

Effect of hydrostatic pressure on the γ -polymorph of glycine

1. A polymorphic transition into a new δ -form

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Abstract. The results of a high-resolution powder diffraction study of the effect of high hydrostatic pressure up to 8 GPa on the pure γ -polymorph of glycine ($P3_1$) are discussed. A phase transition with a jumpwise change of cell volume and cell parameters was observed. The transition starts at about 2.73 GPa and is still not complete even at 7.85 GPa. The crystal structure of the previously unknown high-pressure polymorph of glycine (δ -polymorph) could be solved and refined in the space group Pn. In this structure, glycine zwitter-ions are linked via NH...O hydrogen bonds into layers, which form double-layered bands via additional NH...O hydrogen bonds. The structure of the individual layers in the high-pressure polymorph is similar to that in the previously known α - ($P2_1/n$) and β - ($P2_1$) forms, but the packing of the layers is essentially different. The pressure-induced polymorphic transformation in the γ -glycine can be compared with a change in the secondary structure of a peptide, when a helix is transformed into a sheet.

Introduction

While the majority of crystal structures of organic molecules have been determined at normal pressure conditions, there is a great demand for the observations of structural changes that occur in organic solids in response to high pressure [1–14]. Apart from many other interesting aspects of high-pressure organic crystal studies, including correlations “structure-properties” for new materials and devices, such observations are necessary to assess the theoretical interaction models used to predict crystal packings and conformations of molecules by the minimization of

total non-bonded potential energy. An advantage of the high-pressure studies is that at high pressures the influence of thermal factor on crystal structure can be expected to reduce greatly, thus facilitating computations. The force fields verified on small-molecule crystals, could be, under assumptions, transferred to biological macromolecules; for example – applied for protein folding prediction.

Among molecular organic crystals, those of amino acids attract special attention – as biomimetics, as solid drugs, as materials for molecular electronics, as systems important for geo- and cosmochemistry [8–10, 12–15]. The hot topics of the research are i) the search of high-pressure polymorphs of amino acids, and ii) the studies of the anisotropy of pressure-induced structural distortion not accompanied by a phase transition.

Effect of pressure on the crystals of selected amino acids (L-alanine, α -glycine, L-asparagine) was studied by Raman spectroscopy [16–18]. Recently, a series of pressure-induced polymorphic transitions was reported for cysteine [19]. For glycine, the formation of a high-pressure polymorph was briefly mentioned [20], but we could not find any publications supporting this statement and describing the crystal structure of the high-pressure polymorph. No polymorphic transitions were observed when applying pressure up to 4 GPa (X-ray diffraction) [21], or 23 GPa (Raman spectroscopy) to α -glycine [18]. The effect of pressure up to 4 GPa was compared for α - and γ -polymorphs. During the X-ray diffraction studies of the samples of α -glycine containing the impurity of γ -glycine, sudden changes in the diffraction patterns were observed at about 3.5 GPa: all the reflections characteristic for the γ -form have disappeared, whereas no new reflections appeared [21]. A phase transition in γ -glycine was supposed to take place at this pressure, so that the lines of a new polymorph were masked by the lines of the α -polymorph – the main form in the sample. In order to test this hypothesis, we have obtained a pure polymorph of γ -glycine ($P3_1$, $a = 7.0383(7)$, $c = 5.4813(8)$ at ambient conditions) using a specially developed procedure [22], and have carried out a high-resolution X-ray powder diffraction study

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of this sample at hydrostatic pressures up to 8 GPa. The aims of the present study were: i) to solve and refine the structure of glycine at several pressures and to follow the pressure-induced changes in the H-bond patterns and in the molecular conformations that result or not in a polymorphic transition; ii) to test if there are any pressure-induced phase transitions in γ -glycine in this pressure range, on increasing pressure and on decompression down to ambient pressure. Preliminary results of this study were published in [23] and reported at several International Meetings [24–27].

Experimental

Pure samples of γ -glycine were obtained from a commercial sample of glycine (containing a mixture of α - and γ -polymorphs) [28] following the procedure described in [22]. Preliminary experiments were carried out using a Debye-Scherrer film technique (camera radius 45 mm) with a laboratory X-ray source, $\text{MoK}\beta$ ($\lambda = 0.6323 \text{ \AA}$), focusing Si-monochromator. Hydrostatic pressure was created in a NBS-type lever-arm diamond anvil cell (DAC) with an opening angle 30 deg. [29]. The first experiment was done with an Inconel 718 gasket. It was originally 250 μm thick, pre-indented to 110 μm . For the second experiment a Thyrodur 1.2709 steel was used, that was hardened by heating for six hours at 500 $^\circ\text{C}$ with subsequent cooling [30]. The original thickness of the gasket was 240 μm and it was pre-indented to 120 μm . The hole size in all the experiments was equal to 300 μm . A methanol-ethanol mixture was used as a pressure-transmitting medium [31]. Ruby fluorescence was used for pressure calibration with the accuracy of 0.05 GPa [32, 33]. These studies, as well as direct optical microscopy observations, allowed us to observe a phase transition at about 2.5 GPa. We could not however index the powder patterns of the high-pressure phase and solve the structure, since glycine is a poor diffractor (having only light N, O, C and H atoms), and even with the exposure times equal to 96 hours we could measure reliably only strong lines.

For more detailed studies, a monochromatized synchrotron radiation source at the Swiss-Norwegian Beam Line at ESRF was used ($\lambda = 0.71950 \text{ \AA}$, collimator width and height 0.15 mm). Diffraction patterns were registered with a MAR345 image plate detector (pixel size 0.15 mm, 2300×2300 pixels in image, maximum resolution 1.105 \AA , maximum 2θ 36.942 deg.). The frames were measured with exposing time equal to 900–3600 seconds, with oscillations in $\varphi \pm 3$ degrees. The distance from crystal to detector, the beam center position, the tilt angle and the tilt plane rotation angle were refined using a Si standard put at a diamond anvil of the open DAC in a special calibration experiment. Hydrostatic pressure was created in a DAC of the four-screw type (Merrill-Bassett type cell modified by Mao & Bell [34–36]). To achieve large sample volume, “Thyrodur 1.2709” – steel was used as a gasket material, with the hole size equal to 0.270 mm. After the gasket was preliminary pressed to the thickness of 0.077 mm, it was hardened by heating at 500 $^\circ\text{C}$ and subsequent cooling [30].

A methanol-ethanol mixture was used as a pressure-transmitting medium [31]. It was specially dried to have no traces of water, because even traces of water are known to influence on the polymorphic transformations in glycine [22]. The sample in the DAC was centered with respect to the beam very carefully, so that no reflections from steel gasket could be observed in the measured diffraction pattern.

Fit2D program [37] was used for processing diffraction data measured with the synchrotron source (calibration, masking, integration). The unit cell dimensions were determined with the indexing program TREOR [38] using the first 19 peak positions. Automatic indexing was carried out for the two extreme cases – i) a sample at the lowest measured pressure (0.63 GPa), ii) a sample at the highest measured pressure (7.85 GPa). At pressures below 3.38 GPa the powder diffraction patterns were indexed as trigonal, a few weak lines of the high-pressure phase were ignored. Starting from the pressure of 4.17 GPa the powder diffraction patterns were indexed as monoclinic, a few weak lines of the low-pressure phase were ignored. To characterize the quality of indexing, the indexes of reliability M_N and F_N were used (1) and (2).

$$M_N = \frac{\sin^2 \theta_N}{\bar{\varepsilon} \cdot n_N} \quad (1)$$

where $\sin^2 \theta_N$ – the value of $\sin^2 \theta$ for the N -th line at the powder diffraction pattern, $\bar{\varepsilon}$ – an average error in $\sin^2 \theta$, n_N – the number of theoretically possible lines at the powder diffraction pattern up to the N -th.

$$F_N = N / (\langle \Delta 2\theta \rangle n_{\text{poss}}) \quad (2)$$

where n_{poss} – the number of possible diffraction lines up to the N -th observed, $\langle \Delta 2\theta \rangle$ – a mean discrepancy between the observed and calculated values of 2θ angles.

The values of these parameters for the sample at different pressures are summarized in Table 1.

A Program Collection ULM [39] was used to refine the cell parameters from the measured values of theta-angles and the hkl -indices ascribed to the diffraction lines. For the phases present as minor components the cell parameters were not refined, but calculated from the d_{hkl} for the few stronger lines with unambiguous indexing.

The structure was solved by the grid search procedure [40]. The starting model of the glycine zwitter-ion was built in Cartesian coordinates using the data of the ambient-pressure single-crystal diffraction analysis [41]. The structure was refined with the use of bond restraints by the MRSA program [42]. The strength of restraints was a function of interatomic separation [42, 43]; MRSA's option to control the “rigidity” of the bonds in the course of the refinement procedure was used. For the intramolecular bonds N–H and C–H (an r.m.s. deviation in the bond lengths equal to 0.03 \AA) H atoms were placed in geometrically calculated positions at the stage of refinement using as starting values the data from ambient pressure single crystal diffraction analysis [41] and then refined using bond restraints with a common isotropic displacement parameter U_{iso} fixed to 0.05 \AA^2 . To fix the origin of the coordinate system, the two of the crystallographic coordi-

Table 1. Parameters characterising structure solution and refinement at several pressures.

P , GPa	R_p	R_b	R_w	R_e
0.63	0.11	0.15	0.09	0.33
1.85	0.12	0.15	0.10	0.30
2.74	0.09	0.12	0.09	0.19
3.27 ^a	0.10	0.17	0.12	0.15
3.37 ^a	0.10	0.17	0.11	0.14
4.17 ^a	0.12	0.23	0.14	0.14
4.67 ^a	0.11	0.22	0.12	0.12
5.83 ^a	0.15	0.19	0.16	0.12
6.47	0.10	0.10	0.11	0.14
7.85	0.14	0.15	0.12	0.12
7.46	0.09	0.11	0.11	0.16
7.10	0.09	0.10	0.11	0.16
6.72	0.13	0.18	0.15	0.19
6.10	0.10	0.12	0.10	0.19
5.10	0.08	0.10	0.10	0.16
4.38	0.07	0.09	0.08	0.16
3.63	0.07	0.09	0.09	0.15
3.11	0.07	0.09	0.08	0.18
2.36	0.10	0.13	0.11	0.16
2.00	0.11	0.13	0.14	0.19
1.39	0.06	0.07	0.06	0.18
0.95	0.07	0.09	0.08	0.18

a: The refinement was carried out for a two-phase (trigonal and monoclinic) system.

R_p – R -pattern: $R_p = \sum |Y_{\text{obs}} - Y_{\text{calc}}| / \sum |Y_{\text{obs}}|$

R_b – R -Bragg factor: $R_b = \sum |Y_{\text{obs}} - Y_{\text{calc}}| / \sum |Y_{\text{obs}} - \text{Background}|$

R_w – R -weighted pattern: $R_w = (\sum w(Y_{\text{obs}} - Y_{\text{calc}})^2 / \sum w Y_{\text{obs}}^2)^{1/2}$

R_{exp} – R -expected: $R_{\text{exp}} = \sum \sigma(Y_{\text{obs}}) / \sum |Y_{\text{obs}}|$

Y_{obs} – the intensity in the i -th Bragg reflection

Y_{calc} – the intensity assigned to the i -th Bragg reflection

$\sigma(Y_e)$ – standard deviation of Y_{obs}

nates of an oxygen atom were fixed automatically by MRIA [42].

PowderCell [44] and Platon [45] were used for structure analysis and graphic representation.

Results and discussion

An irreversible pressure-induced polymorphic transition

The changes in the powder diffraction patterns (after integration) with increasing pressure and on the de-compression are shown in Figs. 1, 2. As was already observed in earlier experiments [21], on increasing pressure up to 2.5 GPa, the structure of γ -glycine compressed anisotropically, so that a/c ratio decreased. At 2.74 GPa the reflections of a new phase could be observed, although γ -polymorph was still the major component at this pressure. The new high-pressure phase was present as the main component in the pressure range 4.17–7.85 GPa, but even at 7.85 GPa the weak peaks of the strongest reflections of the low-pressure phase (γ -glycine) were still present in the diffraction patterns (Fig. 3). At pressures above 5.8 GPa a very large (about 10-fold) broadening of the diffraction

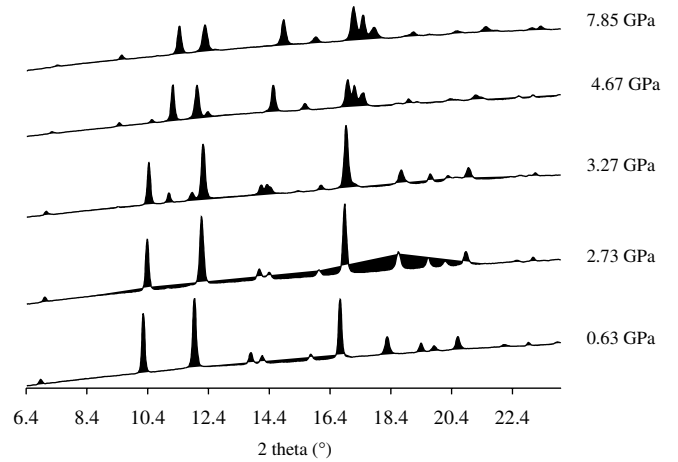


Fig. 1. The changes in the powder diffraction patterns (after integration) with increasing pressure. The parts of the spectra at higher 2 theta angles are not shown.

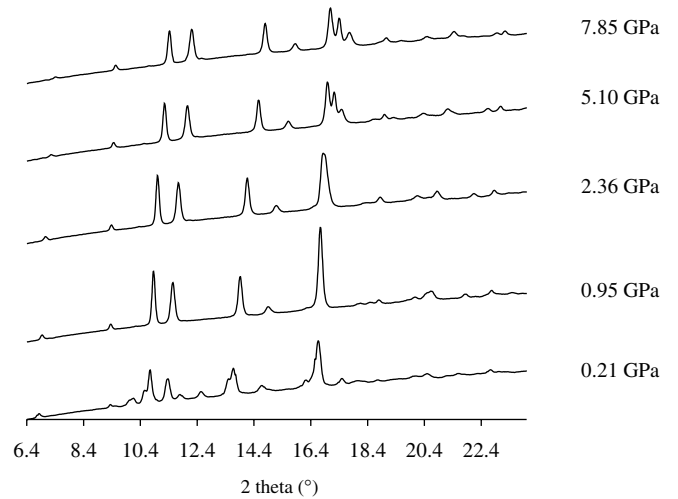


Fig. 2. The changes in the powder diffraction patterns (after integration) on the decompression. The parts of the spectra at higher 2 theta angles are not shown.

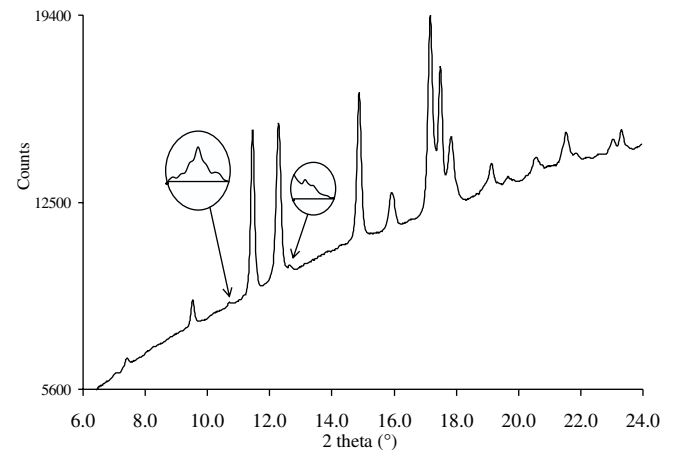


Fig. 3. A powder diffraction pattern (after integration) for a sample compressed to 7.85 GPa. The weak peaks of the strongest reflections of the remaining traces of the γ -polymorph are enlarged.

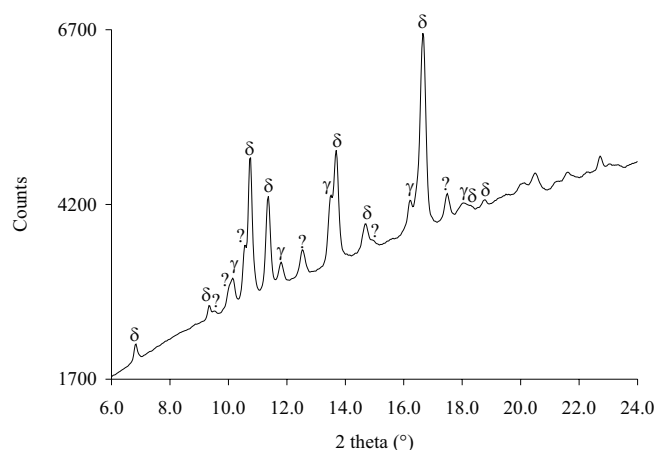
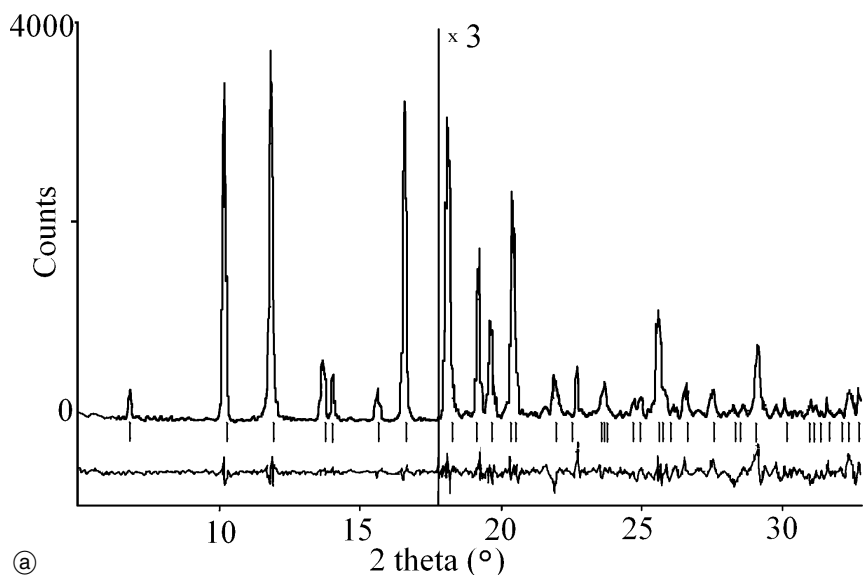


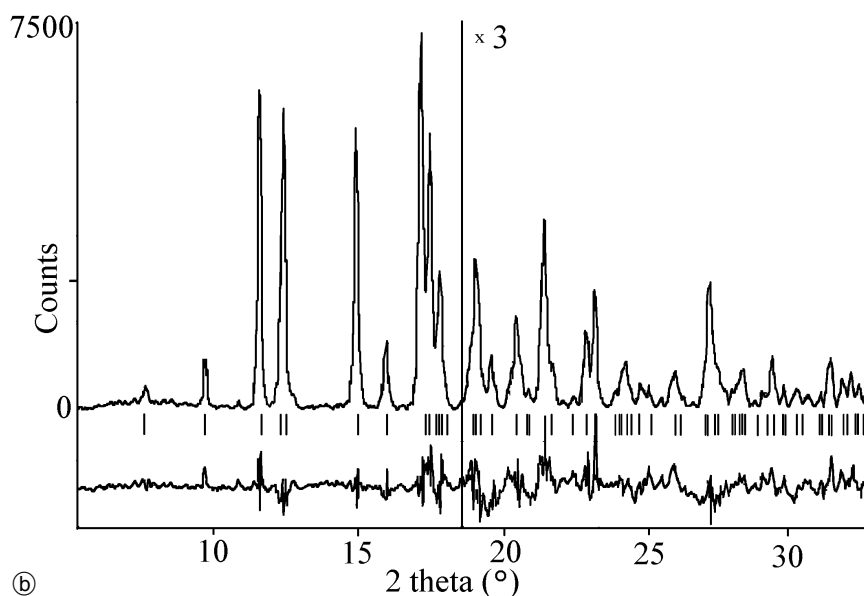
Fig. 4. A powder diffraction pattern (after integration) for a sample after decompression down to 0.2 GPa; the peaks assigned to the γ -form, δ -form, and another phase (?) are marked.

peaks of the remaining γ -phase was observed. This broadening may be explained, for example, if one supposes a slight triclinic distortion of the γ -polymorph (cell parameters a and b become about 0.2 Å different; α -, β -, γ -angles deviate at 0.5–1 deg. from 90 deg and 120 deg., correspondingly).

On decompression, the high-pressure phase did not disappear completely even at ambient pressure. At about 3.3 GPa the amount of the initial γ -polymorph started to increase noticeably. When pressure reached 0.2 GPa, some additional lines appeared, that could not be assigned either to the high-pressure polymorph, or to the γ -glycine: (2θ (deg): 9.99, 10.55, 12.52, 13.45, 14.94, 16.19, 17.47, 21.19, 25.11) (Fig. 4). These lines could not be ascribed also either to the α -, or to the β -phases of glycine. Attempts to index the third phase automatically failed — a solution was suggested by the program, but the cell volume per a glycine zwitter-ion in the proposed cell was



(a)



(b)

Fig. 5. Typical Rietveld plots showing the observed and difference profiles. The reflection positions are shown below the observed profile; for clarity, for the 2 theta values higher than 18° the intensities are multiplied by 3 ((a) the starting γ -polymorph at 0.63 GPa, (b) — a new δ -polymorph at 7.85 GPa).

equal to 65 \AA^3 only, whereas in the γ - and in the high-pressure polymorphs it was about 75 \AA^3 . Probably, some of the reflections of the third phase that are necessary for a correct indexing are masked by the reflections of the γ - and the high-pressure forms.

The structure of the new high-pressure polymorph

Parameters characterizing structure solution and refinement at several pressures are summarized in the Table 1¹. At pressures below 4.17 GPa, the results of structure solution and refinement were in a good agreement with the structure of γ -polymorph known from single-crystal diffraction data [41 and refs. therein]. The structure was solved in the space group $P3_1$ (No. 144). At pressures above 4.17 GPa, the structure of a new high-pressure polymorph (termed δ -polymorph) was solved in the space group Pn (standard setting Pc , No. 7). In Fig. 5, typical Rietveld plots for the starting γ -polymorph (a) and for a new high-pressure polymorph (b) are shown; the values of pressure equal to 0.63 GPa and to 7.85 GPa were selected as examples.

The intramolecular bond lengths and angles in the starting, γ -, and in the new, high-pressure polymorph (δ) were close (within the error limits) to those obtained from single-crystal diffraction data of all glycine modifications at ambient pressure. We have tried to refine the structure having fixed the values of intramolecular bond lengths ($C-C = 1.53 \text{ \AA}$, $C-N = 1.48 \text{ \AA}$, $C-O = 1.25 \text{ \AA}$) and have compared the result with the refinement with “free” intramolecular geometry. The comparison of the results of refinement with a) completely free and b) absolutely rigid geometrical parameters of zwitter-ions has shown that neither of two extreme variants is optimum: for absolutely rigid molecules the R -factors were noticeably worse, but if the bond lengths were not constrained at all, in some cases non-realistic values of the bond lengths and angles in the zwitter-ions could be obtained.

The packing of zwitter-ions in the δ -polymorph has some common structural patterns with that in the three other polymorphs previously known at ambient pressure (α -form, $P2_1/n$ [46], β -form, $P2_1$ [47], and γ -form, $P3_1$ [48]). The zwitter-ions of glycine in the δ -polymorph form head-to-tail chains linked via the $NH\dots O$ hydrogen bonds, which are similar to those present in all the three previously described glycine polymorphs (Fig. 6). The lengths of the intermolecular distances (the $N1-O1$, $N1-O2$) and angles ($O1-N1^i-O2$, torsion angles $N1^iO1C1C2$, $N1^iO2C1C2$, $N1^iO1C2N1$) within a chain vary slightly from polymorph to polymorph. At high pressures, in the δ -polymorph both the $N1-O2$ and the $N2-O1$ distances satisfy the criteria of classifying a $NH\dots O$ contact as a hydrogen bond (distance $N1-O2 = 2.964(10) \text{ \AA}$, distance $N1-O1 = 2.736(15) \text{ \AA}$ at 7.85 GPa), whereas in the α -, β -, and γ -polymorphs at ambient pressure, and also in the δ -form at pressures below the phase transition point, only a $N1H\dots O2$ contact would be considered as a hydrogen bond following standard criteria of a crystallographic computing program. On

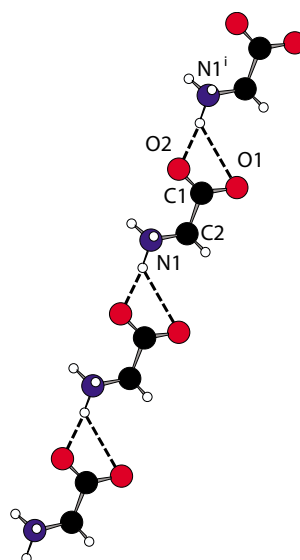


Fig. 6. A chain of zwitter-ions present in all the four polymorphs of glycine. Large white circles – O, black circles – C, dashed circles – N, small white circles – H. (In the electronic version: red circles – O, black circles – C, blue circles – N, small white circles – H.)

increasing pressure, the two $NH\dots O$ hydrogen bonds in a chain of the δ -polymorph behaved differently – the longer one compressed, whereas the length of the shorter one remained practically constant within the error. This resulted also in the distortion of the $O1-N1^i-O2$ angle (Fig. 7 a, b). Previously, different changes in the distances $N1-O1$ and $N1-O2$ resulting in distortions of bonds and

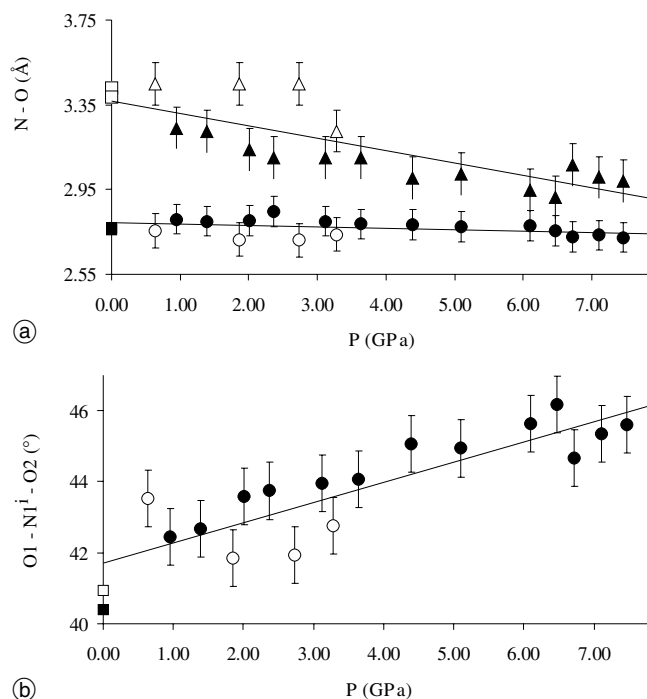


Fig. 7. The changes in the selected distances and angles within a chain in the starting γ -, and in the new high-pressure, δ -polymorphs of glycine versus pressure: (a) the distances $N-O$ in the $NH\dots O$ hydrogen bonds, \circ – $N1-O2$ for γ -phase, \triangle – $N1-O1$ for γ -phase, \bullet – $N1-O2$ for δ -phase, \blacktriangle – $N1-O1$ for δ -phase, \blacksquare – $N1-O2$ for α -phase and β -phase, \square – $N1-O1$ for α -phase and β -phase; (b) the $O1-N1^i-O2$ angle, \circ – for γ -phase, \bullet – for δ -phase, \blacksquare – for α -phase, \square – for β -phase. Atom labeling is explained in Fig. 6.

¹ The atomic coordinates and displacement parameters were deposited as CIFs at Cambridge Structural Data Centre (Nos. CCDC 250992–251017 and CCDC 231174).

torsion angles was observed on cooling for α , β , γ -polymorphs of glycine [41] and L-serine [49]. The interrelation between the compression of intermolecular hydrogen bonds and the distortion of angles and the rotation of molecules or molecular fragments was observed previously for a number of structures [1–14, 50, 51]. It is remarkable, that the distortion of the chains of zwitter-ions in the γ - and in the δ -polymorphs was continuous in all the pressure range from ambient to 7.85 GPa, despite a polymorphic transformation (Fig. 7).

The chains of the glycine zwitter-ions are, in turn, linked via additional hydrogen bonds with each other to give not the helices, as in the original γ -glycine, but layers, similar to those in the α - and β - forms. The stacking of the layers in the δ -form is essentially different from those in the α -, and in the β -polymorphs: the layers in the δ -polymorph are double, as in the α -form, but the individual layers in the double-layer band are not related with each other by inversion, as in the α -form, but solely by a glide plane, so that the structure of the δ -form remains polar, as the structure of the parent γ -form (Fig. 8).

It is worthy noting that the δ -form was formed only when pressure was applied to the γ -polymorph. Although the structure of the α -form is built from layers very simi-

lar to those in the δ -form, pressure as high as 23 GPa seems not to induce any phase transitions in the α -glycine [18]. Probably, a rearrangement of a centrosymmetric structure of α -glycine into a polar structure of δ -glycine, as well as the reverse transformation on decompression, are kinetically hindered. A γ – δ transformation and the reverse one are also kinetically hindered – on increasing pressure, the transition was observed in a wide pressure range, on decompression it was not completely reversible. Still, a rearrangement requiring rotation of $2/3$ of the chains formed by zwitter-ions with respect to each other along the axis parallel to the chain axis (Fig. 8) seems to proceed easier, than a transformation involving inverting every second H-bonded layer in the structure. It is possible also that piezoelectric properties of the γ -glycine [47, 48] are important for the mechanism of the γ – δ transformation: electric field induced in the crystal by applying hydrostatic pressure may influence on the reorientation of the dipoles of zwitter-ions. It is interesting to study the effect of pressure on another polar piezoelectric polymorph of glycine – β -polymorph – and to test if a β – δ transformation can be induced. Recently, a reversible phase transition in the β -polymorph was observed by Raman spectroscopy at about 0.76 GPa [52, 53], but the

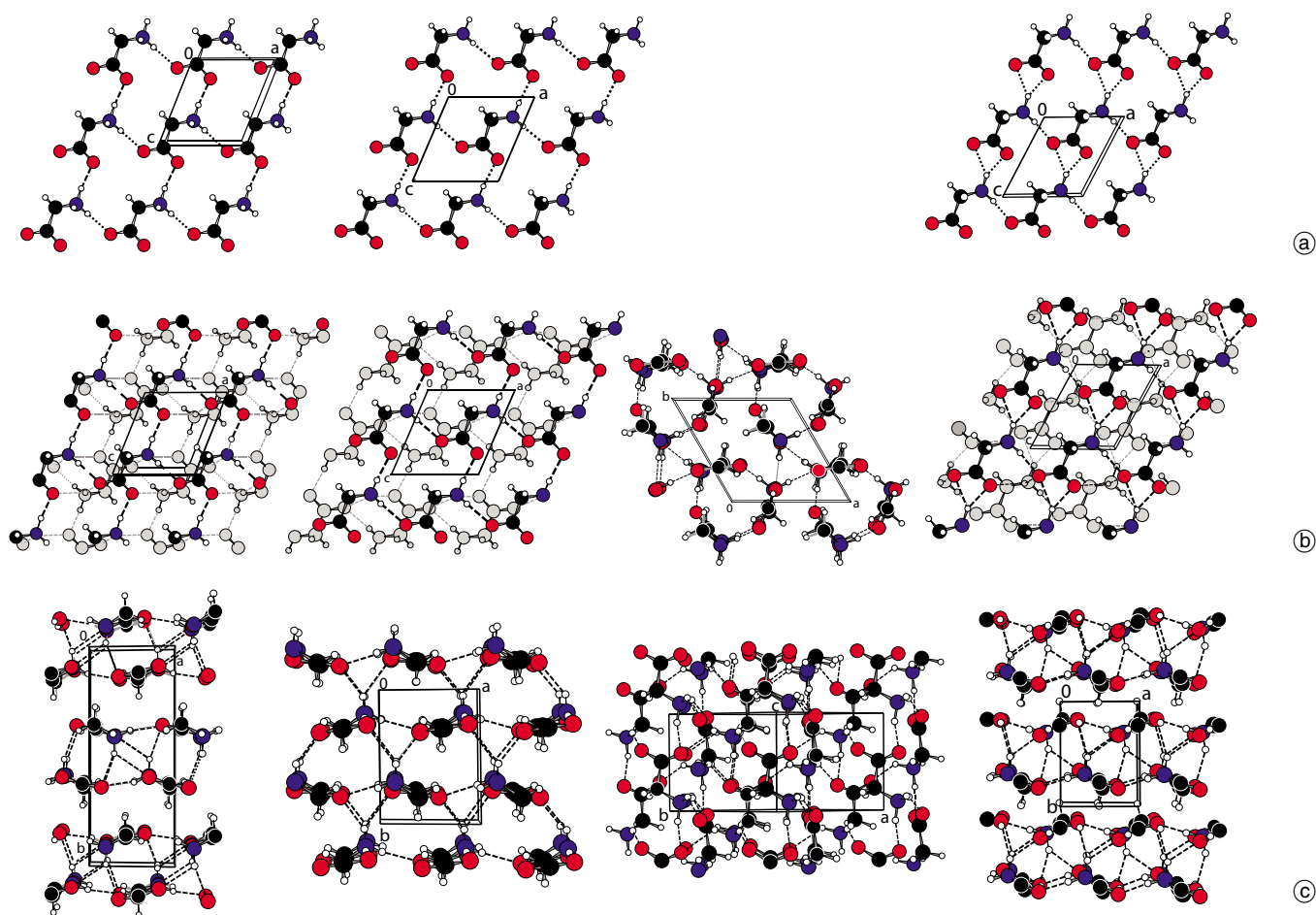


Fig. 8. The fragments of crystal structures of the four polymorphs of glycine in two projections. Upper row – individual layers in the α -, β - and δ - polymorphs (a), the fragments of $(a \times c)$ planes in the α - and β -polymorphs, a fragment of a $(a \times b)$ -plane in the γ -polymorph, a fragment of a $(a \times c)$ -plane in the δ -polymorph (b) lower row – the fragments of the same polymorphs viewed in the projections normal to those in the upper row (c). The colours are selected as in Fig. 6. All the atoms in the layers one level below are coloured grey. Dashed and dotted lines show various types of $\text{NH} \dots \text{O}$ hydrogen bonds.

structure of the new phase formed as a result of this transformation is unknown and has still to be solved by a diffraction experiment.

Conclusions

The structure of γ -glycine was shown to undergo a partly reversible polymorphic transformation into a previously unknown polymorph of glycine, the δ -form, in a wide pressure range between 2.7 GPa and 7.8 GPa. The structural “synthone” – a chain of zwitter-ions, that is present in the three previously known polymorphs of glycine (α -, β -, and γ -) – is present also in the structure of the high-pressure δ -form. Although the chains of zwitter-ions in the δ -polymorph form layers similar to those in the α -form, the δ -polymorph could be formed when applying pressure not to the α -polymorph (which is stable at least to 23 GPa) [18], but to the γ -polymorph, in which such layers are not present, but can be formed from linked chains of zwitter-ions aligned parallel to the crystallographic c -axis if part of the zwitter-ions rotate with respect to each other along the chain axis. This transformation seems to be kinetically hindered (is observed in a wide pressure range and is not completely reversible on decompression).

Detailed studies of the response of the polymorphs of crystalline amino-acids to increasing pressure can be helpful to achieve a better understanding of the effect of pressure on peptides. In particular, the compressibility of the hydrogen bonds, or the flexibility of torsion angles can be compared and correlated with the “softness” of a structure along selected directions. The pressure-induced polymorphic transformation in the γ -polymorph can be compared with a change in the secondary structure of a polypeptide chain from a helix into a layer [54]. Further detailed studies of other related systems under pressure are required, in order to make some generalizations.

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