organic papers

β-Glycine

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.001 Å
R factor = 0.025
wR factor = 0.076
Data-to-parameter ratio = 13.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of β-glycine, $C_2H_5NO_2$, has been refined. Single crystals of the metastable β-polymorph of glycine were obtained by cooling a saturated solution of glycine containing acetic acid. The crystal of the β-polymorph was preserved in dry air for several months. As the humidity of the air increased, a polymorphic transformation into the α-form was observed. The cell parameters of β-glycine have already been determined by Kozhin [*Kristallografiya* (1978), **23**, 1211–1215], but the coordinates have not been published so far.

Comment

Three polymorphs (α, β and γ) are known for glycine. The structures of the α- and γ-polymorphs have been refined from ambient and low-temperature data (Jönsson & Kvick, 1972; Kvick *et al.*, 1980). The structure of the β-polymorph was first reported by Iitaka (1959) and later described in more detail (Iitaka, 1960). The cell parameters of β-glycine, (I), have been determined by Kozhin (1978), but the coordinates have not been published so far and the structure was not refined again after these early publications. The data published by Iitaka were obtained by a photographic technique, the structure was refined to an R factor of 4.3, and no H-atom coordinates were reported. Maybe one of the reasons for this situation is the difficulty in obtaining single crystals of the β-polymorph.

$$^+H_3N \longrightarrow CH_2 \longrightarrow COO^-$$
(I)
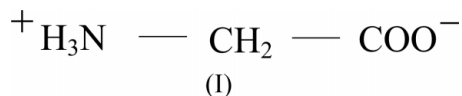
We have grown a crystal of the β-polymorph and have re-solved and rerefined its crystal structure at ambient temperature (T = 294 K), using a Stoe Stadi-4 four-circle diffractometer. The main structural features previously reported by Iitaka were confirmed. Glycine exists in the structure in the form of zwitterions, $^+H_3NCH_2COO^-$ (Fig. 1), which are linked together by electrostatic interactions and a three-dimensional network of hydrogen bonds (Fig. 2). The geometry of the zwitterions is similar to that in the α- and γ-polymorphs (Iitaka, 1960). The two C—O bonds are almost equivalent, in contrast to the data previously published by Iitaka in 1960. The difference in the torsion angles of the zwitterions in the α-, β- and γ-polymorphs is about 10° [161.8 (1)° in α at ambient temperature (Jönsson & Kvick, 1972), 157.41 (8)° in β (our data), 167.1 (1)° in γ at ambient temperature (Kvick *et al.*, 1980)]. Both O atoms and the NH_3 group are involved in the formation of hydrogen bonds. Although Iitaka could not locate H atoms in the structure, his representation of the hydrogen-bond network was correct, as
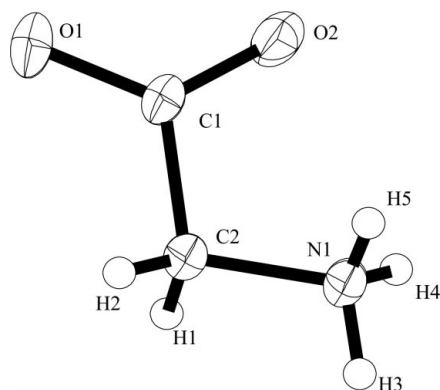
Figure 1
The molecular structure of glycine. Displacement ellipsoids are plotted at the 50% probability level.

confirmed by our more precise data. The shortest hydrogen bonds link zwitterions in layers parallel to the *ac* plane. The third H atom of an NH_3 group is located between the two O atoms of the neighbouring layer, forming a bifurcated hydrogen bond [2.23 (2) Å and 2.30 Å] linking zwitterions in the *b* direction. All the layers are linked with each other by these bifurcated hydrogen bonds in a three-dimensional network. The crystal structure is polar (space group $P2_1$). The distance between the neighbouring layers is equal to half a translation along *b*.

The structure of an individual layer of zwitterions in the β-polymorph is similar to that in the α-polymorph. The topology of the layers is the same for non-H atoms. The intermolecular hydrogen bonds within the layer are longer in the β-polymorph [1.87 (2) Å and 1.97 (2) Å] than they are in the α-polymorph (1.77 Å and 1.92 Å). The linkage between the layers in the β-polymorph is different from that in the α-polymorph (Iitaka, 1960). In the latter, the bifurcated hydrogen bonds link layers of zwitterions related by mirror planes in double-layer dimer-packages. Only van der Waals interactions exist between these double layers. The formation of double layers in the α-polymorph accounts for the fact that the *b* cell parameter in the α-polymorph is approximately doubled, compared with the *b* cell parameter in the β-polymorph.

Iitaka reported in his early paper (Iitaka, 1960), that the β-polymorph of glycine is stable in dry air for an indefinitely long time, but transforms easily into either the α- or γ-polymorphs, depending on the conditions, for example, if the air is humid.

In our experiments, the crystal of the β-polymorph was preserved in dry air for several months. This was confirmed not only by optical microscopy observations, but also by several X-ray diffraction data collections during this time period. As the humidity of the air increased, a polymorphic transformation into the α-form was observed. The crystals lost transparency, but preserved their original shape. X-ray diffraction data could be collected from the crystal after the transformation. Reflections became broader, after the trans-

formation, than they were in the diffraction pattern from the original crystal, but the structure could still be refined (to $R = 0.22$). The orientation matrix after the transformation was determined. Having compared the orientation matrices before and after the transformation, we could calculate the angles between the crystallographic axes of the product α-polymorph with respect to the crystallographic axes of the parent β-polymorph. Molecular layers (normal to the *b* direction) rotated at an angle of about 27° in the course of the β–α transformation.

A comparison of the structures of the α- and β-polymorphs allows one to suppose that the β–α transformation requires a reconstruction of the hydrogen-bond network and involves changes in the orientation of the zwitterions in every second layer of the parent structure of the β-polymorph. The effect of water vapour on the transformation may be related to this structural reconstruction during the transformation.

Experimental

Single crystals of the metastable β-polymorph of glycine were obtained by cooling a saturated solution of glycine containing acetic acid (volume ratio water–acid equal to 5:1) from 323 K down to 288 K. 30 ml of this solution were placed in a 50 ml glass vessel of 4 cm diameter. Simultaneously crystals of the α-polymorph crystallized in the same vessel. According to the data previously described in the literature (Iitaka, 1960; Kvick *et al.*, 1980), the β-polymorph crystallizes from a water–ethanol solution, whereas crystallization from a water solution with acetic acid has been reported to give the γ-polymorph.

Crystal data

$C_2H_5NO_2$	$D_x = 1.576$ Mg m^{-3}
$M_r = 75.07$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 26
$a = 5.0935$ (11) Å	reflections
$b = 6.274$ (2) Å	$\theta = 15.1$–24.7°
$c = 5.3847$ (12) Å	$\mu = 0.14$ mm^{-1}
$\beta = 113.19$ (2)°	$T = 294$ (1) K
$V = 158.18$ (8) Å^3	Prism, colourless
$Z = 2$	$0.5 \times 0.4 \times 0.2$ mm

Data collection

Stoe Stadi-4 four-circle diffractometer	894 independent reflections
	823 reflections with $I > 2\sigma(I)$
Scan width (ω) = 1.42–1.87°, scan ratio $2\theta{:}\omega$ = 1.00; I(Net) and $\sigma(I)$ calculated according to Blessing (1987)	$R_{int} = 0.039$
	$\theta_{max} = 37.5$°
	$h = -8 \rightarrow 8$
	$k = -10 \rightarrow 10$
Absorption correction: ψ scan (*X-RED*; Stoe, 1998)	$l = -9 \rightarrow 9$
	2 standard reflections
$T_{min} = 0.909$, $T_{max} = 0.998$	frequency: 180 min
6548 measured reflections	intensity decay: 4.3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.0031P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	
$wR(F^2) = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{max} < 0.001$
894 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
67 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
All H-atom parameters refined	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.58 (7)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2528 (9)	C1—O2	1.2529 (11)
N1—C2	1.4753 (11)	C1—C2	1.5281 (11)
O1—C1—O2	125.78 (8)	O2—C1—C2	117.15 (7)
O1—C1—C2	117.03 (7)	N1—C2—C1	111.79 (6)
O1—C1—C2—N1	−157.41 (8)	O2—C1—C2—N1	25.03 (12)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H4$\cdots$O1^i	0.88 (2)	1.97 (2)	2.8509 (13)	176.6 (17)
N1—H3$\cdots$O2^{ii}	0.899 (16)	1.866 (16)	2.7626 (11)	174.4 (17)
N1—H5$\cdots$O2^{iii}	0.89 (3)	2.30 (2)	2.9795 (15)	132.6 (14)
N1—H5$\cdots$O1^{iv}	0.89 (3)	2.23 (2)	2.9785 (13)	140.7 (16)

Symmetry codes: (i) $1 + x, y, z$; (ii) $x, y, z - 1$; (iii) $1 - x, y - \frac{1}{2}, 1 - z$; (iv) $-x, y - \frac{1}{2}, 1 - z$.

The structure was solved and refined in the space group $P2_1$, since the crystals are piezoelectric (Iitaka, 1961), and this fact excludes the existence of a centre of symmetry. Attempts to treat the structure as a twin resulted in less precise results. Anomalous scattering effects were not treated. Friedel pairs were merged.

Data collection: *STADI*4 (Stoe & Cie, 1997); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *X-STEP* (Stoe & Cie, 1998) and *Pcw* (Kraus & Nolze, 1999); software used to prepare material for publication: *SHELXL*97.
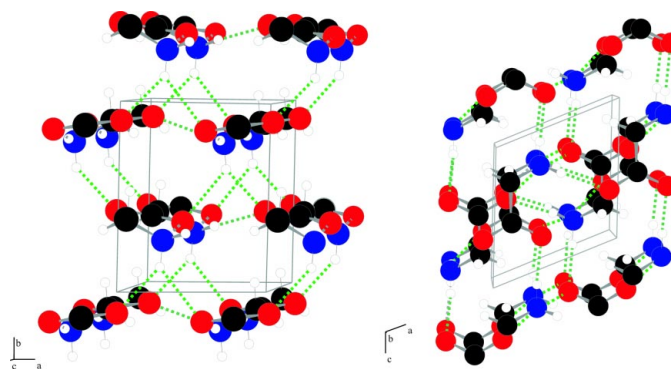
Figure 2
The three-dimensional network of hydrogen bonds in β-glycine.

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