THE UNIT CELL AND SPACE-GROUP OF β-GLYCINE.

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ABSTRACT.

The dimensions of the structural unit cell of β-glycine, all determined by purely röntgenographic measurements, are $a_0 = 5.07$ Å, $b_0 = 6.23$ Å, $c_0 = 5.37$ Å, all ± 0.01 Å, $\beta = 113° 27' \pm 15'$. β-glycine crystallizes either in the space-group $C_{2h}^2 - P2_1/m$ or in the space-group $C_2^2 - P2_1$.

Faceted crystals of β-glycine were investigated by means of the Weissenberg X-ray goniometer,[1] and the reflection goniometer. The crystals were prepared by dissolving 1 gram of glycine in 10 cc. of distilled water, cooling the solution in ice, and adding 20 cc. of cooled 96 per cent ethyl alcohol slowly and with stirring. Acicular crystals precipitated which were freed from the solution in a sintered silica filter under partial vacuum and dried quickly in an evacuated desiccator. The β-form inverts to the α-form in air but can be preserved for some time in an evacuated desiccator. Representative crystals of β-glycine are shown in Fig. 1. It was found that the use of more concentrated aqueous solutions caused precipitation of the α-form with the β-form.

The crystals of β-glycine selected for X-ray investigation by the equi-inclination method were elongated parallel to the *b*-axis and almost equi-dimensional in cross-section (about 0.1 mm. in diameter). After the exposure of the Weissenberg photographs, the crystals were placed under the polarizing microscope in an immersion liquid, and proved not to have inverted to the α-form. A rotation photograph was taken with the crystal rotating around the *b*-axis, and Weissenberg resolutions were made of the equator and first layer-line, also a rotation photograph and an equator Weissenberg resolution about the *a*-axis. The dimensions of the monoclinic unit cell, all determined by purely röntgenographic measurements, are $a_0 = 5.07$ Å, $b_0 = 6.23$ Å, $c_0 = 5.37$ Å, all ± 0.01 Å, $\beta = 113° 27' \pm 15'$. The axial ratio calculated from the unit cell dimen-

[1] The X-ray study of β-glycine was suggested to the authors by Mr. L. H. Adams in connection with some compressibility measurements carried out by him.

sions is $a:b:c = 0.814:1:0.862$. The angles between the faces in the prismatic zone (parallel to the b-axis) were also measured on a reflection goniometer and the value of β was found to be $113° 22' \pm 5'$, in good agreement with the X-ray determination. A comparison of the unit cell dimensions determined by the authors with those determined by Bernal is given in Table I.

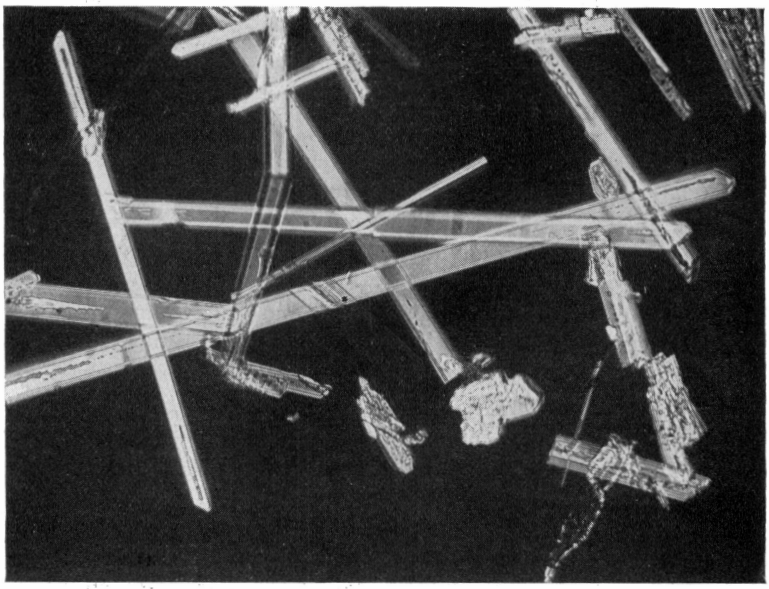

Fig. 1. Faceted crystals of β-glycine. Crossed nicols. 100 x.

The Weissenberg photographs were indexed by the graphical construction of Schneider.[2] According to a preliminary report on *The crystal structure of the natural amino acids and related compounds* by J. D. Bernal,[3] β-glycine crystallizes in the space-group C_s^2n, but this is not correct, since there are no systematic absences of spectra from (*hol*) planes. Comparison of the Weissenberg photographs of the equator and first layer-lines taken with the crystal rotating around the b-axis shows that the lattice is primitive and without glide planes.

[2] Z. Krist., 69, 41-48, 1928.
[3] Z. Krist., 78, 363-369, 1931.

The *b*-axis appears to be a screw axis, since the odd orders from the clino-pinacoid were absent on the equator Weissen-

TABLE I.
Comparison of the Dimensions of the Structural Cells of β- and α-Glycine.

		a_0	b_0	c_0	β
β-glycine	Ksanda and Tunell	5.07	6.23	5.37	113° 27′
	Bernal	5.18	6.18	5.29	114° 20′
α-glycine	Ksanda and Tunell	5.06	11.93	5.43	111° 29′
	Bernal	5.04	12.1	5.41	111° 38′†
	Hengstenberg and Lenel*	5.1	11.9	5.43	111° 38′†

* Z. Krist., 77, 424-436, 1931.
† The value of the β-angle was taken by Hengstenberg and Lenel from the literature; the same value appears in Bernal's table.

berg photograph taken with the crystal rotating around the *a*-axis. The space-group of β-glycine is accordingly either C_{2h}^2—$P2_1/m$ or C_2^2—$P2_1$, the characteristically missing spectra of these two space-groups being the same. The crystals were tested for a piezo-electric effect,[4] but none could be detected; the question as to the crystal class of β-glycine therefore cannot be answered definitely without further evidence.

The density calculated from the unit cell dimensions on the assumption that the cell contains 2 molecules of $CH_2(NH_2)COOH$ is 1.592. The calculated value agrees sufficiently well with unpublished measurements of the density, made in the Geophysical Laboratory by L. H. Adams and R. E. Gibson, to establish the number of molecules in the unit cell as two.

In order to facilitate the future identification of β-glycine by the powder method, the planar spacings and relative intensities of the diffraction lines in a powder photograph of β-glycine taken with Cu-radiation filtered through nickel foil are assem-

[4] The authors are indebted to Messrs. S. B. Hendricks and M. E. Jefferson of the U. S. Department of Agriculture, Bureau of Chemistry and Soils, for their kindness in making this test.

TABLE II.

Planar spacings and relative intensities of diffraction lines of powder spectra of β- and α-glycine taken with Cu-K radiation filtered through nickel foil. Powder specimens were rotated uniformly during the exposure. Estimated intensities of the diffraction lines are based on a scale of ten, where ten represents the intensity of the strongest line in each case.

Line No.	β-form			α-form		
	Intensity estimated	d/n	hkl	Intensity estimated	d/n	hkl
1	10	4.912	001	3	5.960	020
2	1	4.640	100	7	4.689	100
3	2	4.360	$\bar{1}01$	4	4.415	110, $\bar{1}01$
4	9	3.773	110	2	4.129	$\bar{1}11$
5	7	3.115	020	8	3.696	120
6	6	2.871	101	5	3.129	031
7	5	2.656	$\bar{1}02$, 021	4	3.043	130
8	8	2.454	002, $\bar{1}12$	10	2.974	040
9	5	2.302	200, 012	7	2.520	002, 041, 140
10	5	2.194	210, $\bar{2}02$	8	2.450	$\bar{1}41$, $\bar{2}11$
11	3	2.057	$\bar{2}12$	2	2.363	131
12	2	1.969	$\bar{2}21$	3	2.327	200
13	3	1.899	102, 130	2	2.212	$\bar{1}32$
14	2	1.853	220	3	2.139	$\bar{2}02$, 051
15	6	1.722	$\bar{1}13$	2	2.098	150, $\bar{2}12$
16	4	1.643	003, $\bar{1}32$, $\bar{2}13$	4	2.040	$\bar{1}51$, 141
17	6	1.593	$\bar{2}31$, 032	2	1.995	230, $\bar{2}22$
18	1	1.561	040	4	1.927	102
19	2	1.514	310, $\bar{2}32$	4	1.908	112, $\bar{2}41$
20	2	1.492	$\bar{2}23$	3	1.857	$\bar{2}32$

TABLE II.—Continued.

21	2	1.450	023,	$\bar{3}22$,	$\bar{3}03$		5	1.793	221,	$\bar{1}61$			
22	3	1.407	$\bar{3}13$				2	1.742	132				
23	6	1.358	113,	141			2	1.705	$\bar{2}51$,	$\bar{2}42$			
24	2	1.332	$\bar{1}04$,	$\bar{2}04$			1	1.650	250,	$\bar{2}13$			
25	1	1.304	$\bar{1}14$,	$\bar{2}14$			6	1.625	161,	$\bar{1}33$			
26	2	1.253	$\bar{4}01$,	$\bar{4}02$			3	1.603	071,	023,	$\bar{3}02$		
27	2	1.235	004,	330,	$\bar{3}04$,	$\bar{4}12$	3	1 567	300,	$\bar{1}71$			
28	5	1.210	051,	014,	$\bar{3}14$		4	1.521	260,	320			
29	1	1.194	$\bar{1}51$,	$\bar{4}03$			1	1.491	080,	$\bar{3}32$			
30	1	1.183	$\bar{3}33$				4	1.471	171,	251,	202		
31	3	1.169	400,	$\bar{4}22$			1	1.440	$\bar{1}53$,	$\bar{1}72$			
32	2	1.151	133,	203			4	1.422	$\bar{3}13$,	081,	$\bar{3}42$		
33	1	1.127	$\bar{1}52$,	213,	302		2	1.386	$\bar{3}23$				
34	1	1.113	052,	312			3	1.348	$\bar{3}33$				
35	3	1.093	250,	340			1	1.323	$\bar{2}04$,	181			
36	6	1.076	114,	$\bar{4}04$,	$\bar{2}52$		1	1.316	242				
37	2	1.064	322,	$\bar{3}43$			1	1.288	331				
38	1	1.030	124,	411			2	1.269	$\bar{1}34$				
39	1	1.003	233,	$\bar{5}02$,	$\bar{2}53$		6	1.233	360,	304,	$\bar{3}53$,	$\bar{2}82$	
40	..	....	....				4	1.181	400,	0 10 0,	351,	262	
41	..	....	....				1	1.158	302,	420,	$\bar{2}54$,	0 10 1	
42	..	....	....				2	1.134	322				
43	..	....	....				1	1.120	104				
44	..	....	....				3	1 107	272,	$\bar{2}83$,	083		
45	..	....	....				1	1.085	$\bar{3}73$,	$\bar{1}$ 10 2			
46	..	....	....				2	1.071	$\bar{4}04$,	$\bar{2}15$,	134,	342,	2 10 1
47	..	....	....				1	1.060	371,	$\bar{1}93$,	225		
48	..	....	....				2	1.049	$\bar{2}74$,	$\bar{4}61$,	$\bar{4}62$,	1 11 0	
49	..	....	....				1	1.025	183				
50	..	....	....				1	1.017	$\bar{4}71$,	$\bar{4}72$,	381,	1 10 2	

bled in Table II. The lines were indexed by an application of Bernal's graphical method in which all possible spacings in the β-glycine structure down to $d/n = 1.000$ Å were taken account of. The β-form when freshly crystallized has a great tendency to invert to the α-form, and in order to obtain a powder photograph of β-glycine unmixed with α-glycine care must be taken to remove all adsorbed water from the surface of the β-glycine. The crystals should be thoroughly washed with alcohol and immediately placed in a desiccator over phosphorus pentoxide and the desiccator evacuated with a vacuum oil pump in order to remove the last traces of moisture from the crystals. The crystals grown for the powder spectrum

TABLE III.

The Optical Properties of β- and α-glycine.*

	Optical character	α	β	γ
β-glycine	Biaxial (—)	1.490	1.608	1.652
α-glycine	Biaxial (—)	1.502	1.618	1.670

* Determined by N. L. Bowen.

were exceedingly small, prepared by quick precipitation; they were thoroughly dried and without grinding were mounted on a fine thread of Pyrex glass by means of a film of vacuum grease. The specimen was rotated uniformly during the exposure.

Rotation, Weissenberg, and powder photographs were also taken of crystals of α-glycine for the purpose of comparison. The values found for the dimensions of the monoclinic structural cell of α-glycine, all obtained by purely röntgenographic measurements, are $a_0 = 5.06$ Å, $b_0 = 11.93$ Å, $c_0 = 5.43$ Å, all $\pm$ 0.01 Å, $\beta = 111° 29' \pm 15'$. The axial ratio calculated from the unit cell dimensions is $a:b:c = 0.424:1:0.455$. The planar spacings and relative intensities of the diffraction lines in a powder photograph of α-glycine taken with Cu-radiation filtered through nickel foil are assembled in Table II. The lines were indexed by an application of Bernal's graphical method in which all possible spacings in the α-glycine structure down to $d/n = 1.000$ Å were taken account of. A comparison of the values of the unit cell dimensions determined by the authors and previous investigators is given in Table I.

The optical properties of β- and α-glycine have been determined by means of the immersion method by Dr. N. L. Bowen and are collected in Table III.