

The Crystal and Molecular Structure of *O*-Carbamoylhydroxylamine, an Isomer of Hydroxyurea

INGRID KJØLLER LARSEN

Chemical Laboratory C, The Royal Danish School of Pharmacy, Copenhagen, Denmark

The crystal and molecular structure of *O*-carbamoylhydroxylamine, $O=C(NH_2)ONH_2$, has been determined from three-dimensional X-ray data and refined by least-squares method to an *R*-value of 0.105. The crystals are orthorhombic, space group *Pbca*, $Z = 8$, with $a = 8.445$, $b = 13.47$, $c = 5.758$ Å. The molecule is planar with the exception of the hydrogen atoms of the O-bonded amino group. The molecules are connected by a three-dimensional system of $NH \cdots O$ hydrogen bonds, the carbonyl oxygen atom being acceptor for all of them.

Two isomeric compounds, hydroxyurea $O=C(NH_2)NHOH$ (*N*-carbamoylhydroxylamine) and so called isohydroxyurea $O=C(NH_2)ONH_2$ (*O*-carbamoylhydroxylamine) are formed by substituting ammonium sulphate with hydroxylammonium sulphate in the classical Wöhler synthesis. The constitutions of both compounds have been established by chemical and physico-chemical methods.¹⁻³ In addition the molecular structure of hydroxyurea in the crystalline state has been established in this laboratory,⁴ and as a continuation of this work the present X-ray investigation of *O*-carbamoylhydroxylamine has been carried out. Recently a second X-ray determination of the structure of hydroxyurea⁵ has been carried out, based on data from an automatic diffractometer and consequently resulting in lower standard deviations.

EXPERIMENTAL

O-Carbamoylhydroxylamine, $CH_4N_2O_2$, M.W. 76.06, was synthesized according to the method of Kofod.⁶ The compound crystallizes most frequently as very thin, rhomboid plates. Single crystals suitable for X-ray study were obtained by recrystallization from a mixture of 30 % anhydrous ether in absolute ethanol. Slow evaporation was performed at 5°C. The melting point was 72–74° (decomp.). Examination of the crystals under the polarizing microscope indicated orthorhombic crystals.

Needleshaped crystal fragments, 0.2×0.3 mm² in cross section ($\mu = 12.8$ cm⁻¹ for $CuK\alpha$), were cut out of the crystals with the needle axes in the direction of the diagonals of the rhombs. The fragments were coated with silicone grease and placed in Lindemann

tubes to protect them against the humidity of the air, which causes decomposition in a few days.³

Oscillation and Weissenberg photographs showed systematic extinction of $Ok\bar{l}$ reflections when k is odd, $hk0$ when h is odd, and $h0l$ when l is odd, indicating the space group $Pbca$. The unit cell dimensions were determined from zero-level Weissenberg photographs: $a = 8.445 \text{ \AA}$, $b = 13.47 \text{ \AA}$, $c = 5.758 \text{ \AA}$ (estimated error about 0.2 %), $V = 655 \text{ \AA}^3$ ($\lambda = 1.5405 \text{ \AA}$ was used in the computations). The assumption of 8 molecules in the unit cell leads to a calculated density of 1.551 g/cm^3 in good agreement with the observed value of 1.538 g/cm^3 , measured by flotation in a mixture of pentane and tetrachloromethane.

Multiple film equi-inclination Weissenberg photographs were collected, using Ni-filtered Cu radiation of levels hkl for $0 \leq l \leq 5$ and hkl for $0 \leq h \leq 6$. The intensities were measured on a Flying Spot Integrating Microdensitometer (Joyce-Loebl & Co.). Of the 828 independent reflections within the sphere of reflection a total of 613 were observed ~ 74 %. The intensities were brought on a common relative scale, using the least-squares method of Hamilton, Rollett and Sparks.⁷ No corrections for absorption or extinction were made.

STRUCTURE DETERMINATION

Solution of the structure was achieved by means of the sharpened Patterson projection $^sP(xy)$ ⁸

$$\sum_{hk} \sum_{\hat{f}} \left| \frac{F(hk)}{\hat{f}} \right|^2 \exp[(2B - B_1) \sin^2\theta/\lambda^2] \cos 2\pi(hx + ky); B_1 = 1.5$$

combined with packing considerations. Refinement with two-dimensional data was carried out according to the method of Bhuiya and Stanley.^{9,10} In the initial computations the f -curve of nitrogen was used for the five heavy atoms. When the R -value ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) had dropped to 0.23,

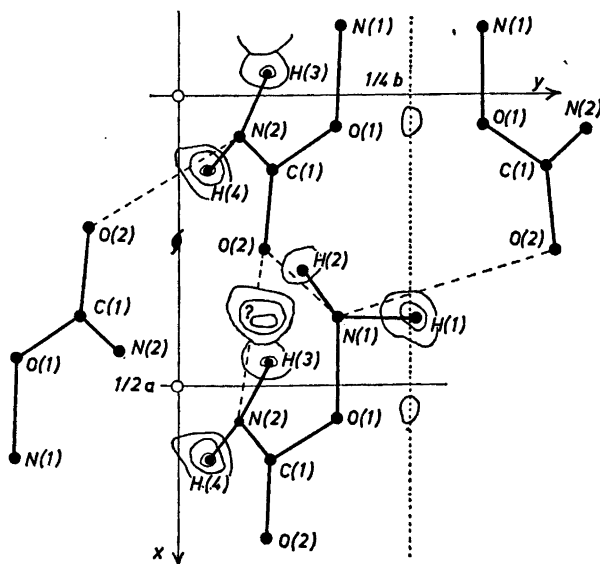


Fig. 1. Projection along the c -axis of sections of the difference map.

it was possible in the electron density map $\rho(xy)$ to distinguish between oxygen and nitrogen, and this was subsequently confirmed in the three-dimensional electron density map $\rho(xyz)$.

Refinement with three-dimensional data was carried out by means of the least-squares program ORFLS.¹¹ After 2 cycles of refinement of positional parameters, isotropic temperature factors and 1 scale factor the R -value was 0.18. After 2 cycles of refinement, using anisotropic temperature factors, the R -value was 0.13. The weighting scheme used was that introduced by Hughes,¹² atomic scattering factors were taken from *Intern. Tables*.¹³

Four strong reflections, (040), (041), (131) and (002), were apparently seriously affected by extinction (F_o was systematically smaller than F_c). They were removed and the three-dimensional electron density and difference synthesis were calculated (Program: ERFR 2).¹⁴

The difference map showed peaks at or close to the expected sites of the four hydrogen atoms of the molecule, *i.e.* in a distance of about 1 Å from N(1) and N(2) and in directions favourable for hydrogen bonding, *cf.* Figs. 1 and 3. In addition a fifth peak appeared half-way between H(2) and H(3) and in a distance of about 1 Å from N(1). This peak, indicated by a sign of interrogation in Fig. 1, was not interpreted as hydrogen for the following reasons: If peak(?) and H(1) or peak(?) and H(2) are interpreted as hydrogen atoms, very distorted NH₂-groups must be accepted. A choice of the peaks H(1) and H(2) as hydrogen atoms, on the other hand, produces a rather regular pyramidal configuration of the N(1)-atom, *cf.* Fig. 2. Finally, the peak(?) is located only 1.5 Å from H(3), and not near any direction, which might correspond to a hydrogen bond. A difference Fourier synthesis, based on structure factors including H(1)–H(4), was calculated. This still showed the extra peak, and no other spurious peaks were found.

Introduction of the four hydrogen atoms H(1), H(2), H(3), and H(4) lowered the R -value to 0.105 (B was arbitrarily fixed as 2.0 Å² for all H-atoms). Two cycles of refinement of the parameters of the heavy atoms using anisotropic temperature factors and refinement of the positional parameters of the hydrogen atoms did not lower the R -value and all the parameter shifts were very small (less than 1/3 of the standard deviations) and considered insignificant. The unobserved reflections were not included in the refinements, but were calculated as a control. None of them had unexpectedly high values.

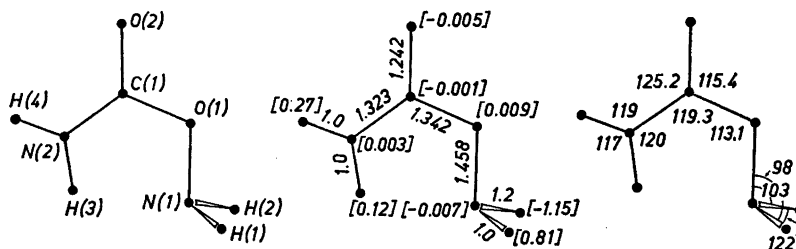


Fig. 2. Bond lengths (Å) and angles (°). The numbers in angular parentheses are the distances (Å) of the atoms from the least-squares plane through the five heavy atoms.

The computations were performed on a GIER computer (The H. C. Ørsted Institute) and IBM 7090 (NEUCC). The final atomic parameters are given in Tables 1 and 2, interatomic distances and angles in Tables 3 and 4, observed and calculated structure factors in Table 5.

Table 1. Final positional parameters as fractions of cell edges. Standard deviations times 10^4 (10^3 for the H-atoms) in parentheses.

Atom	x	σx	y	σy	z	σz
N(1)	0.3806	(5)	0.1798	(4)	0.5057	(7)
O(1)	0.5422	(4)	0.1665	(2)	0.5893	(6)
C(1)	0.6293	(5)	0.1070	(3)	0.4528	(7)
O(2)	0.7674	(4)	0.0925	(3)	0.5187	(5)
N(2)	0.5653	(4)	0.0695	(3)	0.2623	(7)
H(1)	0.380	(9)	0.255	(7)	0.500	(10)
H(2)	0.300	(9)	0.133	(5)	0.625	(15)
H(3)	0.467	(9)	0.100	(5)	0.200	(16)
H(4)	0.633	(9)	0.033	(5)	0.150	(14)

Table 2. Anisotropic temperature parameters U_{ij} Å² ($\times 10^2$).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	1.88	4.50	3.53	1.15	-0.10	-0.55
O(1)	2.31	3.40	2.42	0.75	-0.49	-0.75
C(1)	1.45	1.93	1.83	-0.17	-0.22	0.24
O(2)	1.48	3.77	3.24	0.06	-0.64	0.51
N(2)	1.74	3.22	2.77	0.40	-0.35	-1.02

Table 3. Intramolecular distances and angles. Standard deviations (times 10^3 for the distances) in parentheses.

Atoms	Distance (Å)
O(1)-N(1)	1.458 (5)
O(1)-C(1)	1.342 (5)
C(1)-O(2)	1.242 (5)
C(1)-N(2)	1.323 (5)
N(1)- - -N(2)	2.570 (6)
N(1)-H(1)	1.010 (90)
N(1)-H(2)	1.240 (80)
N(2)-H(3)	0.990 (80)
N(2)-H(4)	0.990 (80)
Atoms	Angle (°)
N(1)-O(1)-C(1)	113.1 (0.3)
O(1)-C(1)-N(2)	119.3 (0.4)
O(1)-C(1)-O(2)	115.4 (0.3)
O(2)-C(1)-N(2)	125.2 (0.4)
O(1)-N(1)-H(1)	98 (4)
O(1)-N(1)-H(2)	103 (4)
C(1)-N(2)-H(3)	120 (5)
C(1)-N(2)-H(4)	119 (5)
H(3)-N(2)-H(4)	117 (7)
H(1)-N(1)-H(2)	122 (5)

Table 4. Intermolecular distances and angles. Standard deviations (times 10^3 for the distances) in parentheses.

Atoms	Distance (Å)
N(2)---O(2) ^I	3.007 (5)
N(1)---O(2) ^{II}	3.130 (5)
N(1) ^{III} ---O(2) ^I	3.216 (6)
N(2) ^{IV} ---O(2) ^{II}	2.954 (5)
N(1)---O(2) ^I	3.378 (5)
N(2)---N(2) ^{IV}	3.495 (5)
N(1)---O(1) ^{III}	3.449 (5)

Atoms	Angle (°)
C(1) ^I -O(2) ^I ---N(2)	129.6 (0.2)
C(1) ^I -O(2) ^I ---N(1) ^{III}	96.7 (0.2)
C(1) ^{II} -O(2) ^{II} ---N(1)	119.7 (0.2)
C(1) ^{II} -O(2) ^{II} ---N(2) ^{IV}	135.3 (0.2)
N(2) ^{IV} ---O(2) ^{II} ---N(2) ^V	77.2 (0.1)
N(2) ^V ---O(2) ^{II} ---N(1) ^{VI}	80.0 (0.1)
N(1) ^{VI} ---O(2) ^{II} ---N(1)	65.7 (0.1)
N(1)---O(2) ^{II} ---N(2) ^{IV}	73.5 (0.1)

I means $(x-0.5, y, 0.5-x)$	IV means $(1-x, -y, 1-z)$
II means $(x-0.5, y, 1.5-z)$	V means $(x, y, z+1)$
III means $(x, 0.5-y, z-0.5)$	VI means $(x, 0.5-y, z+0.5)$

DISCUSSION OF THE STRUCTURE

The structural feature of particular interest of *O*-carbamoylhydroxylamine is the geometry of the molecule compared with the geometry of the isomeric compound hydroxyurea.^{4,5}

The molecular skeleton was found to be planar, as was the case for hydroxyurea. The deviations of the heavy atoms from the least-squares plane through these atoms are insignificant (Fig. 2). The deviations of the N(2)-bonded H-atoms from this plane are larger, but probably not significant. The N(1)-bonded H-atoms, on the other hand, are not included in the coplanarity, H(1) and H(2) are situated approximately symmetrically on each side of the molecular plane.

In the crystalline state the *O*-carbamoylhydroxylamine molecule has adopted a conformation, in which the carbonyl group and the N—O bond are situated *trans* with respect to the central C—O single bond. A similar *s trans* conformation was found in hydroxyurea with respect to the central C—N single bond. This arrangement is the opposite of the observations of Schmidt,¹⁵ concerning saturated and unsaturated carboxylic acids, esters and amides. In all these structures, and also in a series of *n*-aliphatic amides¹⁶ and in acrylamide,¹⁷ the flat or nearly flat molecules have adopted O=C—C—C *cis* conformation. The reason for *trans* conformation in *O*-carbamoylhydroxylamine and hydroxyurea may be, that this arrangement provides as much space as possible around the carbonyl oxygen atom. This seems to be favourable, because the oxygen atoms of both compounds are acceptors for more than two hydrogen bonds, four and three, respectively. In the stable and

Table 5. Observed and calculated structure factors.

H	K	L	F(OBS)	F(CALC)															
					10	0	C	6.794	7.951	4	14	1	1.487	1.441					
					10	1	C	2.947	3.315	4	15	1	4.017	4.166					
					10	2	C	2.423	2.064	5	1	1	11.943	11.715					
					10	3	C	2.988	2.985	5	2	1	18.247	18.456					
					10	4	C	3.940	4.275	5	3	1	8.612	8.047					
					10	5	C	3.311	3.646	5	4	1	7.817	7.144					
					10	6	C	1.886	1.813	5	5	1	4.999	4.382					
					0	2	1	7.565	8.128	5	6	1	4.182	3.260					
					0	4	1	18.430	31.388	5	7	1	5.485	4.917					
					0	6	1	6.441	6.540	5	8	1	4.965	4.261					
					0	8	1	9.804	10.142	5	9	1	3.859	3.208					
					0	10	1	2.327	1.412	5	10	1	10.389	10.568					
					0	12	1	3.388	2.793	5	11	1	6.965	6.589					
					0	14	1	3.589	2.926	5	13	1	3.641	3.546					
					0	16	1	2.754	2.101	5	14	1	4.594	4.628					
					1	1	1	20.300	25.375	5	15	1	1.787	2.038					
					1	2	1	20.121	27.165	6	2	1	4.707	3.555					
					1	3	1	25.235	37.407	6	3	1	7.374	7.065					
					1	4	1	19.993	26.906	6	4	1	5.280	4.727					
					1	5	1	9.444	10.033	6	5	1	3.126	3.160					
					1	6	1	12.376	14.050	6	6	1	2.893	2.494					
					1	7	1	5.286	5.478	6	7	1	5.854	5.679					
					1	8	1	13.804	16.414	6	8	1	0.705	0.403					
					1	9	1	8.341	8.510	6	10	1	2.913	2.893					
					1	11	1	8.311	7.030	6	11	1	1.397	1.554					
					1	12	1	5.460	4.676	6	12	1	3.160	3.166					
					1	13	1	2.131	1.780	7	1	1	9.227	8.857					
					1	14	1	4.840	4.423	7	3	1	4.973	4.459					
					1	15	1	5.369	4.559	7	4	1	13.576	15.038					
					1	16	1	1.494	1.679	7	5	1	8.390	8.294					
					1	17	1	3.272	3.255	7	6	1	6.862	6.303					
					1	18	1	3.888	3.051	7	7	1	2.297	1.844					
					2	1	1	14.800	16.297	7	8	1	9.298	10.256					
					2	2	1	6.214	5.674	7	9	1	4.596	4.534					
					2	3	1	7.369	7.160	7	10	1	4.924	5.121					
					2	4	1	17.065	20.096	7	11	1	4.287	4.652					
					2	5	1	9.699	10.774	8	1	1	2.753	2.359					
					2	6	1	4.226	2.906	8	2	1	2.744	2.275					
					2	7	1	7.807	8.733	8	3	1	2.304	2.797					
					2	8	1	7.881	8.020	8	4	1	6.534	5.998					
					2	9	1	1.635	0.254	8	6	1	3.349	2.810					
					2	10	1	2.093	1.209	8	8	1	1.929	1.649					
					2	12	1	2.536	2.630	8	9	1	1.752	1.940					
					2	14	1	1.744	1.833	8	10	1	3.016	2.856					
					2	15	1	2.072	1.897	9	1	1	2.971	2.557					
					2	16	1	1.668	2.064	9	2	1	6.893	7.126					
					3	2	1	8.882	7.017	9	4	1	3.530	3.283					
					3	3	1	3.319	2.280	9	5	1	3.376	3.656					
					3	4	1	7.963	6.868	9	6	1	3.544	3.976					
					3	5	1	2.212	1.466	9	8	1	3.964	3.997					
					3	6	1	4.310	3.677	10	1	1	2.504	2.309					
					3	7	1	0.744	0.738	10	4	1	3.201	3.438					
					3	8	1	9.449	8.903	0	0	2	26.796	42.950					
					3	9	1	6.220	5.187	0	2	2	15.297	18.423					
					3	10	1	4.739	4.152	0	4	2	16.852	21.965					
					3	11	1	0.932	1.030	0	6	2	7.776	7.219					
					3	12	1	2.984	2.778	0	8	2	2.237	1.406					
					3	13	1	5.208	4.984	0	10	2	11.781	12.311					
					3	16	1	3.054	2.056	0	12	2	5.728	4.993					
					4	1	1	7.837	6.393	0	14	2	11.148	11.083					
					4	2	1	9.472	8.768	0	16	2	3.497	3.800					
					4	3	1	11.306	10.729	1	0	2	1.663	1.618					
					4	4	1	0.664	0.444	1	1	2	12.500	13.571					
					4	5	1	8.033	7.253	1	2	2	1.191	1.155					
					4	6	1	2.777	2.192	1	3	2	6.149	4.795					
					4	7	1	10.429	10.125	1	4	2	1.801	1.295					
					4	8	1	0.668	0.486	1	5	2	12.492	13.143					
					4	9	1	0.706	1.459	1	6	2	3.183	2.675					
					4	10	1	0.731	0.989	1	7	2	11.394	11.623					
					4	11	1	0.736	1.045	1	8	2	2.170	2.385					
					4	12	1	1.629	1.154	1	9	2	1.840	1.507					
					4	13	1	1.930	2.094	1	10	2	1.220	0.902					

Table 5. Continued.

1	11	2	6.864	6.012	7	4	2	3.752	3.294	3	10	3	7.665	6.697
1	12	2	2.081	2.080	7	5	2	2.763	2.168	3	11	3	0.926	1.047
1	13	2	3.927	3.003	7	6	2	5.646	5.664	3	12	3	1.226	1.078
1	15	2	0.820	1.234	7	7	2	1.185	0.926	3	13	3	1.412	1.715
1	16	2	0.721	0.677	7	8	2	1.132	0.898	3	14	3	1.470	1.779
2	0	2	20.907	22.256	7	10	2	1.513	1.564	3	15	3	0.904	1.103
2	1	2	11.839	11.789	7	11	2	1.425	1.463	4	1	3	14.275	13.400
2	2	2	18.231	18.231	7	12	2	2.277	2.151	4	2	3	13.184	11.866
2	3	2	1.658	0.709	8	0	2	14.649	16.180	4	3	3	8.553	7.275
2	4	2	10.340	10.104	8	1	2	7.073	6.544	4	4	3	1.306	0.904
2	5	2	6.787	6.443	8	2	2	3.988	3.450	4	5	3	1.304	1.437
2	6	2	20.183	22.449	8	3	2	5.119	5.314	4	6	3	5.492	5.158
2	7	2	10.261	10.157	8	4	2	7.177	6.943	4	7	3	3.072	2.931
2	8	2	4.013	2.641	8	6	2	6.939	6.621	4	8	3	3.665	2.557
2	9	2	7.016	6.962	8	7	2	2.813	1.617	4	9	3	7.388	7.189
2	10	2	5.405	5.205	8	8	2	3.894	3.732	4	11	3	3.387	3.025
2	11	2	7.364	6.943	8	9	2	4.486	4.561	4	12	3	4.014	3.578
2	12	2	3.908	3.212	8	10	2	3.530	4.046	4	13	3	3.344	3.467
2	13	2	1.094	1.212	9	0	2	1.975	2.002	4	14	3	1.532	1.921
2	14	2	2.675	2.143	9	1	2	2.986	3.212	5	1	3	8.598	8.179
2	15	2	0.944	1.176	9	2	2	1.036	1.132	5	2	3	5.136	4.280
2	16	2	0.648	0.932	9	5	2	2.635	2.703	5	3	3	8.520	7.734
3	0	2	1.277	1.283	9	6	2	2.581	2.581	5	4	3	1.299	1.070
3	1	2	11.469	11.003	9	8	2	1.980	1.734	5	7	3	1.352	1.485
3	2	2	9.286	7.937	10	0	2	1.512	0.880	5	8	3	1.988	1.924
3	3	2	4.840	3.694	10	1	2	1.296	1.529	5	9	3	1.308	1.043
3	4	2	2.217	1.100	10	3	2	2.366	2.541	5	10	3	3.965	3.828
3	5	2	8.683	8.063	10	4	2	1.197	2.458	5	11	3	4.879	4.955
3	6	2	12.078	11.812	0	2	3	18.235	21.428	5	12	3	1.619	1.942
3	8	2	3.415	2.936	0	4	3	2.950	2.557	5	13	3	1.906	1.785
3	9	2	0.903	0.664	0	6	3	6.927	6.051	6	1	3	10.366	9.743
3	10	2	5.085	4.453	0	8	3	7.040	6.303	6	2	3	7.632	6.727
3	11	2	0.931	0.880	0	10	3	13.100	12.801	6	3	3	8.454	7.857
3	12	2	2.553	2.454	0	12	3	5.547	5.220	6	4	3	6.389	5.720
3	13	2	4.244	3.573	0	14	3	4.234	3.521	6	5	3	1.417	1.132
4	0	2	3.449	3.258	1	1	3	3.570	3.127	6	7	3	1.318	0.270
4	1	2	1.606	1.629	1	2	3	10.556	10.253	6	8	2	3.744	3.650
4	2	2	10.732	9.551	1	3	3	8.380	7.864	6	9	3	4.356	3.965
4	3	2	5.509	4.050	1	4	3	14.816	15.730	6	10	3	3.273	3.331
4	4	2	1.226	1.106	1	5	3	4.410	3.231	6	11	3	3.096	2.821
4	5	2	9.484	9.125	1	6	3	7.930	8.167	7	1	3	8.409	7.755
4	6	2	9.436	9.170	1	7	3	1.152	0.508	7	2	3	4.124	3.641
4	9	2	2.806	2.175	1	8	3	10.259	10.726	7	3	3	3.514	3.391
4	11	2	2.042	2.200	1	9	3	2.031	1.664	7	4	3	7.759	7.425
4	12	2	3.124	3.062	1	10	3	1.966	1.840	7	5	3	5.446	4.818
4	13	2	4.785	4.442	1	11	3	4.542	3.802	7	6	3	4.377	4.156
4	14	2	4.458	4.475	1	12	3	3.587	3.088	7	7	2	2.927	2.252
5	0	2	15.127	14.182	1	13	3	4.174	3.616	7	8	3	3.657	3.969
5	1	2	4.715	3.279	1	14	3	2.779	2.842	7	9	3	1.009	0.923
5	2	2	5.952	4.503	1	15	3	1.688	1.608	7	10	3	1.223	1.200
5	3	2	3.645	2.253	2	1	3	4.859	3.513	7	11	3	2.988	3.475
5	4	2	10.256	8.930	2	2	3	12.907	11.763	8	1	3	1.518	1.674
5	5	2	2.452	2.236	2	4	3	5.276	4.976	8	2	3	7.147	6.738
5	6	2	5.165	4.602	2	5	3	5.792	5.007	8	3	3	3.790	4.024
5	10	2	1.352	1.252	2	6	3	4.487	3.747	8	4	2	2.742	2.468
5	12	2	4.307	3.969	2	7	3	3.384	3.143	8	5	3	2.505	2.095
5	13	2	0.656	0.417	2	8	3	6.840	6.478	8	6	3	1.054	0.427
5	14	2	3.137	3.444	2	9	3	9.522	9.797	8	7	3	1.932	2.152
6	0	2	3.682	2.829	2	10	3	7.723	6.875	8	8	3	1.196	1.070
6	1	2	2.713	1.764	2	12	3	3.194	3.086	8	9	3	2.713	2.753
6	2	2	2.942	2.354	2	13	3	5.095	5.030	9	2	3	2.396	2.148
6	3	2	15.173	15.548	2	14	3	1.021	1.340	9	3	3	2.209	2.598
6	4	2	3.318	2.298	2	15	3	2.752	2.778	9	4	3	4.105	4.426
6	5	2	9.612	9.203	3	1	3	5.060	3.841	9	5	2	3.483	4.050
6	7	2	13.111	13.871	3	2	3	14.999	14.010	9	6	3	1.079	1.699
6	9	2	2.749	2.582	3	3	3	7.031	6.321	0	0	4	18.711	20.255
6	10	2	4.455	4.448	3	4	3	1.806	0.892	0	2	4	7.174	6.584
6	11	2	2.794	2.936	3	5	3	3.781	3.648	0	4	4	6.706	6.231
6	13	2	1.063	0.979	3	6	3	3.590	2.803	0	6	4	12.764	13.260
7	0	2	6.300	5.767	3	7	3	2.276	1.844	0	8	4	7.037	6.298
7	1	2	2.775	2.115	3	8	3	3.181	2.442	0	10	4	7.631	6.871
7	2	2	4.101	3.791	3	9	3	2.208	2.162	0	12	4	2.923	2.736

Table 5. Continued.

0	14	4	0.708	0.566	7	3	4	3.243	2.813	7	2	5	2.438	2.908
1	0	4	2.087	2.062	7	4	4	2.573	2.288	7	3	5	2.745	2.283
1	1	4	5.800	5.229	7	6	4	3.679	3.298	0	0	6	3.106	2.729
1	3	4	3.465	2.781	7	8	4	0.945	0.980	0	10	6	3.189	3.276
1	5	4	4.048	3.350	7	9	4	0.737	0.859	1	0	6	1.683	1.586
1	7	4	9.670	9.927	8	0	4	4.151	4.501	1	1	6	3.140	2.995
1	8	4	3.599	3.026	8	2	4	3.558	3.591	1	3	6	4.516	4.458
1	10	4	1.337	1.380	8	3	4	1.990	1.816	1	4	6	1.127	1.042
1	11	4	6.906	6.483	8	4	4	3.239	3.083	1	7	6	2.135	1.870
1	12	4	1.862	1.831	8	5	4	2.201	2.169	2	0	6	9.595	9.226
1	14	4	1.718	1.601	8	6	4	3.053	3.378	2	1	6	7.774	7.278
2	0	4	8.353	7.738	0	2	5	3.232	3.296	2	2	6	0.921	0.820
2	1	4	7.200	6.338	0	4	5	8.591	7.525	2	3	6	3.260	3.106
2	2	4	2.338	1.932	0	6	5	1.430	1.355	2	4	6	4.351	4.109
2	3	4	7.762	6.952	0	8	5	4.683	4.224	2	5	6	1.459	1.465
2	4	4	7.239	6.481	0	10	5	0.997	1.137	2	6	6	0.794	0.809
2	5	4	7.527	7.435	0	12	5	0.499	0.710	2	7	6	2.531	2.700
2	6	4	1.766	1.540	1	1	5	0.445	0.526	2	8	6	3.218	3.258
2	7	4	7.312	7.088	1	2	5	2.068	1.743	2	9	6	3.524	3.839
2	8	4	2.066	1.540	1	3	5	3.471	3.861	3	0	6	7.988	7.800
2	10	4	1.678	1.859	1	4	5	9.048	8.718	3	1	6	0.817	0.832
2	12	4	3.514	3.275	1	6	5	2.418	2.221	3	2	6	1.976	2.214
2	13	4	3.617	3.283	1	7	5	4.158	3.832	3	3	6	2.733	2.401
2	14	4	1.983	2.259	1	8	5	5.393	5.239	3	4	6	4.899	4.559
3	0	4	1.137	0.983	1	9	5	0.836	1.158	3	6	6	3.161	3.283
3	1	4	8.055	7.016	1	10	5	0.507	0.923	3	7	6	3.761	4.009
3	2	4	4.048	3.130	1	11	5	0.576	0.659	4	0	6	1.811	1.349
3	3	4	5.932	5.189	2	1	5	8.047	7.454	4	1	6	5.125	4.018
3	4	4	4.123	3.812	2	2	5	4.297	3.864	4	2	6	5.146	4.173
3	5	4	3.423	2.842	2	3	5	1.928	1.113	4	3	6	0.574	1.003
3	6	4	7.064	6.846	2	4	5	7.602	6.661	4	6	6	5.924	6.409
3	7	4	1.162	1.118	2	5	5	7.915	7.500	4	7	6	3.376	3.913
3	8	4	5.369	5.015	2	7	5	2.993	2.904	5	0	6	2.665	3.204
3	9	4	1.362	1.272	2	8	5	4.127	3.806	5	3	6	1.013	1.515
3	10	4	5.594	5.723	2	9	5	2.693	2.740	5	4	6	3.121	3.486
3	12	4	0.966	1.140	2	10	5	0.886	1.319	6	1	6	1.673	2.017
3	13	4	2.600	2.645	2	11	5	1.678	1.907	0	4	7	3.872	3.868
4	0	4	5.572	5.225	2	12	5	0.592	0.953	1	1	7	2.382	2.910
4	1	4	1.052	0.279	3	1	5	1.769	1.395	1	2	7	1.096	1.645
4	2	4	8.027	6.864	3	2	5	9.616	8.663	1	4	7	2.248	2.290
4	3	4	9.079	8.557	3	3	5	7.917	6.878	1	5	7	0.962	1.521
4	5	4	8.304	8.124	3	4	5	5.688	5.087	2	1	7	1.679	1.814
4	6	4	9.494	8.722	3	5	5	5.162	4.862	2	2	7	1.897	2.456
4	7	4	4.710	4.271	3	7	5	3.469	3.411	2	3	7	2.972	3.357
4	8	4	2.356	2.295	3	9	5	3.837	3.685	2	4	7	2.897	1.867
4	9	4	3.839	4.021	3	10	5	4.467	4.410	3	2	7	5.404	6.027
4	10	4	1.767	1.543	3	11	5	1.049	1.374					
4	11	4	1.527	1.456	4	1	5	2.629	2.020					
5	0	4	15.533	14.672	4	2	5	7.615	7.179					
5	1	4	1.440	1.329	4	3	5	3.678	3.067					
5	3	4	1.336	1.238	4	4	5	4.282	4.094					
5	4	4	8.214	7.576	4	5	5	2.391	2.270					
5	5	4	1.464	1.515	4	6	5	4.679	4.059					
5	6	4	1.169	0.673	4	7	5	3.771	3.351					
5	7	4	1.746	1.811	4	8	5	5.407	5.270					
5	8	4	1.474	1.495	4	9	5	1.757	1.509					
5	10	4	1.637	1.919	4	10	5	0.394	0.710					
5	11	4	1.337	1.458	5	1	5	5.188	4.851					
5	12	4	2.436	2.769	5	2	5	1.962	1.511					
6	0	4	9.776	8.934	5	3	5	5.114	4.462					
6	2	4	3.329	2.691	5	4	5	6.119	5.403					
6	3	4	3.516	3.309	5	6	5	0.859	1.191					
6	4	4	3.412	3.109	5	7	5	0.807	0.974					
6	5	4	2.803	2.503	5	8	5	3.624	4.149					
6	6	4	5.094	5.032	5	9	5	1.186	1.432					
6	7	4	4.899	4.793	6	1	5	1.007	1.291					
6	8	4	3.676	3.436	6	2	5	0.996	0.957					
6	9	4	1.183	1.355	6	3	5	4.150	4.018					
6	10	4	1.342	1.560	6	4	5	1.415	1.362					
7	0	4	5.217	4.849	6	6	5	2.077	2.078					
7	1	4	3.332	2.822	6	7	5	2.374	2.512					
7	2	4	1.904	1.838	7	1	5	2.001	2.214					

unstable form of chloroacetamide^{18,19} *trans* conformation of C=O and C—Cl was found with respect to the C—C single bond. The explanation suggested by Katayama¹⁹ is, that the electrostatic force between the two large dipoles of the C=O and C—Cl bonds will bring the molecule to *trans* conformation of these bonds. This explanation may be valid for hydroxyurea too, but not for *O*-carbamoylhydroxylamine.

The bond lengths and angles in *O*-carbamoylhydroxylamine (Table 3 and Fig. 2) are in good agreement with corresponding bonds and angles in hydroxyurea.^{4,5} The C=O bond in *O*-carbamoylhydroxylamine (1.242 Å) is shorter than the C=O bond in hydroxyurea (1.253 Å), but probably not significant¹³ (Vol. II, p. 90).

The C—O single bond has no corresponding bond in hydroxyurea, but is of normal length. The N—O bonds of the two molecules are not directly

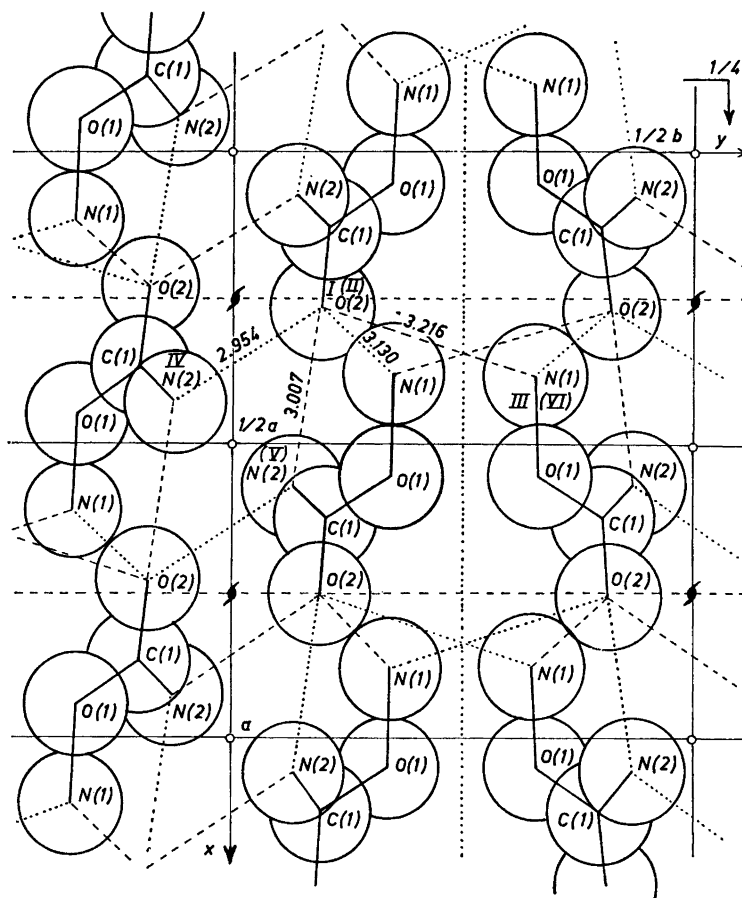


Fig. 3. The structure viewed along the *c*-axis. Broken lines indicate hydrogen bonds between atoms in the same layer of molecules, dotted lines hydrogen bonds to atoms above or below this layer.

comparable, because of different hybridization of the two nitrogen atoms, *i.e.* plane trigonal configuration in hydroxyurea and pyramidal configuration in *O*-carbamoylhydroxylamine. The length of the bond in the last molecule (1.458 Å) is in agreement with that found for the N—O bond in hydroxylamine²⁰ (1.47 ± 0.03 Å).

The large difference between the two angles adjoining the carbonyl bond observed in hydroxyurea is even more prominent in *O*-carbamoylhydroxylamine (Fig. 2). The explanation earlier suggested⁴ is not applicable in this case, but the observation follows the correlation of bond length with bond angles observed by Katayama,¹⁹ *i.e.* when the C—N bond length of amides,

$$\text{O}=\text{C} \begin{array}{l} \diagup \text{NH}_2 \\ \diagdown \text{X} \end{array}$$
 is about 1.30 Å the N—C—O angle is larger than the X—C—O

angle, and when the C—N bond length is about 1.38 Å the X—C—O angle is larger than the N—C—O angle. These relations are explained by the existence of repulsion between the non-bonded N and O atoms.

The most prominent feature of the *intermolecular* contacts is the three-dimensional system of hydrogen bonds, involving all the hydrogen atoms of the molecule. The carbonyl oxygen atom O(2) is acceptor for all of them, whereas the oxygen atom O(1) is not involved in hydrogen bonding (Table 4 and Fig. 3). The carbonyl oxygen atom is acceptor for hydrogen bonds from four different molecules, and the directions to the donor atoms form a rather regular, tetragonal pyramid (Table 4).

The NH—O hydrogen bonds are rather long, 2.95–3.22 Å. This is in agreement with observations by Lindgren and Olovsson,²¹ who found a lengthening of the NH—X bonds with increased coordination number of X in a series of ammonium and alkylammonium halides. The NH—O bond across the *c*-glide plane (3.216 Å) must be very weak. This is in agreement with the physical fact, that the crystals seemed indisposed to grow in the *b*-direction. None of the non hydrogen bonded *intermolecular* contacts are remarkable short.

Acknowledgement. The author wishes to thank Professor B. Jerslev for her great interest in this work and valuable comments on the manuscript.

REFERENCES

1. Exner, O. and Horák, M. *Chem. Listy* **52** (1958) 1613.
2. Davies, M. and Spiers, N. A. *Spectrochim. Acta* **15** (1959) 487.
3. Kofod, H. *Oxyurinstof*, (Diss.), University, Copenhagen 1960.
4. Larsen, I. K. and Jerslev, B. *Acta Chem. Scand.* **20** (1966) 983.
5. Berman, H. and Kim, S. H. *Acta Cryst.* **23** (1967) 180.
6. Kofod, H. *Acta Chem. Scand.* **7** (1953) 938.
7. Hamilton, W. C., Rollet, J. S. and Sparks, R. A. *Acta Cryst.* **18** (1965) 129.
8. Weissberger, A. *Physical Methods in Organic Chemistry*; Lipscomb, W. N. *X-Ray Crystallography*, Interscience, New York 1960, p. 1695.
9. Bhuiya, A. K. and Stanley, E. *Acta Cryst.* **16** (1963) 981.
10. Danielsen, J. ALGOL program D45, University of Aarhus, Denmark.

11. Busing, W. R., Martin, K. O. and Levy, H. A. (1962), Full Matrix Least-Squares Program (FORTRAN), Oak Ridge National Laboratory, Oak Ridge, Tennessee.
12. Hughes, E. W. *J. Am. Chem. Soc.* **63** (1941) 1737.
13. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962.
14. Sly, W. G., Shoemaker, D. P. and Van den Hende, J. H. (1962), Two- and Three Dimensional Crystallographic Fourier Summation Program for the IBM 7090 Computer, Massachusetts Institute of Technology, Esso Research and Engineering Company, Massachusetts.
15. Leiserowitz, L. and Schmidt, G. M. J. *Acta Cryst.* **18** (1965) 1058.
16. Turner, J. D. and Lingafelter, E. C. *Acta Cryst.* **8** (1955) 549.
17. Isakov, I. V. *Zh. Strukt. Khim.* **7** (1966) 898.
18. Penfold, B. R. and Simpson, W. S. *Acta Cryst.* **9** (1956) 831.
19. Katayama, M. *Acta Cryst.* **9** (1956) 986.
20. Meyers, E. A. and Lipscomb, W. N. *Acta Cryst.* **8** (1955) 583.
21. Lindgren, J. and Olovsson, I. *Acta Cryst.* **B 24** (1968) 554.

Received October 4, 1967.