ACTA CHEMICA SCANDINAVICA 12 (1958) 1768—1776

The Crystal Structure of Acetaldehyde-ammonia

EINAR WANG LUND

Kjemisk Institutt, Universitetet i Oslo, Blindern, Norway

In the solid state acetaldehyde-ammonia is found to be the trihydrate of trimethyl-hexahydrotriazine. The methyl groups are bonded equatorially to the carbon atoms of the hydrogenated triazine ring. The C—C and C—N distances are normal. Oxygen atoms of the waters of crystallization are interconnected by hydrogen bonds of length 2.70 Å to form a six-membered puckered ring. Hydrogen bonds probably exist between oxygen atoms and nitrogen atoms of adjacent rings.

In a previous short communication [1] a preliminary account of the crystal structure of acetaldehyde-ammonia has been given. This article is a more complete description of the structure.

The general tendency of aldehydes to polymerize has led several authors to the assumption that acetaldehyde-ammonia is a trimer. Among others Delépine [2] presented the idea that acetaldehyde-ammonia in the solid state actually is a trihydrate of 2,4,6-trimethyl-hexahydro-1,3,5-triazine. Delépine based this assumption mainly on the fact that the compound is easily dehydrated *in vacuo* over concentrated sulphuric acid. The anhydrous product formed under such conditions has been found by the author to cyrstallize in the cubic space group $Pa3$ with the lattice constant $a = 14.56$ Å.

The molecular structure proposed by Delépine was also the main result of an X-ray crystallographic determination made by Moerman [3]. The structure reported by Moerman was, however, rather improbable with respect to interatomic distances and bond angles. Therefore a re-investigation of the structure using Fourier methods has been carried out.

Crystals of acetaldehyde-ammonia in the form of rhombohedra were obtained by adding gaseous ammonia to an ice-cold solution of acetaldehyde in dry ether. Rotation and Weissenberg photographs showed that the Laue symmetry of the crystals is $D3d$- $\bar{3}m$ and that the unit cell with hexagonal axes has the dimensions: $a = 11.29$ Å, $c = 15.87$ Å. With the value of the density reported by Moerman $d = 1.06$ gcm^{-3} these dimensions led to a number of 18 units of $CH_3CHO{\cdot}NH_3$ in the hexagonal unit cell. Inspection of Weissenberg diagrams showed no systematic extinctions of reflexions other than those given by a rhombohedral structure based on a hexagonal unit cell. Therefore the possible space groups are D_{3d}^5—$R\bar{3}m$, D_3^7—$R32$ or C_{3v}^5—$R3m$. Of these only D_{3v}^5—$R\bar{3}m$ contains a center of symmetry.

The first X-ray study of acetaldehyde-ammonia was made by Hassel and Mark [4] who determined the cell dimensions and the space group. They based the space group determination on the statement made by Groth [5] that acetaldehyde-ammonia belongs to the ditrigonal scalenohedral class D_{3d}—$\bar{3}m$. Hassel and Mark found therefore unambigously from the sets of reflexions present that the only possible space group is D_{3d}^5—$R\bar{3}m$.

In order to support the crystal class determination, investigation was made for the presence of piezoelectricity. This was kindly undertaken by Mr. Erik Blomgren at the Chemistry Department of the University of Uppsala, Sweden. Mr. Blomgren could state very positively that no piezoeffect was present. This negative result together with the statement of Groth and the fact that the space group $R\bar{3}m$ is the only of the three groups mentioned that has a 36-fold general position led to the choice of this space group as the most probable. The final result is considered to be a confirmation of the correctness of this choice.

The arrangement of symmetry elements in this space group is such that any Fourier projection will give considerable amount of overlap of nonequivalent atoms and no resolved peaks suitable for determination of atomic coordinates. Therefore the computation of a Fourier section was considered necessary in order to get details of the structure. The asymmetric part of the "monomer" contains (apart from the hydrogen atoms) two carbon atoms, one nitrogen atom and one oxygen atom which have to be placed in one of the special 18-fold positions. The only possible one from steric considerations is that which involves a plane of symmetry. This plane with the equation $y = -x$ then contains all the important atoms in the asymmetric unit and is therefore highly suitable as the plane for a Fourier section.

In order to obtain the necessary intensities double sets of equi-inclination Weissenberg photographs were taken with Cu-K radiation. With rotation about c sets of photographs were from $l = 0$ to $l = 7$ and with rotation about a sets were taken for $h = 0$ to $h = 3$. Intensities of reflexions were estimated visually using a standard scale with known relative values. After correction for Lorentz and polarization factors the intensities were interrelated and brought to the same relative scale. Later the observed values of the structure factors were normalized to the set of calculated values.

The trial structure used in order to obtain signs of the structure factors was partly based on the main features of the structure of Moerman, *viz.* a hydrogenated, methyl substituted triazine ring with center in $(0,0,z)$, the nitrogen atoms of the ring being loosely connected to oxygen atoms by means of hydrogen bonds. A satisfactory agreement between absolute values of observed and calculated structure factors was obtained with the parameter z having a value about 1/4 and oxygen atoms forming a puckered six-membered ring with center in $z = \frac{1}{2}$.

After some refinement, including the introduction of the effect of hydrogen atoms in the calculated structure factors, a final Fourier map was obtained which is reproduced in Fig. 1. In this map contour lines are drawn for arbitrary equidistant values of the function $\varrho\ (x,\bar{x},z)$. The peaks corresponding

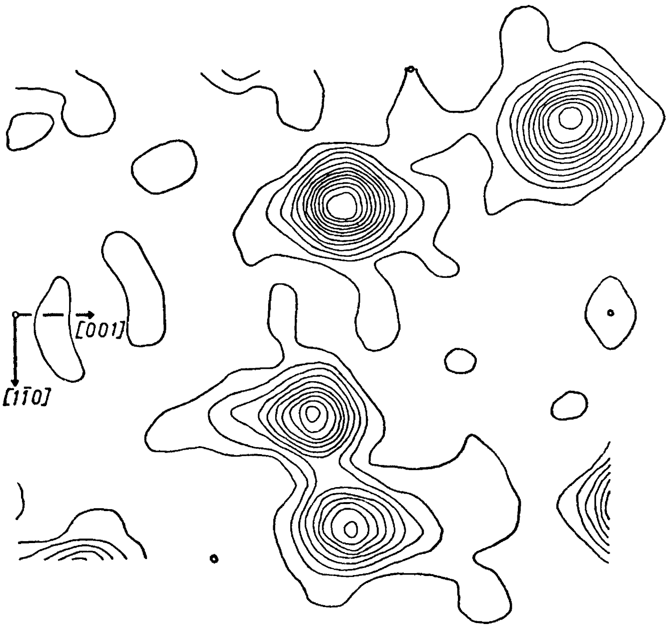

Fig. 1. Fourier section in the plane $y = -x$. Contour lines are drawn at arbitrary equidistant values of the function $\varrho\ (x,\bar{x},z)$.

to nitrogen, oxygen and two carbon atoms are well resolved and the positions of the maxima are assumed to determine atomic coordinates of these atoms which are listed in Table 1.

The main features of the structure formed by carbon, nitrogen and oxygen atoms can be described as follows. Alternating carbon and nitrogen atoms form a six-membered puckered ring of the *cyclo*hexane type. The N—C distance is found to be 1.47 Å. The angles in the ring, ∠NCN and ∠CNC are 114.6° and 109.0°, respectively. To each carbon atom of the ring is linked a methyl group in equatorial position. The C—C distance found is 1.53 Å. The angle between the C—C direction and the threefold axis (negative *c*-axis for the molecule in question) is found to be 109.1° whereas the angle ∠NCC amounts to 109.5°. The oxygen atoms closest to the substituted triazine ring are situated at a distance 2.87 Å from the nitrogen atoms. A hydrogen bond is probably established between these atoms. The angle between the N—O direction and the threefold axis is 115.5°. The N—O direction is thus not far from that corresponding to a bond directed equatorially away from the nitrogen atom.

Oxygen atoms more distant from the triazine ring in question lie at 3.20 Å from the nitrogen atoms in a direction making 19° with the threefold axis. These oxygen atoms are, however, at the shorter distance of 2.87 Å from nitrogen atoms of other substituted triazine rings. On account of the symmetry

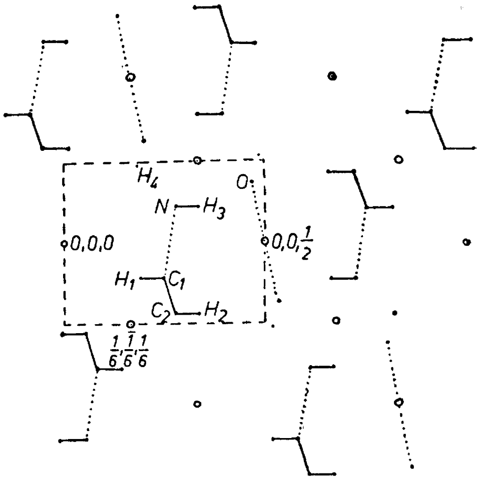

Fig. 2. General survey of positions of atoms and symmetry centers in the plane of the Fourier section. C—C, C—H and N—H bonds lying in the plane are shown by full lines. Nitrogen and carbon atoms belonging to the same hydrotriazine ring are interconnected by dotted lines; the same applies to oxygen atoms of one oxygen ring. The asymmetric unit of Fig. 1 is outlined by a broken line.

six oxygen atoms form a puckered ring. In this ring the O—O distance found is 2.70 Å and the angle ∠OOO is 106.3°. These oxygen atoms are therefore assumed to be interconnected by hydrogen bonds.

Introduction of hydrogen atoms in the calculation of structure factors improved the correspondence with the observed values. The positions of the hydrogen atoms were chosen from chemical facts using reasonable bond distances and valency angles. In spite of the trimerization of the molecule it is highly reasonable that the arrangement $CH_3 \cdot CH \cdot NH$ is retained whereas the remaining two hydrogen atoms of the monomer are probably connected to oxygen. For the methyl groups there are two equilibrium positions consistent with the presence of a symmetry plane through the C—C bond. The one which makes van der Waals' distances most favourable has a C—H bond parallel to the threefold axis. For steric reasons free rotation of methyl groups is improbable. The hydrogen atoms connected to carbon and nitrogen atoms of the ring are assumed to be in axial positions with C—H and N—H distances equal to 1.09 Å and 1.00 Å, respectively. These two hydrogen atoms and one of the methyl hydrogen atoms are thus assumed to lie in the plane of the Fourier section and the extensions of the peaks may indicate their presence.

Between two adjacent oxygen atoms of the oxygen ring one hydrogen atom is assumed to be located. The space group symmetry requires this hydrogen atom either to be located half way between the oxygen atoms or to be disor-

Table 1. Atomic coordinates determined from the Fourier section.

	x	z
C_1	0.071	0.250
C_2	0.145	0.281
N	−0.073	0.277
O	−0.128	0.467

Table 2. Assumed coordinates of hydrogen atoms.

	x	y	z
H_1	0.071		0.181
H_2	0.145		0.350
H_3	−0.073		0.346
H_4	−0.159		0.181
H_5	0.093	−0.251	0.258
H_6	0.037	−0.173	0.509

derly distributed over two symmetrically located positions equidistant from the two oxygen atoms. The latter alternative was chosen, with O—H distance equal to 0.96 Å. For the calculation of structure factors this arrangement corresponds to placing half a hydrogen atoms in a general 36-fold position.

The position of the other hydrogen atom connected to oxygen was assumed to be equatorial to the oxygen ring with an angle ∠OOH equal to 109°. This hydrogen atom will then be located about 0.7 Å from the line of length 2.87 Å connecting the oxygen atom and the nearest nitrogen atom.

The coordinates thus chosen for hydrogen atoms and used in the calculation of structure factors are listed in Table 2. In Fig. 2 is shown the arrangement of atoms and symmetry centers over a greater area of the plane of the Fourier section with the inclusion of hydrogen atoms.

The atomic scattering factors used for carbon, nitrogen and oxygen are those calculated by Berghuis *et al* [6]. For hydrogen the scattering factor given by McWeeny [7] was applied. The calculated structure factors were corrected with an isotropic temperature factor $\exp(-B \sin^2\Theta/\lambda^2)$ with $B = 4.14$ Å^2. A test for an expected anisotropic vibration with the trigonal axis as a preferred direction had no positive result.

In Table 3 a list of observed and calculated structure factors is given. Calculated values for all 415 reflexions with $\sin \Theta/\lambda$ less than 0.6 are included. That only 136 reflecions are observed is partly due to too short exposure of Weissenberg diagrams of higher layer lines. Of the observed structure factors 96 % have a value greater than 10. It is assumed that the value 8 is an average lower limit of the values of structure factors which are observable from the diagrams taken. For unobserved reflexions only that part of a calculated structure factor which exceeds 8 is considered as an error in computing the R-factor.

The over all R-factor with the limit of 8 as observable is found to be 0.24. To this value the contribution from five of the strongest reflexions with $|F_{\rm calc}| > 90$ is 0.04. These strongest reflexions are assumed to be affected by extinction and to be less accurately observed due to the difficulty in estimating their intensities visually. The R-factor for $hk0$-reflexions only is 0.10, for $0kl$-reflexions 0.24. To the latter value the strong reflexions mentioned contribute 0.07. The R-factor including only reflexions with $F_{\rm obs} \neq 0$ is 0.16.

It is believed that the structure is more accurate than an over all R-factor of 0.24 generally would imply. The reasons for this are the difficulty in obtain-

Table 3. Observed and calculated structure factors.

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
110	40	39	762		−6	1.10.3		1
220	63	55	402	18	11	204	81	−93
330	37	36	512	18	13	314		−8
440	40	36	622	20	−22	424		−6
550	60	58	732		−7	534		−11
660		3	842		0	644	26	24
300	99	−99	702	17	18	754		−8
410	63	−53	812	30	29	504	19	21
520	17	−20	922		−1	614		−6
630	20	11	10.0.2	11	8	724		2
740		1	11.1.2		0	834		3
850	11	−12	022	53	−68	804	14	−6
600	32	−23	132	68	65	914	22	−22
710	9	8	242	37	33	10.2.4		3
820	15	−12	352	38	−35	11.0.4		−10
930		2	462	21	−18	014	124	189
900	18	−16	572		2	124	22	17
10.1.0	6	−8	052	56	54	234		17
201	6	−13	162		1	344	25	26
311	24	23	272		4	454	48	45
421	24	−25	382		−10	564	18	20
531		10	492	13	13	674		0
641		−11	082	21	26	044	106	−131
751		−2	192		3	154	64	−63
501	58	56	2.10.2		4	264		9
611		−4	0.11.2		4	374		−11
721	15	16	003		−13	484		−6
831		5	113	22	23	074	12	12
941		4	223		−13	184		0
801	26	−33	333	26	−30	294		−4
911		0	443	23	23	0.10.4		1
10.2.1		−7	553		−3	105	66	−90
11.0.1		10	663		−2	215	43	43
011	59	−73	303	71	80	325	35	−36
121	60	61	413	48	−45	435		6
231	76	−73	523	36	40	545	16	−18
341	23	17	633		8	655		−9
451	15	−13	743		2	765		3
561		−6	853		4	405	40	42
671		3	603	14	−10	515		−4
041	10	−5	713		−9	625		20
151	27	24	823		−8	735		0
261		9	933		−3	845		5
371		2	903		0	705	17	−21
481		5	10.1.3		3	815		2
071	22	−22	033	49	−43	925		−4
181		−1	143	18	13	10.0.5		17
291		2	253	19	−22	025	6	6
0.10.1		9	363		12	135	18	−13
1.11.1		−4	473		−3	245		9
102	88	−137	583		−1	355	16	−4
212	40	−40	063	26	25	465		−11
322	54	54	173		−12	575		3
432	22	−15	283		14	055	62	70
542	56	−50	393		3	165		1
652		3	093	16	−22	275		4

Table 3. (Continued.)

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
385		9	487		−5	20.10	14	−19
085		−7	077		9	31.10		−18
195		5	187		−3	42.10		−4
2.10.5		−5	297		10	53.10		−12
0.11.5		−5	0.10.7		−13	64.10		−6
006	73	−68	108	23	24	50.10		5
116	37	−34	218	21	−30	61.10		3
226	19	16	328		−3	72.10		−3
336		15	438		−11	83.10		7
446	26	−24	548		9	80.10		7
556		−15	658		2	91.10		11
666		−1	408	29	30	01.10	33	−24
306	48	−63	518		19	12.10	15	16
416		2	628		−10	23.10		7
526		−16	738		15	34.10		−2
636	23	−25	848		−1	45.10		−3
746		4	708		−7	56.10		−9
606	14	14	818		−11	04.10	38	38
716		8	928		−1	15.10		8
826		12	10.0.8	19	−20	26.10		8
936		1	028	64	73	37.10		−5
906	29	26	138	22	−17	07.10		2
10.1.6		0	248		−3	18.10		−9
036	57	58	358	33	32	0.10.10		2
146	49	44	468		8	10.11	50	45
256		2	578		7	21.11		6
366		−2	058	65	−79	32.11		22
476		−9	168		−3	43.11		5
066	17	6	278		−6	54.11		20
176		7	388		−8	65.11		5
286		−9	088		6	40.11		−1
396		4	198		6	51.11		−7
096		−4	009	53	−71	62.11		6
1.10.6		5	119	15	−10	73.11		−7
207	51	69	229		−8	70.11		9
317		13	339		4	81.11		−11
427		1	449		−19	10.0.11	7	−8
537	27	33	559		−12	02.11	13	−27
647		6	309	25	37	13.11	23	−23
757		4	419		−12	24.11		−7
507	42	−45	529		11	35.11		−6
617		9	639		−12	46.11		10
727		−11	749		−11	05.11	35	−31
837		−7	609	20	−25	16.11		−3
807		−7	719		7	27.11		−3
917		−7	829		−4	08.11		12
017	36	27	909	22	20	19.11		3
127	37	−38	039	12	−12	00.12	13	−22
237		−1	149	42	42	11.12		11
347		−14	259		−7	22.12		−18
457		18	369		−11	33.12		−13
567		−2	479		4	44.12		4
047	32	−26	069	18	21	55.12		−5
157		−5	179		−1	30.12		2
267		−13	289		6	41.12		20
377		10	099		−1	52.12		−1

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
63.12		6	07.13		3	03.15	10	−17
60.12		11	18.13		− 1	14.15	27	−20
71.12		−10	10.14		− 7	25.15		− 3
90.12	12	−12	21.14		0	06.15	14	−12
03.12	15	24	32.14		− 6	20.16		10
14.12	27	−23	43.14		− 2	31.16		1
25.12		17	54.14		2	42.16		0
36.12		6	40.14		− 9	50.16		11
06.12		−17	51.14		0	01.16		−10
17.12		− 4	62.14		− 1	12.16		5
09.12		10	70.14		3	23.16		−16
20.13		7	02.14		2	34.16		2
31.12		− 6	13.14		10	04.16		4
42.13		3	24.14		− 3	15.16		3
53.13		− 3	35.14		5	10.17		5
50.13	20	−31	05.14	13	13	21.17		− 5
61.13		− 4	16.14		5	32.17		5
72.12		− 1	00.15	23	28	40.17	15	−20
80.13	15	18	11.15		0	02.17		− 6
01.13	16	−12	22.15		6	13.17		11
12.13		−10	33.15		8	05.17	11	11
23.13		17	44.15		1	00.18		− 1
34.12		− 7	30.15		− 1	11.18		0
45.13		−10	41.15		14	22.18		1
04.13	30	32	52.15		− 3	30.18		2
15.13		16	60.15		5	03.18		− 1
26.13		− 5						

ing reliable estimated values of intensities for higher layer lines, too short exposure time for some of the diagrams and extinction effects on five of the strongest reflexions.

The values of interatomic distances and bond angles given above and listed in Table 4 are assumed to be accurate to about one per cent. It is seen that the C—C and C—N bond lengths found are normal. The O—O distance and the shortest N—O distance are assumed to correspond to hydrogen bonds. In comparison with an ideal *cyclo*hexane ring the hydrotriazine ring does not have a center of symmetry geometrically, the angles at N and at C being somewhat different.

It may be of interest to point out that the six-membered ring formed by oxygen atoms in this structure is very similar to the structure element in

Table 4. Interatomic distances and bond angles.

C−C	1.53 Å	∠NCN	(ring)	114.6°
C−N	1.47 Å	∠CNC	(ring)	109.0°
N−O	2.87 Å	$\angle NC_1C_2$		109.5°
N−O′	3.20 Å	∠OOO		106.3°
O−O	2.70 Å			
methyl-methyl	3.74 Å			

hexagonal ice. In ice the O—O distance is about 2 % longer and there are no centers of symmetry whereas in acetaldehyde-ammonia a center of symmetry of the space group is the mid-point of the six-membered ring of oxygen atoms.

The author wishes to acknowledge a grant from *Axel Auberts fond.*

REFERENCES

1. Lund, E. W. *Acta Chem. Scand.* **5** (1951) 678.
2. Delépine, M. *Bull. soc. chim. France* **19** (1898) 15.
3. Moerman, N. F. *Z. Krist.* **98** (1938) 447.
4. Hassel, O. and Mark, H. *Z. physik. Chem.* **111** (1924) 357.
5. Groth, P. *Elemente der physikalischen und chemischen Krystallographie,* München und Berlin 1921, p. 242.
6. Berghuis, J., Haanappel, I-M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
7. McWeeny, R. *Acta Cryst.* **4** (1951) 513.

Received August 13, 1958.