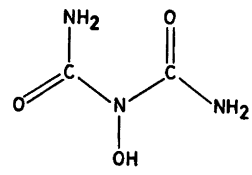
Acta Chemica Scandinavica B 30 (1976) 533—541

The Crystal Structures of 3-Hydroxybiuret and 3-Hydroxybiuret Hemihydrate

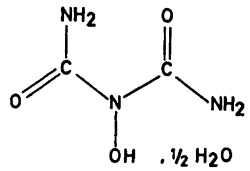
INGRID KJØLLER LARSEN

The Royal Danish School of Pharmacy, Department of Chemistry BC, Universitetsparken 2, DK-2100 Copenhagen, Denmark

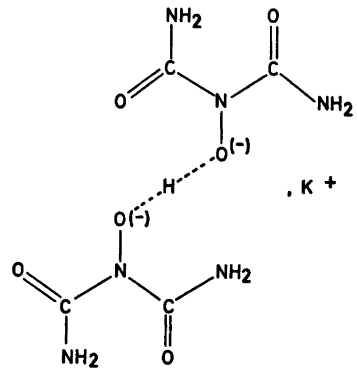
The crystal structures of 3-hydroxybiuret $HON(CONH_2)_2$ and 3-hydroxybiuret hemihydrate $HON(CONH_2)_2 \cdot \frac{1}{2}H_2O$ have been determined using three-dimensional diffractometer-collected X-ray data. The structures were solved by direct phasing techniques and Patterson methods and refined by full-matrix least-squares calculations to give a final R-value of 0.040 for 3-hydroxybiuret and 0.035 for 3-hydroxybiuret hemihydrate. The conformations of the molecules were found to be the same in the two crystal structures, *i.e.* with an *intra*-molecular NH···O=C bond. This conformation was also found in the crystal structure of the potassium acid salt of the compound.[1] The molecules are connected by three-dimensional systems of hydrogen bonds in both structures. The pK_A value of 3-hydroxybiuret was determined to 9.18 ± 0.06.



3-HB



3-HB.½ H_2O



3-HBK

Scheme 1.

The structure determination of 3-hydroxybiuret, $HON(CONH_2)_2$, was undertaken as part of an X-ray study of hydroxylamine derivatives, which are inhibitors of DNA synthesis in several cell systems. The crystal structure of the potassium acid salt of the compound (3-HBK) has been described earlier.[1]

In this paper the crystal structures of the hemihydrate (3-HB.$\frac{1}{2}H_2O$) and the anhydrous compound (3-HB) are reported. Knowledge of the molecular structure of 3-HB in three different crystal structures provides the opportunity to observe the effect of different environments on the dimensions and conformation of the molecule.

As earlier proposed by Zinner and Hitze,[2] it now seems to be evident that the compound prepared by Losee and Bernstein [3] is 3-hydroxybiuret and not the isomeric compound

N,O-dicarbamoylhydroxylamine as postulated. The 3-HB used in the present study was prepared by the same method as that used by Losee and Bernstein, and the melting point reported by these authors is identical with that found for 3-HB (158–160 °C). No other physical data were reported.[3]

EXPERIMENTAL

3-Hydroxybiuret was obtained by treatment of the potassium acid salt[1] with a strongly acidic ion-exchange resin [Amberlite IR-120 (H)], using hydrochloric acid (4 M) as an eluent. Recrystallization of the crude product from aqueous ethanol gave thin, colourless crystals, m.p. 158–160 °C. The pK_A value of the compound was determined to 9.18 ± 0.06 by electrometrical titration in aqueous solution at 22 °C, according to the method described by Albert and Serjeant.[4] The pH values were measured on a Radiometer pH meter 26. Crystals suitable for X-ray work of 3-HB and 3-HB.$\frac{1}{2}H_2O$ were obtained by diffusion (at room temperature) of ether into saturated solutions of the compound in ethanol and aqueous ethanol, respectively.

Some crystal data of 3-HB and 3-HB.$\frac{1}{2}H_2O$ are given in Table 1. The density of 3-HB was measured by flotation in a mixture of bromobenzene and methyl iodide, and of 3-HB.$\frac{1}{2}H_2O$ in a mixture of carbon tetrachloride and methyl iodide. The melting points were determined with a hot stage microscope (Mikroskop Heiztisch Ernst Leitz G.m.b.H., Wetzlar).

The lattice parameters of both compounds were calculated from series of diffractometer-measured θ-values. The intensity data sets were collected on a NONIUS three-circle automatic diffractometer by the moving crystal-stationary detector technique, using graphite monochromatized Mo$K\alpha$-radiation ($\lambda = 0.71069$ Å). The scan speed was 1.2 °/min and each reflexion was scanned over a range of 1.2 °. Background counts were taken for half the scanning time at each of the scan range limits. One standard reflexion was measured for every 25 reflexions.

The crystal of 3-HB chosen for data collection was of the size $0.10 \times 0.14 \times 0.60$ mm³, and was mounted in a glass capillary, oriented with the *c*-axis parallel to the ϕ-axis of the goniostat. Intensities of reflexions were measured in the range $2.5° < \theta < 25.0°$, and each of the 467 independent reflexions were measured twice; 662 of the 934 reflexions (*hkl* and $\bar{h}kl$) had $I_{net} \geq 2.5\ \sigma(I)$ and were considered observed. The reflexions from both octants were used independently in the least-squares refinement.

The crystal of 3-HB.$\frac{1}{2}H_2O$ chosen for data collection was of the size $0.16 \times 0.32 \times 0.80$ mm³.

Table 1. Crystal data for 3-HB and 3-HB.$\frac{1}{2}H_2O$.

	3-HB	3-HB.$\frac{1}{2}H_2O$
Mol. formula	$C_2H_5N_3O_3$	$C_2H_5N_3O_3.\frac{1}{2}H_2O$
Mol. weight	119.1	128.1
Melting point, °C	156–157	158–160
Space group	$P2_12_12_1$	$C2$
a, Å	10.868(7)	19.821(5)
b, Å	11.698(7)	4.093(1)
c, Å	3.603(2)	6.286(2)
β, °		92.96(3)
V, Å³	458.06	509.14
Z	4	4
D_x, g cm^{-3}	1.73	1.67
D_m, g cm^{-3}	1.73	1.68
μMo$K\alpha$, cm^{-1}	1.72	1.69

The hemihydrate of 3-HB has a great tendency to form double crystals, which usually could be observed on the Weissenberg films (double spots). The crystal chosen for data collection also proved to be imperfect in spite of the fact that the Weissenberg films seemed to be normal. The imperfection of the crystal was observed only on the recorder of the diffractometer (double maxima of the peaks within the θ scan range of 1.2 °). The crystal was mounted in a glass capillary and oriented with the *b*-axis parallel to the ϕ-axis of the goniostat. Intensities of reflexions were measured in the range $2.5 < \theta < 25.0°$; 492 of the 511 independent reflexions had $I_{net} \geq 2.5\ \sigma(I)$ and were considered observed.

The data of 3-HB and 3-HB.$\frac{1}{2}H_2O$ were corrected for Lorentz and polarization effects, but no corrections for absorption or extinction were made.

STRUCTURE DETERMINATION

3-HB. The structure was solved by direct methods in a straightforward way using the programs of the X-RAY system.[5] An *E*-map based on 133 $E(hkl)$'s with $|E(hkl)| \geq 1.4$ revealed the positions of the eight non-hydrogen atoms of the molecule. A structure factor calculation based on these eight positions resulted in a conventional *R*-value of 0.24. Two cycles of full-matrix least-squares refinement in which positional as well as individual atomic, isotropic thermal parameters were varied, reduced the *R*-value to 0.087. The five hydrogen atoms were located in the difference Fourier map, and two cycles of anisotropic least-squares refinement with all H-atom parameters fixed

Table 2. Fractional coordinates and thermal parameters for 3-HB and 3-HB.$\frac{1}{2}H_2O$. The thermal parameters are $\times 10^3$ and of the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
3-HB									
N(1)	0.6226(3)	0.4816(3)	1.0744(11)	3.4(2)	2.7(1)	3.9(2)	−0.1(1)	0.1(2)	−0.7(2)
C(2)	0.5400(3)	0.4117(3)	0.9156(12)	3.1(2)	2.8(2)	2.9(3)	−0.4(1)	0.5(2)	0.5(2)
O(2)	0.4347(2)	0.4383(2)	0.8381(9)	2.3(1)	3.8(1)	5.8(2)	0.1(1)	−0.2(2)	0.4(2)
N(3)	0.5812(2)	0.3008(2)	0.8333(10)	2.2(1)	2.6(1)	3.8(2)	−0.3(1)	−0.6(2)	−0.3(2)
O(3)	0.4963(2)	0.2313(2)	0.6522(9)	2.5(1)	4.2(2)	4.3(2)	−0.7(1)	0.1(2)	−0.8(2)
C(4)	0.6950(3)	0.2516(3)	0.9077(12)	2.8(2)	2.5(2)	3.3(2)	0.0(1)	0.4(2)	0.4(2)
O(4)	0.7794(2)	0.3116(2)	1.0323(8)	2.6(1)	3.2(1)	5.2(2)	−0.3(1)	−1.3(1)	−0.4(1)
N(5)	0.7048(3)	0.1428(3)	0.8293(13)	2.7(2)	2.9(2)	6.7(3)	0.2(1)	−1.1(2)	−0.4(2)
3-HB.$\frac{1}{2}H_2O$									
N(1)	0.0735(1)	0.3286(14)	0.8521(4)	2.84(12)	5.83(18)	3.73(18)	0.51(14)	−0.64(9)	−0.82(16)
C(2)	0.1332(1)	0.2074(13)	0.9134(4)	2.85(13)	3.05(16)	2.73(12)	−0.44(13)	0.06(10)	0.13(13)
O(2)	0.1635(1)	0.0043(12)	0.8108(3)	3.67(10)	4.08(13)	3.31(9)	0.58(12)	−0.53(7)	−1.02(12)
N(3)	0.1635(1)	0.3277(12)	1.1037(3)	2.45(10)	3.92(14)	3.07(11)	0.15(11)	−0.27(8)	−0.16(12)
O(3)	0.2241(1)	0.1707(12)	1.1668(3)	2.75(9)	3.67(12)	3.61(10)	0.06(10)	−0.65(7)	0.46(10)
C(4)	0.1341(1)	0.5206(13)	1.2573(4)	3.62(14)	3.27(15)	2.85(12)	−0.42(16)	0.59(10)	0.02(15)
O(4)	0.0797(1)	0.6569(13)	1.2183(3)	4.36(13)	5.84(16)	3.89(11)	1.23(12)	0.47(9)	−0.85(13)
N(5)	0.1700(2)	0.5457(13)	1.4418(4)	5.38(15)	5.05(18)	2.68(11)	0.22(16)	−0.01(11)	−0.55(14)
O(6)	0.0	0.0	0.5	3.63(15)	4.57(19)	3.39(13)	0.0	−0.12(11)	0.0

Table 3. Fractional coordinates and thermal parameters ($\times 10^3$) for the hydrogen atoms of 3-HB and 3-HB.$\frac{1}{2}H_2O$.

	x	y	z	U
3-HB				
H(11)	0.697(4)	0.452(4)	1.140(15)	4.05
H(12)	0.596(4)	0.552(4)	1.134(17)	4.05
H(3)	0.428(5)	0.226(4)	0.767(17)	4.56
H(51)	0.641(4)	0.101(4)	0.744(17)	4.81
H(52)	0.772(5)	0.110(4)	0.891(19)	4.81
3-HB.$\frac{1}{2}H_2O$				
H(11)	0.055(2)	0.508(16)	0.934(7)	4.09
H(12)	0.052(2)	0.227(14)	0.732(7)	4.09
H(3)	0.259(2)	0.304(13)	1.126(6)	3.29
H(51)	0.205(2)	0.470(16)	1.456(7)	4.12
H(52)	0.157(2)	0.689(16)	1.545(7)	4.12
H(6)	0.025(2)	−0.156(16)	0.431(7)	3.75

reduced the R-value to 0.049. In the remaining two cycles of refinement the positional parameters of the H-atoms were also varied, but the isotropic thermal parameters were set equal to the parameters of the atoms to which they are bonded, and were still fixed. The final R-value is 0.040.

3-HB.$\frac{1}{2}H_2O$. Several attempts to solve this structure by the direct phasing method failed, and the structure was finally solved from the sharpened Patterson map in combination with packing considerations. Least-squares refinement of a first trial structure converged at a false minimum with an R-value of 0.30. The right solution was achieved after moving the positions of all the atoms of the molecule about 0.5 Å in the x-direction. Full-matrix least-squares refinement of the scale factor, atomic positions, and isotropic thermal parameters yielded an R-value of 0.073. The six hydrogen atoms of the structure were located in the difference map. The hydrogen atoms of the water molecule are symmetry related because the water oxygen atom was found in the special position (0, y, $\frac{1}{2}$). In the succeeding anisotropic least-squares refinement the positional parameters of the H-atoms were also varied, but the isotropic thermal parameters (set equal to the parameters of the atoms to which they are bonded) were fixed. The final R-value is 0.035.

All the refinements were based on F, minimizing the function $\sum w(|F_o|-|F_c|)^2$, where the weights were initially taken as unity but later changed as follows: $w=1/\{1+[(F_o-B)/A]^2\}$ with $A=10.0$ and $B=15.0$ for 3-HB, and A= B=8.0 for 3-HB.$\frac{1}{2}H_2O$. The scattering factors were taken from *International Tables for X-Ray Crystallography*.[6] Final parameters for the heavy atoms of 3-HB and 3-HB.$\frac{1}{2}H_2O$ are given in Table 2, while the hydrogen atom parameters are given in Table 3. The notation of the atoms is given in Figs. 1 and 3. The observed and calculated structure factor data are available

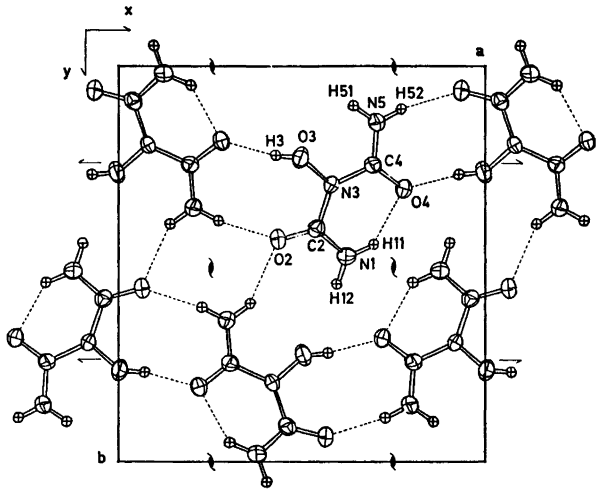


Fig. 1. The structure of 3-HB viewed along the c axis.

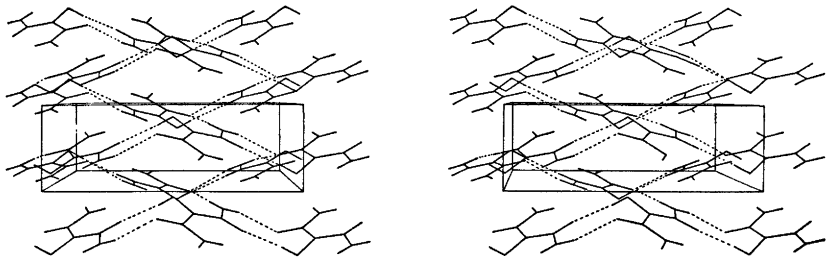


Fig. 2. Stereoscopic diagram of the molecular packing of 3-HB. The view axis is *b*, the *a* axis is →, and the *c* axis is ↓.

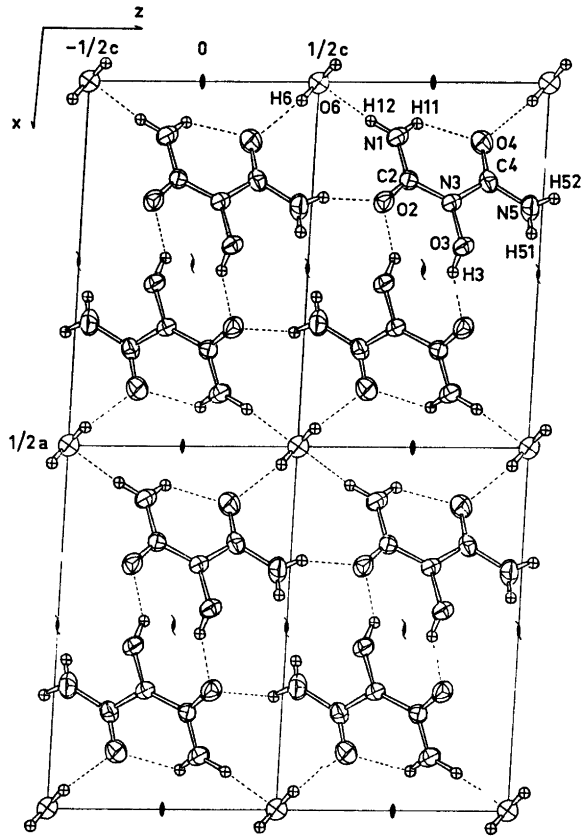


Fig. 3. The structure of 3-HB.$\frac{1}{2}H_2O$ viewed along the *b* axis.

from the author on request. The calculations were performed on a GIER computer and an IBM 360/75 computer, using the following programs: *INDIFF*,[7] a local version of the *N.R.C 2 A Picker Data Reduction Program*,[8] *The X-Ray System*,[5] and *ORTEP*.[9]

DISCUSSION

The molecular arrangement in the crystal of 3-HB is illustrated in Figs. 1–2, and of 3-HB.$\frac{1}{2}H_2O$ in Figs. 3–4. A common feature of the structures is the intensive hydrogen

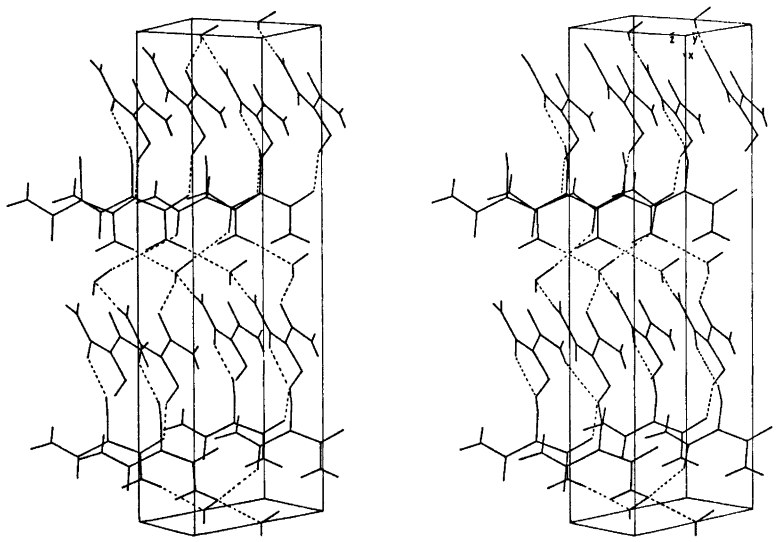


Fig. 4. Stereoscopic diagram of the molecular packing of 3-HB.$\frac{1}{2}H_2O$.

Table 4. Distances and angles concerning the hydrogen bonding systems of 3-HB and 3-HB.$\frac{1}{2}H_2O$.

X–H···Y	Distances (Å) X···Y	H···Y	Angle (°) X–H···Y
3-HB			
N(1)–H(11)···O(4)	2.624(4)	1.91(4)	134(4)
N(5)–H(51)···O(2)$_{1-x,-\frac{1}{2}+y,1\frac{1}{2}-z}$	2.897(4)	2.09(5)	148(4)
N(5)–H(52)···O(2)$_{\frac{1}{2}+x,\frac{1}{2}-y,2-z}$	2.929(4)	2.10(5)	165(6)
O(3)–H(3)···O(4)$_{-\frac{1}{2}+x,\frac{1}{2}-y,2-z}$	2.664(4)	1.82(5)	169(5)
3-HB.$\frac{1}{2}H_2O$			
N(1)–H(11)···O(4)	2.663(5)	1.93(4)	129(4)
N(1)–H(12)···O(6)	2.915(4)	1.97(5)	174(4)
N(5)–H(52)···O(2)$_{x,1+y,1+z}$	2.991(5)	2.11(5)	159(4)
O(3)–H(3)···O(2)$_{\frac{1}{2}-x,\frac{1}{2}+y,2-z}$	2.611(4)	1.77(5)	150(4)
O(6)–H(6)···O(4)$_{x,-1+y,-1+z}$	2.810(3)	1.93(5)	158(5)

bonding, involving all hydrogen atoms except H(12) of 3-HB and H(51) of 3-HB.$\frac{1}{2}H_2O$. The dimensions of the hydrogen bonding systems are given in Table 4. The carbonyl oxygen atoms, O(2) and O(4), are acceptors for two hydrogen bonds in both structures. The hydroxyl oxygen atom, O(3), is donor for one rather strong OH···O bond in each structure, with a carbonyl oxygen atom as the acceptor in both cases. The water oxygen atom of 3-HB.$\frac{1}{2}H_2O$ is donor for two and acceptor for two symmetry related hydrogen bonds. The packing of the molecules is quite different in the two crystal structures of 3-HB, *cf.* Figs. 1 and 3, while the packing of the molecules in 3-HB.$\frac{1}{2}H_2O$ is rather similar to the packing of the 3-HB residues in the crystal structure of the potassium acid salt of 3-hydroxybiuret, 3-HBK.[1]

3-HB. In the crystal structure of 3-HB the molecules are linked into chains in the x-direction by two hydrogen bonds, O(3)–H(3)···O(4)$_{-\frac{1}{2}+x,\frac{1}{2}-y,2-z}$ and N(5)–H(52)···O(2)$_{\frac{1}{2}+x,\frac{1}{2}-y,2-z}$. Each chain is linked to the

Table 5. Bond lengths (Å) and angles (°) for 3-HB, 3-HB.$\frac{1}{2}H_2O$. The dimensions found for the two 3-HB residues in crystal structure of the potassium acid salt of 3-hydroxybiuret,[1] 3-HBK(1) and 3-HBK(2), are given for comparison.

	3-HB	3-HB.$\frac{1}{2}H_2O$	3-HBK(1)	3-HBK(2)
N(1)–C(2)	1.342(5)	1.322(4)	1.335(4)	1.344(4)
C(2)–O(2)	1.218(4)	1.228(5)	1.222(4)	1.229(3)
C(2)–N(3)	1.404(4)	1.401(4)	1.405(4)	1.399(4)
N(3)–O(3)	1.393(4)	1.401(4)	1.390(3)	1.394(3)
N(3)–C(4)	1.390(4)	1.397(5)	1.386(4)	1.388(4)
C(4)–O(4)	1.239(4)	1.228(5)	1.245(4)	1.241(4)
C(4)–N(5)	1.308(5)	1.333(4)	1.334(4)	1.330(4)
N(1)–H(11)	0.91(4)	0.98(6)	0.88(4)	0.86(4)
N(1)–H(12)	0.90(5)	0.95(5)	0.87(4)	0.86(4)
O(3)–H(3)	0.85(5)	0.92(5)	1.31(4)	1.13(4)
N(5)–H(51)	0.91(5)	0.76(5)	0.89(4)	0.93(4)
N(5)–H(52)	0.85(5)	0.92(5)	0.93(4)	0.88(4)
O(6)–H(6)		0.92(6)		
N(1)–C(2)–O(2)	124.8(3)	123.7(3)	123.7(3)	122.6(3)
N(1)–C(2)–N(3)	116.1(3)	117.1(4)	116.1(2)	117.4(2)
O(2)–C(2)–N(3)	119.1(3)	119.1(3)	120.2(2)	120.0(2)
C(2)–N(3)–O(3)	115.3(3)	113.9(3)	115.8(2)	115.4(2)
C(2)–N(3)–C(4)	128.7(3)	127.8(2)	127.7(2)	126.5(2)
O(3)–N(3)–C(4)	116.0(3)	116.4(2)	116.5(2)	117.3(2)
N(3)–C(4)–O(4)	119.6(3)	120.8(2)	122.1(2)	121.2(2)
N(3)–C(4)–N(5)	115.7(3)	115.0(3)	114.6(2)	115.6(3)
O(4)–C(4)–N(5)	124.7(3)	124.2(4)	123.3(3)	123.3(3)
H(11)–N(1)–H(12)	125(4)	125(4)	117(4)	123(4)
H(11)–N(1)–C(2)	118(3)	119(2)	121(3)	118(3)
H(12)–N(1)–C(2)	116(3)	115(3)	120(3)	117(3)
H(3)–O(3)–N(3)	113(4)	107(3)	109(2)	109(2)
H(51)–N(5)–H(52)	120(5)	118(5)	121(4)	123(4)
H(51)–N(5)–C(4)	123(3)	121(4)	118(3)	119(2)
H(52)–N(5)–C(4)	116(4)	120(3)	121(2)	117(3)
H(6)–O(6)–H(6′)		93(5)		

next (antiparallel) chain by the N(5)–H(51)···$O(2)_{1-x,-\frac{1}{2}+y,1\frac{1}{2}-z}$ bond. In this way a three dimensional network of hydrogen bonds is formed, *cf.* Fig. 2.

3-HB.$\frac{1}{2}H_2O$. In the crystal structure of the hemihydrate of 3-HB the molecules form hydrogen bonded pairs by symmetry related OH···O bonds, *cf.* Fig. 3, which are arranged in rows along the long *a*-axis. Each pair is connected with the next pair in the row and the next row of pairs by means of the water molecules. As the water oxygen atoms accept the NH···O bonds from one layer of 3-HB molecules and are donors for the OH···O bonds to another layer, the water molecules also provide for connection in the direction of the short *b*-axis.

The bond lengths and angles for 3-HB and 3-HB.$\frac{1}{2}H_2O$ are given in Table 5, and in addition the dimensions found for the two crystallographically non-equivalent 3-HB residues, 3-HBK(1) and (2), in the crystal structure of the potassium acid salt of 3-hydroxybiuret.[1] Only small differences were found between corresponding bonds and angles (involving non-hydrogen atoms) in the three structures. The negative charge distributed on the two 3-HB residues in the structure of the potassium acid salt does not influence significantly on the bond lengths and angles. The N–O bonds are of equal lengths in the ionized and non-ionized molecules. Greater deviations are observed on the lengths of the carbonyl bonds, *e.g.* C(4)–O(4), and the C(4)–N(5) bonds, but the varia-

Table 6. Least-squares planes (I-III) and angles between them. The angles II:III for 3-HBK(1) and (2) [1] are given for comparison. The equations of the planes are in direct (unit cell) space. Distances (Å) to atoms defining the plane are asterisked.

Plane	
3-HB	
I	$3.3961x + 3.3979y - 3.2586z - 0.2670 = 0$
II	$3.2634x + 3.5929y - 3.2537z - 0.2654 = 0$
III	$3.2210x + 2.6020y - 3.3465z + 0.1362 = 0$
3-HB.½H_2O	
I	$9.5416x + 3.1311y - 2.8400z + 0.6688 = 0$
II	$9.2428x + 2.9831y - 3.2969z + 1.1528 = 0$
III	$9.7349x + 3.2794y - 2.3022z - 0.1237 = 0$

	3-HB			3-HB.½H_2O		
Atom	I	II	III	I	II	III
N(1)	−.017*	.001*		−.021*	.003*	
C(2)	−.018*	−.003*		−.005*	−.009*	
O(2)	−.032*	.001*		−.061*	.003*	
N(3)	.014*	.001*	.002*	.120*	.003*	.002*
O(3)	.079*			.028*		
C(4)	−.009*		−.008*	.008*		−.005*
O(4)	.075*		.003*	.026*		.002*
N(5)	−.091*		.003*	−.095*		.002*
H(11)	−.08			.13		
H(12)	−.06			−.20		
H(3)	−.55			.89		
H(51)	−.17			−.04		
H(52)	−.17			−.07		
Angle II:III	5.1°			10.2°		
	3-HBK(1)			3-HBK(2)		
Angle II:III	3.6°			13.2°		

tions are too small to merit any explanation.

The conformations of the 3-HB molecules (and ions) were found to be roughly the same in the three crystal structures, *i.e.* the conformation with an *intra*-molecular NH···O bond. This conformation was also found in the crystal structures of biuret [10–11] and triuret.[12] None of the 3-HB molecules (or ions) were found to be exactly planar, *cf.* Table 6, but the atoms of each half of the molecules, the "urea-parts", are coplanar in all cases. The angles between the planes of the "urea-parts" are given in Table 6 (angle II:III). The maximum deviation between these angles is about 10°. The standard deviations on the angles are about 0.5°.

The result of the comparison of the molecular geometry of 3-hydroxybiuret in the three crystal structures is as follows: Bond lengths and angles are not affected significantly by the different environments of the molecules (or ions). Even ionization has no significant effect on these molecular dimensions. The conformations of the molecules (and ions) are roughly the same in the three crystal structures and are probably determined by *intra*- rather than by *inter*-molecular forces. Some variations were found in the torsional angles of the molecules (and ions) as reflected in the angles between the "urea-parts". These variations are probably due to the different environments of the molecules (or ions), *e.g.* different hydrogen bonding systems.

Acknowledgement. The author wishes to thank Rita Grønbæk Hazell, University of Århus,

for valuable discussions concerning the solution of the structure of 3-HB.$\frac{1}{2}H_2O$.

REFERENCES

1. Larsen, I. K. *Acta Chem. Scand. A 28* (1974) 787.
2. Zinner, G. and Hitze, M. *Arch. Pharm. 302* (1969) 788.
3. Losee, K. A. and Bernstein, J. Olin Mathieson Chemical Corporation, *U.S. pat.* 3,192,261 (1965); *Chem. Abstr. 64* (1966) P607a.
4. Albert, A. and Serjeant, E. P. *The Determination of Ionization Constants*, Chapmann and Hall, London 1971, p. 9.
5. Stewart, J. M., Kruger, G. J., Amman, H. L., Dickinson, C. and Hall, S. R. *X-Ray 72* Crystal Structure Calculation System, Computer Science Center, University of Maryland, June 1972.
6. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1963, Vol. III.
7. Sørensen, A. M. *INDIFF, An Algol Nonius Three-Circle Diffractometer Input Data Program*, Chemical Laboratory C, The Royal Danish School of Pharmacy, DK-2100 Copenhagen, 1968.
8. Ahmed, F. R. *N.R.C. Crystallographic Program System*, National Research Council Ottawa, Canada 1968.
9. Johnson, C. K. *ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge, Tennessee 1965.
10. Hughes, E. W., Yakel, H. L. and Freeman, H. C. *Acta Crystallogr. 14* (1961) 345.
11. Craven, B. M. *Acta Crystallogr. B 29* (1973) 1525.
12. Ringertz, H. *Acta Crystallogr. 20* (1966) 932.

Received October 27, 1975.