twofold axis simplified the location of the nitrogen atom. A high order superposition function was calculated based on the known nitrogen position. The coordinates of the two oxygen and carbon atoms, respectively, were then deduced from the superposition and Patterson functions. The superposition function was computed with local modifications of programs described in Ref. 6.

The atomic coordinates, together with the inter-layer scale factors and isotropic temperature factors, were refined in a series of least-squares calculations. The total number of parameters varied was 24. After some cycles the agreement factor $R = \sum||F_o|-|F_c||/\sum|F_o|$ was 0.118 and the shifts were no longer significant. A difference Fourier synthesis was calculated, based on the reflexions with sin θ/λ less than 0.5 Å^{-1}. Possible positions for the ten independent hydrogen atoms were deduced from the Fourier maps.

Some cycles of least-squares calculations were made with the ten hydrogen atoms included with fixed parameters. The isotropic temperature factor coefficient B used for the hydrogens was 5 Å^2. (The B values for the methyl carbons were 2.9 and 3.8 Å^2, respectively.) After three cycles the R value dropped to 0.097.

When the observed and calculated structure factors were compared at this stage, it was found that some strong zero-layer reflexions showed a bad agreement. Three reflexions were excluded from the data and two additional cycles of refinement gave an R value of 0.094. The shifts in the last cycle were about one tenth of the standard deviations in question.

Anisotropic temperature factors were now introduced for nitrogen, oxygen, and carbon. The inter-layer scale factors were fixed to the values obtained from the final isotropic refinement, and an overall scale factor was refined. The hydrogen atom parameters were fixed. The total number of parameters varied was 45. After two cycles the R value decreased to 0.078. A difference Fourier, based on the heavy atoms and the reflexions with sin θ/λ less than 0.5 Å^{-1}, was calculated in order to get improved hydrogen positions. However, some peaks assumed to correspond to hydrogen atoms were diffuse. One additional cycle with the redetermined hydrogen positions included gave a final R value of 0.078. In the last cycle, the shifts of all parameters were less than one tenth of their estimated standard deviations.

An attempt was made to refine the hydrogen atom coordinates by least-squares methods. All other parameters were fixed except the overall scale factor. No improvement of the hydrogen atom positions could be obtained because the shifts oscillated.

The least-squares refinement was based on F, minimizing the function $\sum w(|F_o|-|F_c|)^2$. The weights w were calculated as follows:

$w = 1/(a + |F_o| + c|F_o|^2)$. The final values used for a and c were 2.1 and 0.062. An analysis made in the least-squares program showed that these were suitable. Reflexions too weak to be measured were given zero weight in all calculations. In addition, three strong zero-layer reflexions were excluded from the final refinement, which was thus based on 554 observations. The final R value calculated on all 597 observed reflexions was 0.089.

The final atomic parameters are listed in Tables 1 and 2, and the structure factors in Table 5. The root-mean-square components of thermal displacement along the principal axes of the ellipsoids are given in Table 3. Bond distances and angles are listed in Table 4. The standard deviations in these were cal-

Table 1. Atomic coordinates with estimated standard deviations.

Atom	x	y	z
N	0.0312 ± 0.0003	0.4368 ± 0.0003	0.0
O(1)	0.1772 ± 0.0003	0.4055 ± 0.0003	0.5428 ± 0.0012
C(1)	0.2764 ± 0.0004	0.4986 ± 0.0004	0.5308 ± 0.0022
O(2)	0.2266 ± 0.0003	0.1550 ± 0.0003	0.4078 ± 0.0013
C(2)	0.1667 ± 0.0004	0.1242 ± 0.0004	0.1438 ± 0.0016
Hydrogen atoms:			
N: H(1)	0.08	0.43	0.18
H(2)	−0.03	0.38	−0.01
O(1):H(3)	0.11	0.42	0.64
C(1):H(4)	0.40	0.25	0.01
H(5)	0.52	0.32	0.20
H(6)	0.35	0.46	0.44
O(2):H(7)	0.22	0.24	0.42
C(2):H(8)	0.08	0.14	0.14
H(9)	0.20	0.19	0.08
H(10)	0.19	0.04	0.10

Table 2. Anisotropic temperature factor parameters with estimated standard deviations, each multiplied by 10^4. The expression used is: $\exp[-(h^2\beta_{11} + hk\beta_{12} + \ldots)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	63 ± 3	47 ± 3	304 ± 21	5 ± 4	−14 ± 12	−16 ± 11
O(1)	70 ± 3	59 ± 2	296 ± 18	7 ± 4	7 ± 11	−49 ± 11
C(1)	72 ± 4	78 ± 4	681 ± 37	−11 ± 6	62 ± 23	−120 ± 23
O(2)	72 ± 3	58 ± 2	273 ± 16	22 ± 4	−31 ± 11	−29 ± 11
C(2)	81 ± 4	70 ± 4	307 ± 26	20 ± 6	−58 ± 17	−58 ± 16

Table 3. Root-mean-square components, R_i, of thermal vibration along principal axes of the ellipsoids of vibration.

Atom	R_1	R_2	R_3
N	0.16 Å	0.18 Å	0.19 Å
O(1)	0.16	0.20	0.20
C(1)	0.19	0.20	0.29
O(2)	0.17	0.17	0.21
C(2)	0.17	0.19	0.23

culated from the standard deviations of the atomic coordinates. The errors in the unit cell dimensions were also considered. The bond distances listed in Table 4 are not corrected for thermal motion.

The atomic scattering factors used in the calculations were those for neutral O, N, C, and H as given in the *International Tables*.[7]

Computer programs. All calculations were made on the CD 3600 computer in Uppsala, using the programs briefly presented in an earlier paper.[2]

DISCUSSION OF THE STRUCTURE

The structure, illustrated in Figs. 1 and 2, contains a three-dimensional network of hydrogen bonds formed between the CH_3OH molecules and between these and the N_2H_4 molecules. There are two independent methanol molecules, designated below as M(1) and M(2). The centres of the hydrazine

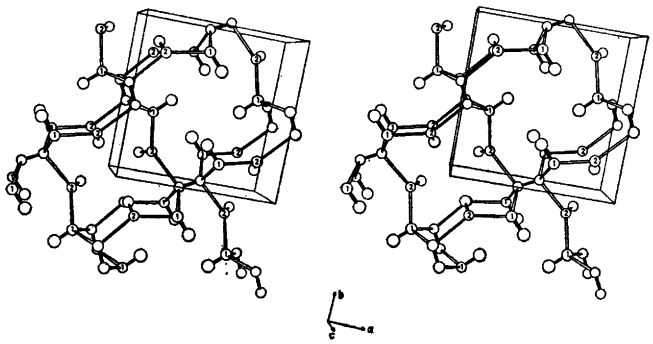

Fig. 1. A stereoscopic pair of drawings showing the structure nearly along the *c* axis. The oxygen atoms of the methanol molecules M(1) and M(2) are numbered 1 and 2, respectively. All other atoms are unlabelled. Covalent bonds are filled, hydrogen bonds are open. The Figs. 1, 2, and 5 were drawn with the program OR TEP, written by C. K. Johnson, Oak Ridge.

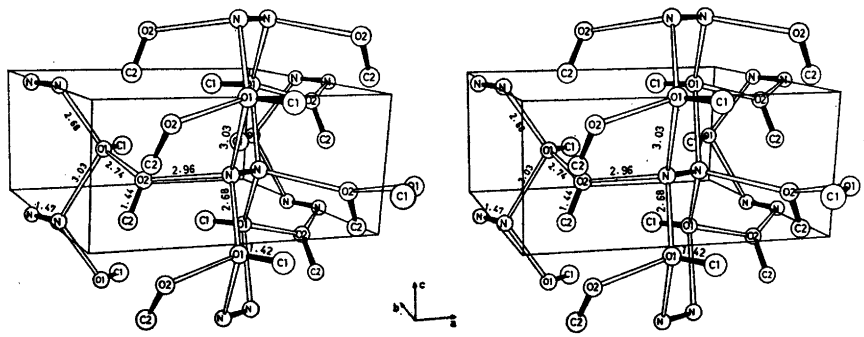

Fig. 2. A stereoscopic pair of drawings showing the details of the hydrogen bonding system.

Table 4. Distances and angles with estimated standard deviations (*cf.* Fig. 4).

Distances

1) Within the molecules		2) Hydrogen bonds	
N—N	1.468 ± 0.006 Å	N—H(1)···O(1)	3.025 ± 0.006 Å
N—H	0.87, 1.00	N—H(2)···O(2)	2.959 ± 0.004
O(1)—C(1)	1.418 ± 0.005	O(1)—H(3)···N	2.682 ± 0.006
O(1)—H	0.85		
C(1)—H	0.95, 0.97, 1.10		
O(2)—C(2)	1.443 ± 0.009	O(2)—H(7)···O(1)	2.737 ± 0.004
O(2)—H	0.89		
C(2)—H	0.83, 0.92, 0.93		

Angles

1) Around nitrogen		2) Around oxygen O(1)	
N—N—O(1)	111.1 ± 0.2°	C(1)—O(1)—N	111.3 ± 0.5°
—O(1)	108.6 ± 0.1	—N	104.9 ± 0.5
—O(2)	111.9 ± 0.3	—O(2)	120.4 ± 0.3
O(1)—N—O(1)	113.6 ± 0.2	N—O(1)—N	113.6 ± 0.2
—O(2)	99.2 ± 0.1	—O(2)	114.5 ± 0.2
O(1)—N—O(2)	112.2 ± 0.1	N—O(1)—O(2)	89.7 ± 0.2
N—N—H	107, 107	C(1)—O(1)—H	120
H—N—H	112		

3) Around oxygen O(2)		4) Around the carbon atoms	
C(2)—O(2)—N	107.7 ± 0.3°	O(1)—C(1)—H	100, 108, 119°
—O(1)	109.7 ± 0.3	H—C(1)—H	85, 113, 124
N—O(2)—O(1)	136.8 ± 0.2		
		O(2)—C(2)—H	88, 107, 114
C(2)—O(2)—H	104	H—C(2)—H	105, 115, 126

5) Around hydrogen atoms involved in hydrogen bonds

N—H(1)···O(1)	177°	O(1)—H(3)···N	149°
N—H(2)···O(2)	169	O(2)—H(7)···O(1)	162

molecules lie on twofold axes. The N_2H_4 molecules are thus parallel to the (001) plane. As shown in Figs. 1 and 2, the M(1) molecules are approximately parallel to the (001) plane, and are grouped close to the fourfold screw axis passing through $(\frac{1}{2},\frac{1}{2},0)$. The M(2) molecules form an angle of about 63° with the (001) plane, and surround the fourfold screw axis through (0,0,0).

Each hydrazine molecule is hydrogen bonded to six methanol molecules; three bonds are generated from each end. Methanol M(2) is involved in one of these bonds and M(1) in the remaining two. These two M(1) molecules are related to each other by a translation of one unit in the *c* direction. The M(1) and M(2) molecules are also bonded to each other by a hydrogen bond. Each M(1) is thus involved in three hydrogen bonds, and M(2) only in two. Details of the structure and the hydrogen bonding system are discussed below.

1. The hydrazine molecule. The N—N distance in the N_2H_4 molecule, 1.468 ± 0.006 Å, is in agreement with values reported earlier, *e.g.* 1.460 ± 0.004 Å in $N_2H_4 \cdot 2C_2H_5OH$.[2] (Consult this paper for further references).

Table 5. Observed and calculated structure factors. Reflexions too weak to be measured are indicated with one asterisk. The $|F_o|$ values for these are given as $F_{min}/\sqrt{2}$ for the reflexions in question. Two asterisks indicate the strong reflexions excluded from the final refinements.

h	k	l	$\|F_o\|$	$\|F_c\|$
2	0	0	5.9	6.4
3	0	0	34.4	43.0**
4	0	0	1.7	1.8
5	0	0	18.8	20.0
6	0	0	4.3	4.4
7	0	0	11.5	11.4
8	0	0	1.6	1.1
9	0	0	6.4	6.3
10	0	0	1.7	1.4
11	0	0	3.9	3.3
12	0	0	3.2	2.5
13	0	0	1.9	1.5
1	1	0	17.5	21.1
2	1	0	5.8	7.3
3	1	0	8.7	9.0
4	1	0	18.0	20.9
5	1	0	1.5	0.7
6	1	0	22.0	24.0
7	1	0	3.9	3.4
8	1	0	7.2	6.7
9	1	0	8.0	7.8
10	1	0	1.1	0.0 *
11	1	0	3.7	3.7
12	1	0	1.5	1.0
13	1	0	2.1	1.7
1	2	0	11.8	13.0
2	2	0	0.5	1.1 *
3	2	0	46.7	54.9**
4	2	0	4.0	5.1
5	2	0	5.4	4.8
6	2	0	8.6	8.4
7	2	0	7.3	7.1
8	2	0	3.0	1.8
9	2	0	1.1	1.6 *
10	2	0	1.1	1.0 *
11	2	0	6.9	7.2 *
12	2	0	1.2	0.4 *
13	2	0	1.7	1.5
0	0	1	36.6	48.1**
1	0	1	5.2	6.4
2	0	1	0.7	0.4 *
3	0	1	11.5	13.4
4	0	1	5.2	4.4
5	0	1	2.3	2.3
6	0	1	13.1	13.9
7	0	1	13.4	14.5
8	0	1	1.1	0.1 *
9	0	1	2.1	1.5
10	0	1	4.0	4.2
11	0	1	2.1	1.5
12	0	1	3.3	3.7
13	0	1	12.2	11.5
1	1	1	13.5	13.3
2	1	1	2.7	2.5
3	1	1	4.1	4.7 *
4	1	1	0.9	2.1 *
5	1	1	6.6	6.5
6	1	1	14.6	14.7
7	1	1	2.6	2.6
8	1	1	1.7	1.3
9	1	1	1.0	0.8 *
10	1	1	1.1	0.3 *
11	1	1	4.6	3.8
12	1	1	16.3	16.0
13	1	1	6.0	5.7
0	2	1	19.2	18.8
1	2	1	21.4	23.3
2	2	1	13.4	13.6
3	2	1	3.2	3.2
4	2	1	6.2	6.7
5	2	1	7.0	7.0
6	2	1	1.1	0.9 *
7	2	1	3.0	2.5
8	2	1	8.3	6.8
9	2	1	0.7	0.3 *
10	2	1	0.8	1.6 *
11	2	1	2.8	2.7
12	2	1	13.4	12.7
13	2	1	6.5	6.4
0	3	1	2.9	2.0
1	3	1	13.4	14.5
2	3	1	4.8	4.7
3	3	1	7.7	7.9
4	3	1	5.7	6.0
5	3	1	4.4	4.5
6	3	1	9.4	9.0
7	3	1	2.1	2.2
8	3	1	5.9	6.3
9	3	1	4.8	4.6
10	3	1	3.2	2.6
11	3	1	1.5	1.1
12	3	1	5.4	5.3
13	3	1	3.3	3.2
0	4	1	1.8	1.0
1	4	1	3.4	2.9
2	4	1	8.5	7.8
3	4	1	3.1	3.1
4	4	1	5.2	4.9 *
5	4	1	1.1	1.5 *
6	4	1	3.1	3.0
7	4	1	1.1	1.0
8	4	1	3.8	3.2
9	4	1	1.4	1.3
10	4	1	6.4	6.7
11	4	1	0.0	0.3
12	4	1	5.3	5.1
13	4	1	2.1	2.8
0	5	1	3.3	3.3
1	5	1	4.9	5.1
2	5	1	1.0	1.1 *
3	5	1	0.8	0.7 *
4	5	1	2.1	2.7
5	5	1	3.8	3.6
6	5	1	3.9	3.6
7	5	1	2.6	2.5
8	5	1	1.0	0.4 *
9	5	1	1.7	1.0 *
10	5	1	1.0	0.4 *
11	5	1	3.5	3.0
12	5	1	0.9	1.2 *
13	5	1	1.2	1.2
0	6	1	1.0	0.4 *
1	6	1	0.9	1.0 *
2	6	1	1.7	1.7
3	6	1	3.5	3.0
4	6	1	4.6	4.7
5	6	1	1.9	1.5
6	6	1	1.3	1.6
7	6	1	2.7	2.4
8	6	1	3.8	3.7
9	6	1	1.8	2.1
10	6	1	10.0	11.1
11	6	1	37.0	36.7
12	6	1	6.9	6.3
13	6	1	11.3	11.6
0	7	1	7.2	7.3
1	7	1	10.5	10.7
2	7	1	6.6	6.3
3	7	1	5.1	4.8
4	7	1	8.5	9.0
5	7	1	2.8	2.4
6	7	1	5.4	5.6
7	7	1	3.8	3.1
8	7	1	1.1	1.1
9	7	1	30.0	29.0
10	7	1	42.5	43.9
11	7	1	11.3	10.8
12	7	1	26.3	28.1
13	7	1	11.1	11.0
0	8	1	10.5	10.0
1	8	1	0.9	1.0 *
2	8	1	3.5	3.9
3	8	1	11.6	11.9
4	8	1	2.6	2.4
5	8	1	2.9	2.5
6	8	1	2.7	1.9
7	8	1	2.6	2.5
8	8	1	29.3	29.1
9	8	1	24.6	25.1
10	8	1	15.4	15.5
11	8	1	13.3	13.0
12	8	1	12.4	13.0
13	8	1	9.6	9.4
0	9	1	15.8	16.0
1	9	1	3.2	3.1
2	9	1	7.6	7.8
3	9	1	5.3	5.2
4	9	1	7.8	7.1
5	9	1	1.2	1.4
6	9	1	6.8	7.0
7	9	1	18.6	19.7
8	9	1	11.1	11.2
9	9	1	15.2	15.3
10	9	1	21.0	21.4
11	9	1	3.8	3.7
12	9	1	10.1	10.8
13	9	1	4.1	3.8
0	10	1	1.9	1.8
1	10	1	2.4	2.2
2	10	1	0.9	1.3 *
3	10	1	3.1	2.7
4	10	1	7.7	7.8
5	10	1	13.5	14.6
6	10	1	16.2	17.1
7	10	1	18.8	19.8
8	10	1	4.8	4.9
9	10	1	9.9	9.9
10	10	1	3.8	4.1
11	10	1	1.6	1.8
12	10	1	6.0	6.0
13	10	1	3.4	3.4
0	11	1	1.0	1.0 *
1	11	1	2.6	2.9
2	11	1	2.7	2.7
3	11	1	13.5	13.2
4	11	1	9.9	10.3
5	11	1	3.7	3.3
6	11	1	15.3	15.3
7	11	1	12.3	13.0
8	11	1	6.2	6.2
9	11	1	4.1	3.7
10	11	1	2.7	2.3
11	11	1	5.4	5.4
12	11	1	3.2	2.6
13	11	1	2.2	1.8
0	12	1	1.4	1.4
1	12	1	8.9	9.5
2	12	1	4.2	3.8
3	12	1	8.0	8.3
4	12	1	5.5	5.2
5	12	1	3.9	3.3
6	12	1	2.0	1.9
7	12	1	2.1	1.2
8	12	1	1.9	1.7
9	12	1	4.6	4.5
10	12	1	3.5	2.7
11	12	1	2.2	2.2
12	12	1	3.8	4.0
13	12	1	1.4	1.5
0	13	1	11.6	12.4
1	13	1	5.1	5.1
2	13	1	2.6	2.6
3	13	1	6.0	5.8
4	13	1	5.0	5.0
5	13	1	9.4	9.5
6	13	1	5.3	5.6
7	13	1	6.1	6.1
8	13	1	8.0	8.3
9	13	1	5.0	5.2
10	13	1	2.7	2.9
11	13	1	2.9	3.3
12	13	1	4.3	3.7
0	0	2	5.1	5.2
1	0	2	3.9	3.4
2	0	2	9.7	10.0
3	0	2	3.2	3.2
4	0	2	2.6	2.5
5	0	2	0.9	0.7 *
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7	0	2	4.3	4.0
8	0	2	2.7	2.6
9	0	2	5.8	6.1
10	0	2	2.6	2.4
11	0	2	2.9	3.7
12	0	2	2.5	2.3
13	0	2	3.8	4.1 *
0	1	2	1.0	0.4 *
1	1	2	5.2	4.7
2	1	2	1.4	1.4
3	1	2	4.5	5.0
4	1	2	3.2	3.4
5	1	2	7.4	6.2
6	1	2	1.3	1.1
7	1	2	1.1	1.2
8	1	2	7.1	5.9 *
9	1	2	1.9	0.3 *
10	1	2	3.4	2.8 *
11	1	2	0.8	0.5 *
12	1	2	1.0	0.8 *
13	1	2	1.2	1.1 *
0	2	2	9.5	0.5 *
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4	2	2	12.1	11.0
5	2	2	13.6	12.5
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7	2	2	5.9	6.3
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9	2	2	5.1	5.3
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4	3	2	6.2	6.6
5	3	2	5.2	5.1
6	3	2	3.8	4.1
7	3	2	4.2	4.7
8	3	2	4.7	4.4
9	3	2	1.7	1.2
10	3	2	25.1	22.2
11	3	2	12.9	11.1
12	3	2	18.1	17.6
13	3	2	4.2	3.8
0	4	2	6.4	6.3
1	4	2	6.5	5.7
2	4	2	9.6	10.0
3	4	2	4.5	4.7
4	4	2	2.1	2.1
5	4	2	3.2	3.2
6	4	2	4.3	4.0
7	4	2	0.8	1.0
8	4	2	13.8	10.8
9	4	2	6.6	6.9
10	4	2	7.4	7.0
11	4	2	9.9	9.8
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0	5	2	8.1	8.6
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2	5	2	3.6	4.0
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5	5	2	0.7	0.6
6	5	2	11.3	10.8
7	5	2	11.7	12.3
8	5	2	9.5	8.8
9	5	2	11.4	11.2
10	5	2	6.2	6.0
11	5	2	8.0	8.5
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13	5	2	3.3	3.4
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1	6	2	8.0	8.0
2	6	2	1.4	1.4
3	6	2	2.8	2.6
4	6	2	2.6	3.2
5	6	2	11.9	11.0
6	6	2	2.9	3.1
7	6	2	8.0	8.0
8	6	2	10.0	10.1
9	6	2	10.4	10.1
10	6	2	5.0	4.9
11	6	2	2.9	3.3
12	6	2	7.5	8.0
13	6	2	0.7	0.8 *
0	7	2	1.1	0.8 *
1	7	2	2.6	2.6
2	7	2	6.0	5.8
3	7	2	5.0	5.0
4	7	2	9.4	9.5
5	7	2	5.3	5.6
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8	7	2	5.0	5.2
9	7	2	2.7	2.9
10	7	2	2.9	3.3
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8	8	2	8.1	8.6
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10	8	2	3.9	4.0
11	8	2	1.4	1.5
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1	9	2	4.6	4.5
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4	9	2	3.8	4.0
5	9	2	1.4	1.5
6	9	2	6.3	6.1
7	9	2	2.1	1.2
8	9	2	2.9	2.7
9	9	2	2.0	1.9
10	9	2	5.0	4.9
11	9	2	2.9	3.3
0	10	2	4.3	3.7
1	10	2	2.9	3.3
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0	11	2	0.7	0.9
1	11	2	11.4	11.7
2	11	2	7.2	7.4
3	11	2	5.1	5.3
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11	11	2	7.3	7.8
12	11	2	10.4	11.5
13	11	2	2.0	2.0
0	12	2	2.0	1.7
1	12	2	0.8	0.7 *
2	12	2	1.6	1.5
3	12	2	2.7	3.1
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6	12	2	3.6	3.6
7	12	2	3.7	4.2
8	12	2	4.2	4.6
9	12	2	2.7	2.7
10	12	2	1.0	0.9
11	12	2	5.5	4.6
12	12	2	3.4	2.9
13	12	2	1.6	2.3
0	13	2	4.3	4.6
1	13	2	5.8	6.4
2	13	2	3.6	3.8
3	13	2	5.2	5.7
4	13	2	5.2	4.7
5	13	2	3.1	2.5
6	13	2	1.7	1.3
7	13	2	4.6	4.1
8	13	2	5.3	4.5
9	13	2	3.3	3.0
10	13	2	0.7	0.3 *
11	13	2	2.3	1.8
0	0	3	7.0	6.4
1	0	3	11.1	9.6
2	0	3	7.0	6.4
3	0	3	4.4	4.7
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5	0	3	6.3	6.9
6	0	3	6.7	6.9
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8	0	3	4.4	4.3
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11	0	3	9.3	9.5
12	0	3	9.4	9.6
13	0	3	2.7	2.2
0	1	3	3.4	3.2
1	1	3	4.0	4.5
2	1	3	1.7	1.8
3	1	3	5.1	4.6
4	1	3	3.5	3.9
5	1	3	3.5	3.7
6	1	3	1.7	1.8
7	1	3	3.0	2.9
8	1	3	1.8	1.8
9	1	3	11.7	10.5
10	1	3	10.1	9.7
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12	1	3	4.6	4.2
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0	2	3	4.8	4.9
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3	2	3	10.4	11.5
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5	2	3	6.5	7.1
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7	2	3	8.4	9.5
8	2	3	3.4	3.3
9	2	3	2.8	2.7
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11	2	3	6.2	6.4
12	2	3	3.6	3.6
13	2	3	4.3	4.3
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2	3	3	3.7	3.7
3	3	3	3.6	3.9
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6	3	3	2.7	2.7
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2	4	3	4.8	5.5
3	4	3	3.2	3.1
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7	4	3	2.3	2.8
8	4	3	2.7	6.5
9	4	3	0.8	0.8
10	4	3	1.4	1.3
11	4	3	3.8	3.6
12	4	3	5.9	5.7
13	4	3	0.4	0.3
0	5	3	1.8	1.9
1	5	3	3.7	4.1
2	5	3	1.2	1.8
3	5	3	8.0	7.9
4	5	3	17.1	16.9
5	5	3	5.1	4.1
6	5	3	3.0	2.6
7	5	3	2.1	2.6
8	5	3	3.2	3.1
9	5	3	9.5	8.4
10	5	3	2.5	1.7
11	5	3	5.8	4.4
12	5	3	4.3	3.6
13	5	3	4.9	4.6
0	6	3	1.8	1.8
1	6	3	2.7	3.0
2	6	3	3.9	3.2
3	6	3	15.0	12.7
4	6	3	6.4	4.4
5	6	3	4.3	4.3
6	6	3	5.5	5.4
7	6	3	6.7	6.4
8	6	3	5.1	4.7
9	6	3	5.4	5.1
10	6	3	5.4	6.3
11	6	3	1.3	1.0
12	6	3	1.8	2.0
13	6	3	1.8	3.1
0	7	3	5.6	5.3
1	7	3	2.4	2.4
2	7	3	8.2	8.7
3	7	3	5.4	5.1
4	7	3	1.8	2.0
5	7	3	3.3	3.3
6	7	3	0.8	0.6
7	7	3	6.2	5.9
8	7	3	3.8	3.6
9	7	3	5.0	5.1
10	7	3	4.0	3.8
11	7	3	3.1	2.8
12	7	3	1.2	1.2
13	7	3	1.8	2.3
0	8	3	4.8	4.3
1	8	3	2.1	1.8
2	8	3	2.3	2.1
3	8	3	1.3	1.7
4	8	3	2.9	2.4
5	8	3	1.2	1.3
6	8	3	1.8	1.3
7	8	3	4.9	4.9
8	8	3	2.5	2.7
9	8	3	4.8	4.6
10	8	3	2.2	2.1
11	8	3	2.2	2.3
12	8	3	0.3	0.6 *
13	8	3	0.7	1.5 *
0	9	3	0.3	0.6 *
1	9	3	1.8	3.1

The nitrogen atoms within a hydrazine molecule are related to each other by a twofold axis passing through the centre of the N—N bond, as was also the case in $N_2H_4 \cdot H_2O$ [1] and $N_2H_4 \cdot 2C_2H_5OH$.[2]

The dihedral angles within a hydrazine molecule are shown in Fig. 3. In the left part of the figure the planes are defined by the nitrogen atoms within a molecule and the nearest oxygen neighbours. The angle φ of internal rotation of the NH_2 groups from the *cis* position is 74°, assuming linear hydrogen bonds. The dihedral angles between the N—N—H planes are illustrated in the right part of Fig. 3, which shows that the angle φ is 67° if the experimental hydrogen positions are used.

Assuming linear N—H···O bonds, the angle φ was 59° in $N_2H_4 \cdot H_2O$ and 73° in $N_2H_4 \cdot 2C_2H_5OH$. In the latter case the corresponding angle was 92° when the planes were defined by N—N—H. According to a recent quantum mechanical calculation the angle φ for free hydrazine in its equilibrium form should be 94°.[8]

2. *The methanol molecules.* The C—O distances in the two independent molecules are 1.418 ± 0.005 and 1.443 ± 0.009 Å, respectively. When a correction for thermal motion is made, assuming riding motion, the C—O distances are 1.438 and 1.448 Å, respectively. Some earlier reported values for this type of bond in the solid state are: 1.42 ± 0.03 Å in the high-temperature form of methanol, 1.44 Å in the low-temperature form,[9] and 1.424 ± 0.003 Å in $N_2H_4 \cdot 2C_2H_5OH$. Spectroscopic and electron diffraction measurements of the C—O distance in methanol in the gas phase give values between 1.421 and 1.434 Å.[10] An average value of 1.43 ± 0.01 Å is given by Lide for a C—O bond distance with carbon exhibiting sp^3 hybridization.[11]

The nearest neighbours of carbon C(1) in adjacent molecules are as follows: three N, two O(2), and one C(2) at 3.46—3.97 Å, and four C(1) at 4.07 Å. Similarly, C(2) has two N, one O(1), three O(2), and one C(1) at 3.50—3.87 Å and four C(2) at 3.89 Å. The methyl group $C(2)H_3$ seems thus to be more closely packed in the structure than $C(1)H_3$.

3. *The hydrogen bonding system.* The nitrogen atoms have three neighbours at possible hydrogen-bond distances, namely two O(1) at 2.682 and 3.025 Å, and one O(2) at 2.959 Å (Table 4, Figs. 2 and 4). It is supposed that the two longer distances represent N—H···O bonds and the third one an O(1)—H···N bond. In addition to the bonds mentioned the oxygens O(1) and O(2) are also bonded to each other by an O(2)—H···O(1) bond (2.737 Å). Oxygen O(1) is thus involved in three hydrogen bonds and O(2) in only two. One of the lone pairs on O(2) is formally not used. Such a situation can be expected as the number of lone pairs per unit $N_2H_4 \cdot 4CH_3OH$ is greater than the number of hydrogen atoms available for hydrogen bonding; ten lone pairs but only eight active hydrogen atoms. The interpretation of the hydrogen bonds given above is confirmed by the difference Fourier syntheses.

The hydrogen bonding system around hydrazine in the present case is similar to that in $N_2H_4 \cdot H_2O$ [1] and $N_2H_4 \cdot 2C_2H_5OH$.[2] The number of hydrogen bonds around hydrazine is normal (six) in these three structures. The N—H···O bond lengths are as follows: $N_2H_4 \cdot H_2O$: 3.113 and 3.149 Å, $N_2H_4 \cdot 2C_2H_5OH$: 3.041 and 3.060 Å, and in the present case 2.959 and 3.025 Å. The variation of these bond distances may depend on differences in the coordination number

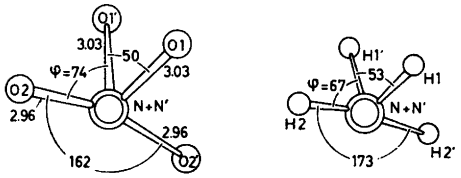

Fig. 3. View down the N—N axis of an N_2H_4 molecule showing the dihedral angles between planes defined by N—N···O (left) and N—N—H (right).

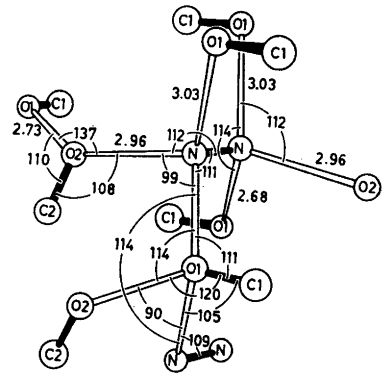

Fig. 4. Hydrogen bond distances and angles. The orientation is the same as in Fig. 2. A twofold axis passes through the centre of the N—N bond.

of the acceptor atoms. In $N_2H_4 \cdot H_2O$ each lone pair on oxygen accepts two hydrogen atoms from N—H···O bonds, thus giving oxygen the coordination number six. The corresponding coordination number in the ethanol compound is four, and that in $N_2H_4 \cdot 4CH_3OH$ four for O(1) and only three for O(2). The shorter of the bonds in the latter case is the N—H···O(2) bond. It is assumed above that the electronegativities of hydrogen and the methyl and ethyl groups are approximately equal.

As mentioned earlier the two independent methanol molecules are bonded to each other by an O(2)—H···O(1) bond of length 2.737 Å. A similar bond exists in solid methanol; 2.66 Å in the high temperature form and 2.68 Å in the low temperature form.[9] A shorter O—H···O bond can be expected in solid methanol as compared with the present case, due to a difference in coordination number of the acceptor atoms.

The O—H···N bond, 2.682 Å, is short for a bond of this type. The comparable bonds in $N_2H_4 \cdot H_2O$ and $N_2H_4 \cdot 2C_2H_5OH$ were 2.790 and 2.730 Å, respectively.

The ideal bond angles subtended at nitrogen and oxygen in the present case could be expected to be approximately tetrahedral, but some large deviations are observed (Table 4, Fig. 4). The greatest variations are found at O(1) and O(2); *e.g.* the angle N···O(2)···O(1) and one of the N···O(1)···O(2) angles are 137° and 90°, respectively. Such deviations are not unusual. (Note that oxygen O(2) accepts only one hydrogen atom, but has two available lone pairs).

4. Hydrogen positions. The hydrogen positions listed in Table 1 were determined from difference Fourier maps as was described above. Well resolved peaks appeared in regions where the hydrogens bonded to the N, O(2), and C(2) atoms were expected to be located. The hydrogen peaks around O(1) and C(1) were on the other hand smeared out, and the localisation of these hydrogen atoms is accordingly uncertain. Some bond distances and angles

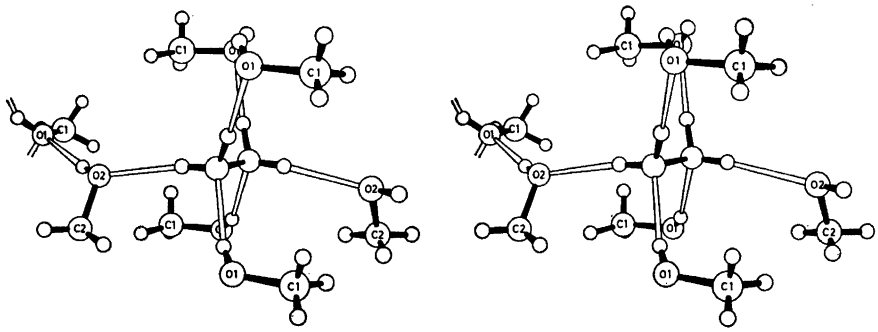

Fig. 5. A stereoscopic pair of drawings showing the location of the hydrogen atoms (small circles). Atom labels on nitrogen are omitted. The orientation is the same as in Fig. 2.

involving hydrogen are listed in Table 4, which indicates that the errors in some of the hydrogen positions are rather large. The hydrogen positions are illustrated in Fig. 5.

As can be seen in Table 4 and Fig. 5, the hydrogen bonds are more or less bent; the O(1)—H···N bond is the most bent (O—H···N angle: 149°). It is to be noticed that the latter bond is the shortest one found in the structure. However, the errors in the angles subtended at hydrogen may be rather large (see above).

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