Crystal and Molecular Structure of ω-Amino Acids, ω-Aminosulfonic Acids and Their Derivatives. IX.

Crystal and Molecular Structure of 3-Amino-2-hydroxy-1-propanesulfonic Acid

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The crystal structure of 3-amino-2-hydroxy-1-propanesulfonic acid was determined by MULTAN system with X-ray intensity data on a diffractometer and refined by the least-squares method to an R-value 0.087 for 1620 reflections. The crystals were orthorhombic, space group Pbca, $Z=8$, with $a=9.909$, $b=12.032$ and $c=10.251$ Å. The molecule takes the zwitterionic form, $H_3^+NCH_2CH(OH)CH_2SO_3^-$. The skeletal conformation of the molecule is planar trans zigzag. The molecules are held together by three-dimensional network of hydrogen bonds.

3-Amino-2-hydroxy-1-propanesulfonic acid acts to lower blood pressure¹⁾ and is a hydroxy derivative of 3-amino-1-propanesulfonic acid, homotaurine, which has strong activity towards the behavior of neurones when applied extracellularly.²⁾

It is of interest to investigate systematically the molecular structures of related compounds and elucidate the relationship between the molecular conformations and their physiological functions.

We previously reported the molecular and crystal structures of 3-guanidino-2-hydroxy-1-propanesulfonic acid³⁾ and 3-guanidino-1-propanesulfonic acid.⁴⁾

In this paper, the authors describe the molecular and crystal structure of 3-amino-2-hydroxy-1-propanesulfonic acid.

Experimental

The compound was recrystallized from aqueous solution as colorless, transparent crystals.

Crystallographic Measurement. The space group was determined from rotation and Weissenberg photographs, and lattice constants were obtained from precise measurement on a diffractometer with Mo $K\alpha$ radiation. Density was measured by the flotation method in a mixture of 1,2-dibromoethane and carbon tetrachloride. The crystal data are listed in Table 1. Three-dimensional intensity data were collected on a computer controlled four-circle diffractometer (Rigaku Denki Co., Ltd.) with Zr-filtered Mo $K\alpha$ radiation. A total of 1749 independent reflections limited within $\sin\theta/\lambda=0.700$ Å^{-1} was scanned by ω-2θ technique at a scan speed of 2° per minute. All the reflections were recorded and corrected for usual Lorentz and polarization effects, no absorption correction being made.

TABLE 1. CRYSTAL DATA OF 3-AMINO-2-HYDROXY-1-PROPANESULFONIC ACID

Molecular formula; $C_3O_4NH_9S$	MW 155.17
Colorless transparent	Orthorhombic
$a=9.909(4)$ Å	$b=12.032(3)$ Å
$c=10.251(4)$ Å	
Volume of unit cell	1222.2 Å^3
D_m	1.688 Mg/m^3
D_x	1.686 Mg/m^3
$Z=8$	$F(000)=656$
Absent spectra; $hk0$ when $h=2n+1$	
$h0l$ when $l=2n+1$	
$0kl$ when $k=2n+1$	
Space group; Pbca	

Structure Determination and Refinement. The structure determination was done by MULTAN system.⁵⁾ As the average value of E^2 with h=even, k=odd and l=odd parity has significantly large one, we tried to rescale the E's so as the average E^2 value of each parity group to have unity, which revealed all the non-hydrogen atoms. Continuation of successive Fourier syntheses with overall isotropic temperature factor reduced the R-factor to 0.21.

Refinement was carried out for all reflections by the block-diagonal least-squares procedure with unit weight. The R-factor was reduced to 0.16 with isotropic temperature factors for all non-hydrogen atoms and decreased further with anisotropic temperature factors to 0.11. In this state, a difference Fourier synthesis revealed the locations of all the 9 hydrogen atoms. They were included in the final least-squares cycles with isotropic temperature factors. The final R-value was 0.087. The observed and calculated structure factors are listed in Table 2.**

Calculations were carried out on NEAC 2200-700 computer, Osaka University, and IBM 360, Seoul National University, Seoul, Korea. The atomic scattering factors were taken from the "International Tables for X-Rav Crystallography."⁶⁾

Results and Discussion

The final atomic parameters are given in Tables 3 and 4, together with their estimated standard deviations. The difference Fourier map is shown in Fig. 1. As shown in Fig. 1, one hydrogen atom of sulfo group is transfered to the amino group. Thus, the molecule occurs in the zwitterionic form, $H_3^+NCH_2CH(OH)$-$CH_2SO_3^-$, as in the cases of related compounds.

Bond Distances and Angles. The interatomic distances and angles are listed in Table 5, together with their standard deviations, and those are acceptable as a whole. In the $-SO_3^-$ group, the average of three S–O distances, three O–S–O angles and three O–S–C1

** Table 2 is kept as a Document at the Office of the Chemical Society of Japan (Document No. 7923).

Table 3. Final positional and thermal parameters (Estimated standard deviations in parentheses) Anisotropic temperature factors are expressed in the form of $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl\}$.

Atom	X	Y	Z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	0.7263(1)	0.5043(1)	0.7580(1)	0.0036(1)	0.0040(1)	0.0060(1)	0.0014(1)	−0.0003(1)	−0.0004(1)
C1	0.6119(4)	0.5601(4)	0.8746(5)	0.0037(4)	0.0035(3)	0.0063(3)	−0.0009(5)	0.0012(7)	−0.0007(6)
C2	0.6043(4)	0.6872(4)	0.8740(5)	0.0029(3)	0.0035(3)	0.0066(4)	−0.0004(5)	0.0006(6)	−0.0005(6)
C3	0.4998(5)	0.7205(4)	0.9757(6)	0.0050(4)	0.0038(3)	0.0092(6)	−0.0001(6)	0.0041(8)	−0.0005(7)
N	0.4876(4)	0.8444(3)	0.9818(5)	0.0039(3)	0.0040(3)	0.0086(5)	0.0011(5)	0.0006(7)	−0.0018(6)
O1	0.6825(4)	0.3885(3)	0.7406(5)	0.0068(4)	0.0037(2)	0.0113(5)	0.0012(5)	−0.0025(7)	−0.0022(6)
O2	0.8606(3)	0.5105(3)	0.8166(4)	0.0032(3)	0.0066(3)	0.0102(4)	0.0019(5)	−0.0007(6)	−0.0009(6)
O3	0.7132(4)	0.5671(3)	0.6380(4)	0.0068(4)	0.0069(3)	0.0065(3)	0.0030(6)	0.0013(6)	0.0016(6)
O4	0.7307(3)	0.7324(3)	0.9079(4)	0.0039(3)	0.0045(3)	0.0126(5)	−0.0016(5)	−0.0016(7)	−0.0000(6)

Table 4. Fractional coordinates of hydrogen atoms

Atom	X	Y	Z	
C1H1	0.516	0.527	0.855	Overall isotropic temperature factor is 2.16 Å^2
C1H2	0.645	0.534	0.970	
C2H1	0.578	0.721	0.774	
C3H1	0.404	0.685	0.949	
C3H2	0.529	0.692	1.072	
NH1	0.564	0.876	1.031	
NH2	0.433	0.863	0.903	
NH3	0.429	0.860	1.041	
O4H1	0.760	0.787	0.842	

Table 5. Bond distances(Å) and angles(°) (Estimated standard deviations are in parentheses)

S-C1	1.779(5)	O1-S-O2	111.5(3)
S-O1	1.470(5)	O1-S-O3	111.4(3)
S-O2	1.462(4)	O2-S-O3	113.8(2)
S-O3	1.449(4)	O1-S-C1	104.5(3)
C1-C2	1.531(7)	O2-S-C1	106.5(2)
C2-C3	1.523(7)	O3-S-C1	108.4(2)
C2-O4	1.409(7)	S-C1-C2	113.9(3)
C3-N	1.497(7)	C1-C2-C3	107.1(4)
		C1-C2-O4	109.9(4)
		C3-C2-O4	109.5(4)
		C2-C3-N	110.2(4)

Table 6. Hydrogen bond lengths(Å) and angles(°)

Bond lengths		Bond angles	
O4-(O4H1)···O1(I)	2.685	C2-O4-O1(I)	113.4
N-(NH1)···O3(II)	2.949	C3-N-O3(II)	108.7
N-(NH2)···O1(III)	2.884	C3-N-O1(III)	101.4
N-(NH3)···O2(IV)	2.984[a)]	C3-N-O2(IV)	130.2[a)]
N-(NH3)···O4(IV)	2.935[a)]	C3-N-O4(IV)	76.9[a)]

(I) (1.5−X, 0.5+Y, Z); (II) (X, 1.5−Y, 0.5+Z); (III) (1.0−X, 0.5+Y, 1.5−Z); (IV) (−0.5+X, 1.5−Y, 2.0−Z).

a) Bifurcated hydrogen bond.

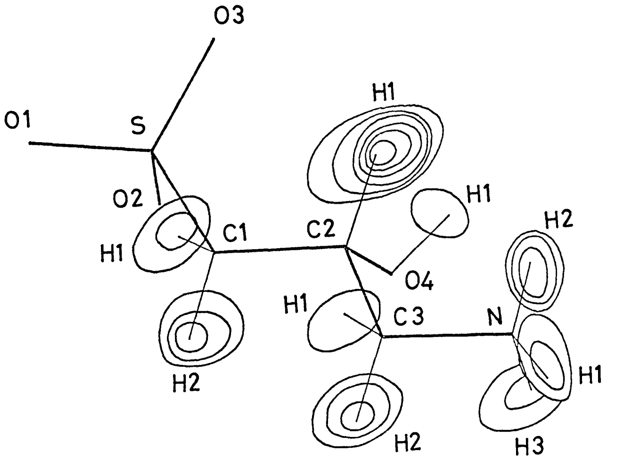

Fig. 1. Difference Fourier map of 3-amino-2-hydroxy-1-propanesulfonic acid. Contours are drawn at intervals of 0.2 e Å^{-3}, starting with the contour of 0.4 e Å^{-3}.

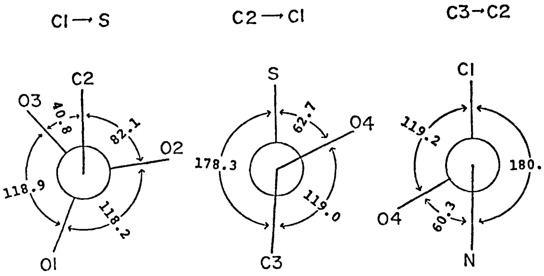

Fig. 2. Torsion angles around three bonds.

angles are 1.460 Å, 112.2° and 106.5°, respectively. These values are very similar to those of other compounds containing a sulfonato group. The C–H, N–H, and O–H distances are within the ranges 1.05—1.13 Å, 0.86—1.00 Å, and 0.99 Å, respectively. It is notable that C2–O4 distance of the hydroxyl group is 1.409 Å, slightly shorter than that found in 4-amino-3-hydroxybutyric acid[7)] (1.425 Å) which is normal C–O single bond, and slightly longer than that of 3-guanidino-2-hydroxy-1-propanesulfonic acid (1.381 Å).

Conformation. The skeletal conformation of this molecule is trans-trans. The tortion angles around C1–C2 and C2–C3 are 178.3 and 180.5°, respectively. However, the corresponding values of 4-amino-2-hydroxybutyric acid and 3-guanidino-2-hydroxy-1-propanesulfonic acid, which contain β-hydroxyl group are 173.7 and 168.8°, 161.9 and 177.8°, respectively.

The torsion angles of sulfonato group are shown in Fig. 2. These values are significantly different from those of homotaurine,[8)] 3-guanidino-1-propanesulfonic acid and 3-guanidino-2-hydroxy-1-propanesulfonic acid.

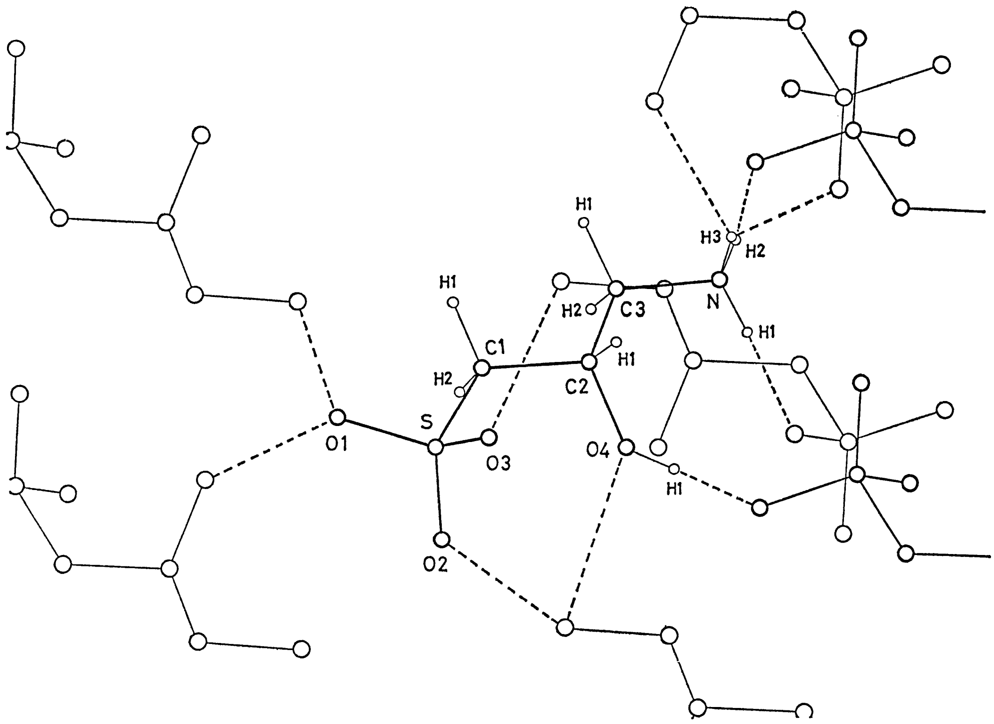

Fig. 3. Hydrogen bonds around original molecule.

Crystal Structure. Distances and angles of hydrogen bonds are listed in Table 6. All feasible hydrogen atoms in the molecule are utilized to form hydrogen bonds, in which one hydrogen atom (NH_3) on the amino group takes part in bifurcated hydrogen bond, and the molecules are held together by a three-dimensional network of NH···O and OH···O hydrogen bonds, as shown in Fig. 3.

The intermolecular contacts between adjacent molecules are in normal van der Waals distances.

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