23. **A New Form of Glycine**

**By Yoichi IITAKA**

Mineralogical Institute, University of Tokyo


In the course of a study of α-glycine, whose piezoelectric properties have hitherto been contradictorily reported,\(^{1,2}\) we have found mixed in certain commercial glycine a new polymorph of glycine. Whereas α-glycine is monoclinic and non-piezoelectric, this substance is trigonal and markedly piezoelectric. These two kinds of glycine crystals are easily recognized and separated from each other in the mixture on account of their piezoelectric behaviours.\(^{2}\) No doubt that we are here dealing with a new form of CH₂(NH₂)COOH, γ-glycine.

**Preparation**

γ-glycine crystals have been obtained after several trials by recrystallizing α-glycine in acid aqueous solution (acetic acid) around 1°C. They invariably turn into monoclinic α-form upon recrystallization in distilled water.

**Elementary Analysis**

The elementary analysis of γ-glycine crystals sorted from the commercial mixture has been carried out for us kindly by Miss S. Shimokochi and Miss T. Mitsui at the Microanalytic Laboratory, Faculty of Agriculture, University of Tokyo. The twice repeated analysis gave the almost identical results as given in Table I.

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>Means</th>
<th>Theoretical, CH₂(NH₂)COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>32.53%</td>
<td>32.75%</td>
<td>32.64%</td>
<td>32.00%</td>
</tr>
<tr>
<td>H</td>
<td>7.45 ..</td>
<td>7.32 ..</td>
<td>7.39 ..</td>
<td>6.71 ..</td>
</tr>
<tr>
<td>N</td>
<td>18.96 ..</td>
<td>18.74 ..</td>
<td>18.85 ..</td>
<td>18.66 ..</td>
</tr>
</tbody>
</table>

**Crystallographic Data**

The crystals of γ-glycine at hand are flat trigonal (bi)-pyramids, measuring up to 0.5 mm. The hemimorphic nature is outwardly not evident. No goniometric measurement was undertaken because of the poor reflexion of faces.

The cell dimensions have been determined by means of a Geiger counter spectrometer (Norelco) using Cu Kα radiation (λ=1.5405 Å).
A New Form of Glycine

For the determination of space group several Weissenberg-Buerger photographs around the c-axis were taken. They revealed the rule that for the (00l) reflexions to occur l shall be 3n, excluding all other space groups than P31 or P32.

The X-ray data of γ-glycine along with those of α- and β-glycine, the two other known polymorphs of glycine, are reproduced in Table II.

<table>
<thead>
<tr>
<th>Form</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β</th>
<th>Unit cell volume</th>
<th>Number of molecules in the cell</th>
<th>Volume per molecule</th>
<th>Piezo-electricity</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ</td>
<td>7.02A</td>
<td>5.47A</td>
<td>—</td>
<td>231.6A³</td>
<td>3</td>
<td>76.9A³</td>
<td>+</td>
<td>P31 or P32</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>5.04A</td>
<td>12.1A</td>
<td>5.41A</td>
<td>111°38'</td>
<td>308 A³</td>
<td>77.2A³</td>
<td>-</td>
<td>P2₁/c</td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>5.18A</td>
<td>6.18A</td>
<td>5.29A</td>
<td>114°20'</td>
<td>154 A³</td>
<td>77.0A³</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

Melting and Transition

γ-glycine when heated changes over irreversibly to α-glycine which melts as known at about 235°C. The transition point from γ-glycine to α-glycine is 165° ± 5°C. This was deduced from a comparison of the X-ray spectrograms (Cu Ka) of unheated and variously heated glycine (Fig. 1). It is to note that γ-glycine when heated several minutes over 175°C loses a fraction of one % of its weight due possibly to sublimation.

Infra-red Absorption and Other Physical Properties

We have been able through courtesy of Prof. Y. Morino and Dr. K. Kuratani, of Chemistry Laboratories, University of Tokyo, to examine the infra-red spectra of γ- and α-glycine, which were obtained by means of a Baird infra-red spectrometer (NaCl). The crystals were powdered and inserted between two rock salt plates after having been dispersed in liquid paraffine. The spectra as reproduced in Fig. 2 are very similar and demonstrate that the γ- and α-glycine are built from the molecules possibly of the same configuration.
The specific gravity measured using a pychnometer and liquid paraffin is 1.63 gr./cm³ against 1.604 gr./cm³ calculated on the basis of the X-ray data.

The indices of refraction measured by the immersion method are \( \omega = 1.587 \) and \( \varepsilon = 1.610 \) (white light), being optically uniaxial positive.

The writer wishes to express his sincere gratitude to Professor T. Ito for his suggestions and encouragement.

References