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A comparative study of pressure-induced lattice strain of α- and γ-polymorphs of glycine

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Abstract. The effect of hydrostatic pressure up to 4 GPa on the two polymorphs of glycine (α – s.g. $P2_1/n$, and γ – s.g. $P3_1$ ($P3_2$)) was studied by X-ray powder diffraction using a synchrotron radiation source ($\lambda = 0.7$ Å, a MAR345 image plate detector). No polymorphic transformations were detected. Relative volume changes and the anisotropy of structural distortion of the two polymorphs were compared. The directions of maximum and minimum lattice strain were related to the directions of weak and strong hydrogen bonds in the structures.

Introduction

Studies of the role of intermolecular interactions in the formation of crystal structures and in determining solid-state properties are attracting in the last years much attention. These studies are important for crystal engineering, for polymorph prediction, for design of supramolecular devices and biomimetic systems. The crystals with intermolecular hydrogen bonds in the structure, and at the same time – with non-spherical and conformationally flexible structure building units (molecules or molecular ions) are especially attractive and challenging. Intermolecular interactions in molecular solids manifest themselves, in particular, in the anisotropy of structural distortion. The role of hydrogen bonds in the anisotropy of structural distortion under pressure was studied recently for some coordination [1–7] and organic [8–13] compounds.

Glycine is interesting in several respects. In the crystals it exists as zwitter-ions linked together by electrostatic interactions and hydrogen bonds. Zwitter-ions of glycine are flexible: the value of the torsion angle may vary in a rather wide range. Three polymorphs are known for glycine (α – $P2_1/n$, β – $P2_1$, γ – $P3_1$ ($P3_2$)). The polymorphs differ in the way, how the stronger and the weaker intermolecular hydrogen bonds link zwitter-ions in the crystal together [14–26]. In the α-polymorph zwitter-ions are linked by hydrogen bonds in double antiparallel layers, the interactions between these double layers being purely van-der-Waals. In the β-polymorph individual parallel layers are linked by hydrogen bonds in a three-dimensional network. In the γ-polymorph zwitter-ions form helixes linked with each other in a three-dimensional network.

Glycine is the smallest amino-acid, and can therefore serve as a model system for studying interactions important in biological systems and factors determining the changes in the secondary structure of biopolymers. Response of intramolecular geometry, of intermolecular hydrogen bonds, and of packing mode of zwitter-ions in the crystal to various external actions (changes in temperature, pressure, electric and magnetic fields, chemical agents) is of particular interest. Comparison of the data for different polymorphs is helpful for understanding the factors influencing the anisotropy of distortion of crystal structures with hydrogen bonds and for studying the interrelations between the properties of individual molecules and the properties of their assembly.

Anisotropy of thermal expansion of the three polymorphs of glycine was compared in [27, 28]. We have started a systematic comparative study of the anisotropy of structural distortion induced by high pressure. The present contribution deals with the data on pressure-induced lattice strain in the two polymorphs, which are stable at ambient conditions – α- and γ-modifications.

Experimental

A commercial powder sample of glycine [29] was used for experiments. According to the X-ray powder diffraction data it contained a mixture of α- and γ-polymorphs, α-polymorph being the main component. We decided to use this mixture of polymorphs for our comparative high-pressure studies. An advantage of using the mixture was that X-ray patterns of both polymorphs were measured at absolutely equal conditions. An obvious disadvantage, at the same time, was that attempts to refine crystal structures of the two polymorphs using the powder data met

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difficulties. Hydrostatic high pressure was created in a Merrill-Bassett diamond anvil cell (DAC) [30] of the four-screw type suggested by Mao & Bell [31]; the cell has been described by Ahsbahs et al. [32]. 220.0250/R/l steel was used as a gasket material, a methanol-ethanol-water mixture [33, 34] – as a pressure-transmitting medium. Ruby fluorescence was used for pressure calibration with the accuracy of 0.05 GPa [35]. A monochromatized synchrotron radiation source at the Swiss-Norwegian Beam Line at ESRF was used ($\lambda = 0.7$ Å, collimator width and height 0.1 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 Å, maximum 2θ 36.942 deg.). The frames were measured with exposing time equal to 1200–3600 seconds, with $\Delta\varphi = 8$ degrees. The distance crystal – detector was adjusted using a Si-standard. 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. Indexing of the diffraction pattern was based on the structural data at ambient pressure and on the continuity of changes in d-values as pressure was increased steadily by small steps. Cell parameters were refined using a program complex Ulm [36]. Deformation (strain) ellipsoids were calculated from the measured changes in lattice parameters as described in [37].

Results and discussion

No polymorphic transitions were observed either in the α-, or in the γ-polymorph as pressure increased up to 4.0 GPa. The diffraction patterns could be indexed assuming continuous anisotropic structural distortion of the ambient-pressure structures. At 4.0 GPa the intensities of reflections of the γ-polymorph fell down, but were fully restored as the pressure decreased back to 1 atmosphere. A full-profile analysis of the powder patterns at different pressures using program MRIA [38] has shown that the preferred orientation was present in the samples of both α- and γ-polymorphs (010 in α-, and 001 – in γ-polymorph) [39]. For the α-polymorph the preferred orientation did not change noticeably with pressure, whereas for the γ-polymorph it increased at about 10 times [39]. One may suppose some structural reorganization of γ-glycine to take place at about 4 GPa. Further detailed studies at this and higher pressures of a pure γ-polymorph are needed to elucidate this problem.

The changes in the cell volumes of the α- and of γ-polymorphs with increasing pressure were continuous and reached at 4 GPa 13.7% for the α-polymorph and 10.6% – for the γ-polymorph (Fig. 1). The γ-polymorph was less compressible at room temperature with increasing pressure, than the α-polymorph, although at ambient pressure the density of the γ-polymorph was slightly lower, than that of the α-polymorph, both of them being almost equal within errors.

Pressure-induced lattice strain for both polymorphs was noticeably anisotropic. The structure of γ-polymorph was least compressible along crystallographic direction **c** (Fig. 2).

Relative linear strain in the plane normal to the **c**-axis was approximately 3 times higher (Fig. 3). As a result, the **a/c** ratio decreased linearly with increasing pressure (Fig. 2). Similar effect was observed on cooling γ-glycine [24, 27, 28]. Nelmes et al. [40] have studied pressure-induced structural distortion of deuterated γ-glycine and have reported a decrease in **a/c** ratio by circa 1.5% at 0.5 GPa, what is in a good agreement with our data (Fig. 2).

One can understand the lowest compressibility of the γ-polymorph along **c**-axis, taking into account that in this direction glycine zwitter-ions are linked in chains by strong hydrogen bonds. In the plane normal to this direction zwitterions are also linked by hydrogen bonds, but the structure can be more readily compressed in this plane if cooperative shifts of zwitter-ions and changes in their torsion angles are involved (Fig. 4). One can suppose that different compression of different types of hydrogen bonds in the structure also accounts for the observed anisotropy of lattice strain. According to the report of Nelmes et al. [40], compressibility of the three types of hydrogen bonds in the structure could be noticed even at pressures as low as 0.5 GPa, medium length hydrogen bonds being most compressible. According to Nelmes et al. [40], the fact that these hydrogen bonds are compressed more readily with pressure than the other, suggests that the torsion angles of glycine molecules change with pressure. For a comparison, we can note, that according to the single-crystal neutron diffraction data, on cooling γ-glycine down to 83 K, the longer hydrogen bonds in the ($\mathbf{a} \times \mathbf{b}$)-plane compressed more readily (1.5–2.6 times), than the shorter ones along **c**-direction [24]. The changes in measured torsion angles on cooling were within the experimental error [24, 28].

Pressure-induced lattice strain in α-glycine was also anisotropic (Fig. 5). Maximum changes were observed for cell parameter **b**, minimum changes – for cell parameter **c**. The value of β-angle increased with pressure. The difference between cell parameters **c** and **a** increased linearly with pressure (Fig. 6). The values of linear strain in the directions of the principle axes of the strain ellipsoid are plotted in Fig. 3. Compression of the structure along **b**-axis (principle axis **2**), i.e. in the direction normal to the

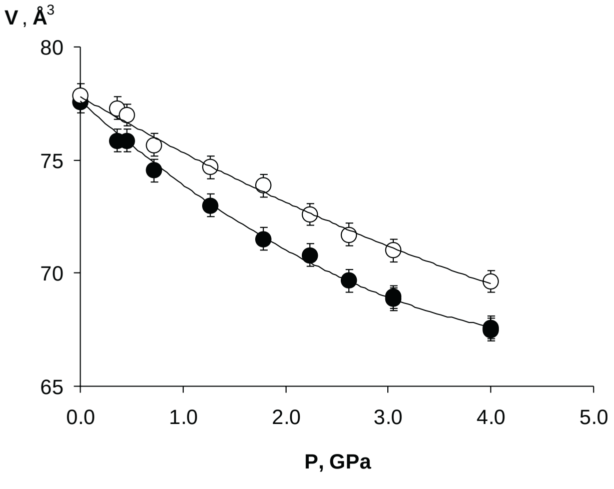

Fig. 1. Volume per zwitter-ion in γ-glycine (white circles) and α–glycine (black circles) versus hydrostatic pressure.

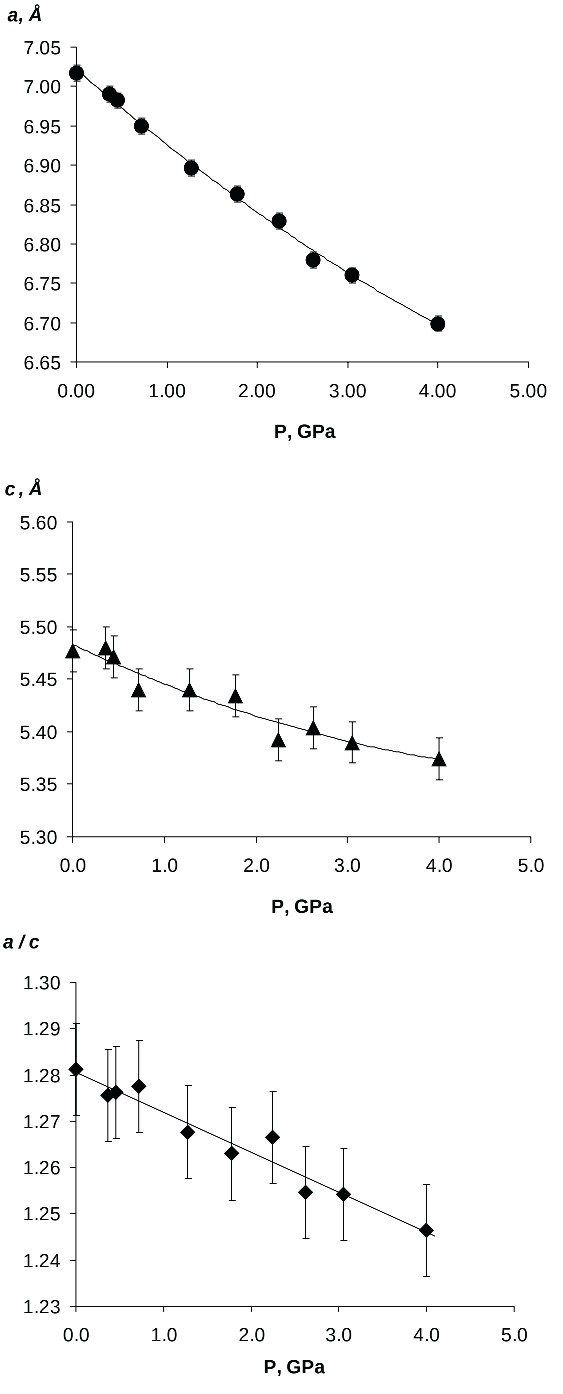

Fig. 2. Cell parameters (*a* and *c*) and their ratio in γ-glycine versus hydrostatic pressure.

double molecular layers linked by hydrogen bonds (Fig. 7), was large, but not the maximum one in the structure. Maximum (principle axis **3**) and minimum (principle axis **1**) values of linear strain were observed within these planes. Directions of **1** and **3** did not coincide either with **a**, or with **c**, and rotated as pressure increased (Fig. 8). Direction of minimum contraction was closer to axis **c**, than to axis **a**. Both the absolute values and the relative changes in cell parameters **c** were close for the α- and the γ-polymorphs (Fig. 9). The value of cell parameter **c** is determined by the intermolecular distance in the head-to-tail arrangement of glycine zwitter-ions (compare Fig. 3 and 7). Hydrogen bonds in this direction are the shortest ones in both polymorphs.

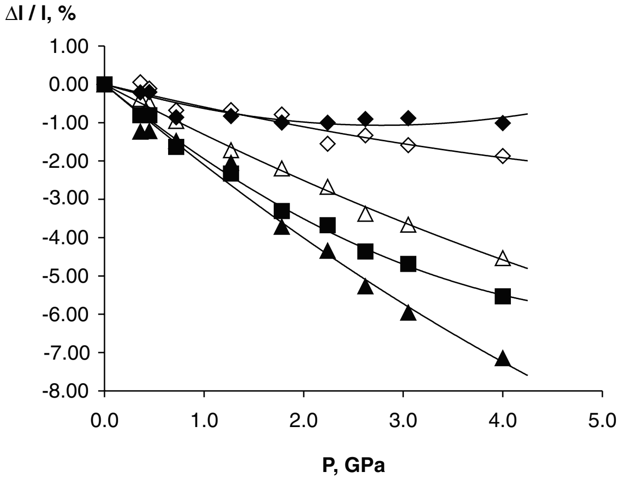

Fig. 3. Relative linear strain in polymorphs of glycine versus pressure. α-glycine – black symbols: rhombs – along axis **1**, squares – along axis 2 || **c**, triangles – along axis **3**; γ-glycine – white symbols: rhombs – along direction **c** (axis **1**), triangles – in the plane normal to **c** (axis **2** & **3**)

The anisotropy of lattice strain of α-glycine on cooling and on heating reported in [27, 28] is somewhat different from that induced by pressure in our experiments, although the main features – a low compressibility of the structure along **c**-direction and a high compressibility in **b**-

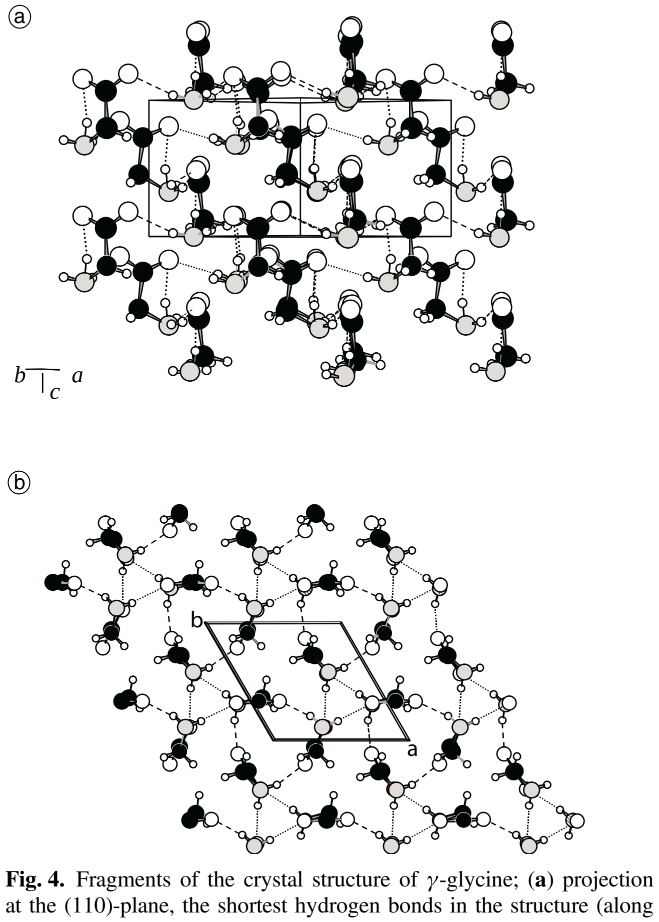

Fig. 4. Fragments of the crystal structure of γ-glycine; (**a**) projection at the (110)-plane, the shortest hydrogen bonds in the structure (along **c**) are shown in addition to hydrogen bonds plotted in Fig. 4b; (**b**) projection at the (001)-plane, dotted lines – longer hydrogen bonds, dashed lines – shorter hydrogen bonds. Notions for atoms: C – black circles, O – large white circles, N – grey circles, H – small white circles.

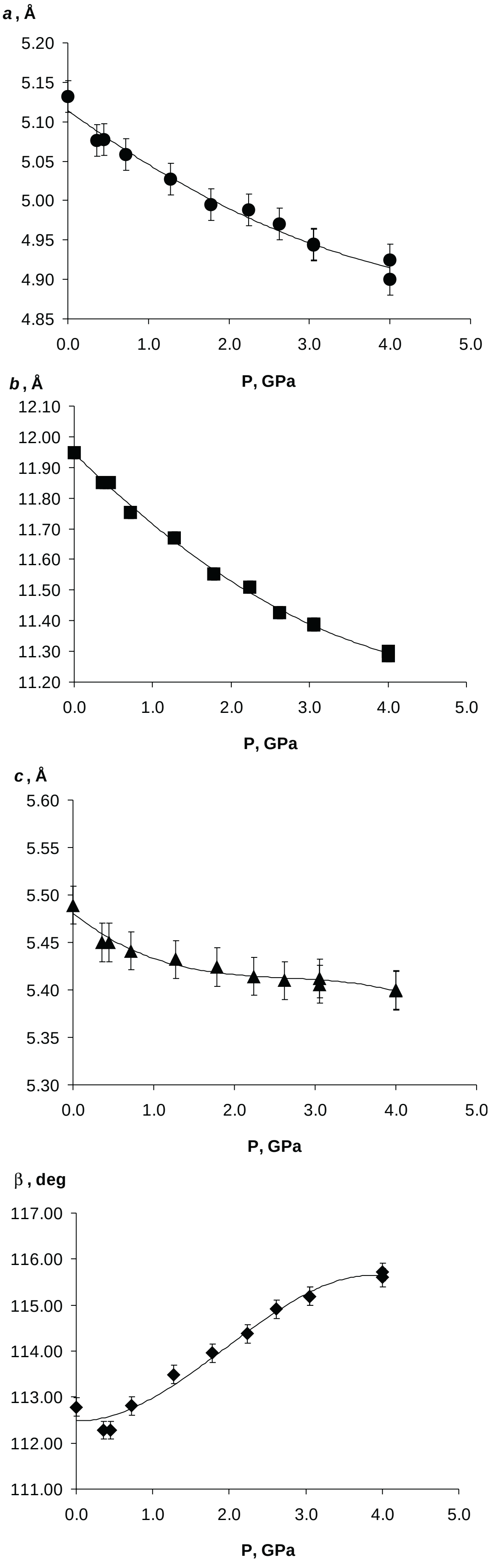

Fig. 5. Cell parameters in α-glycine versus pressure.

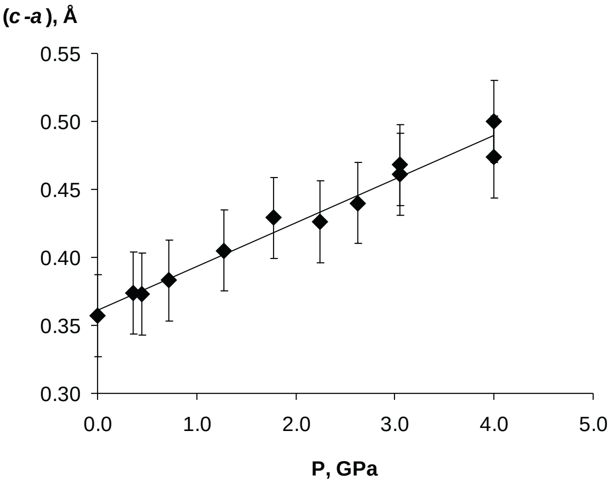

Fig. 6. Difference between cell parameters **c** and **a** in α-glycine versus pressure.

direction — are in a good agreement. A more detailed comparison of the anisotropy of structural distortion of the α-polymorph on cooling and under pressure is given in [28].

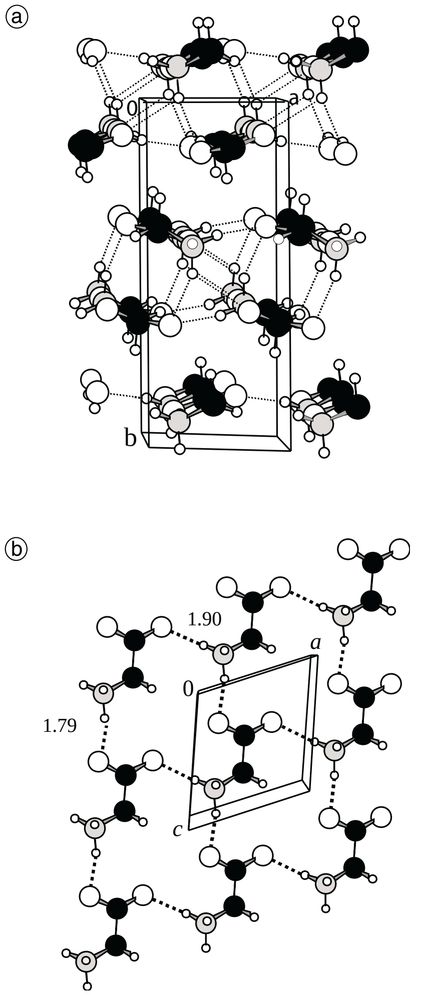

Fig. 7. Fragments of the crystal structure of α-glycine; (**a**) projection along (001)-plane, hydrogen bonds are shown by dotted lines; (**b**) a layer in the (010)-plane, hydrogen bonds are shown by dashed lines, the N–O distances in the H-bonds are indicated at the plot. Notions for atoms: C — black circles, O — large white circles, N — grey circles, H — small white circles.

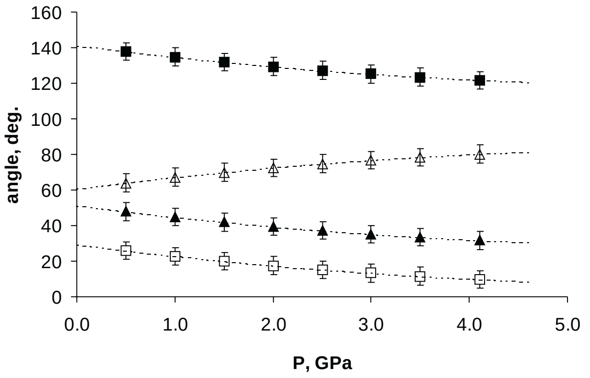

Fig. 8. Angles between crystallographic axes (**a**, **c**) in the α-polymorph of glycine and the principle axes (**1**, **3**) of strain ellipsoids at increased pressures. Black squares – ($\mathbf{1} \times \mathbf{a}$), white triangles – ($\mathbf{3} \times \mathbf{a}$), black triangles – ($\mathbf{3} \times \mathbf{c}$), white squares – ($\mathbf{1} \times \mathbf{c}$).

Conclusions

The measurements of pressure-induced changes in lattice parameters of the α- and γ-polymorphs of glycine have not revealed either phase transitions, or amorphization in the pressure range up to 4 GPa. Both structures turned out to be remarkably stable with respect to hydrostatic loading. Bulk compressibility of the two polymorphs is noticeably lower, than those of the polymorphs of paracetamol, fenacetin or benzoquinone [8–13]. They were comparable with the bulk compressibility of a series of Co(III)-nitropentaammine complexes [1–7], and higher, than that of sodium oxalate [41]. The slightly denser α-polymorph turned out to be more compressible, than γ-polymorph. This illustrates that in anisotropic molecular crystals density may be less important for the compressibility, than the mode of molecular packing, the structure and the strength of intermolecular hydrogen bonds [42].

The anisotropy of lattice strain can be related to the directions of stronger and weaker hydrogen bonds in the structures. Despite different crystal structures of the α- and γ-polymorphs of glycine, close values of linear strain were measured along particular crystallographic directions, in which packing of molecules and the parameters of intermolecular hydrogen bonds are similar. Similar effect was reported for lattice strain in α- and γ-glycine on cooling [27, 28].

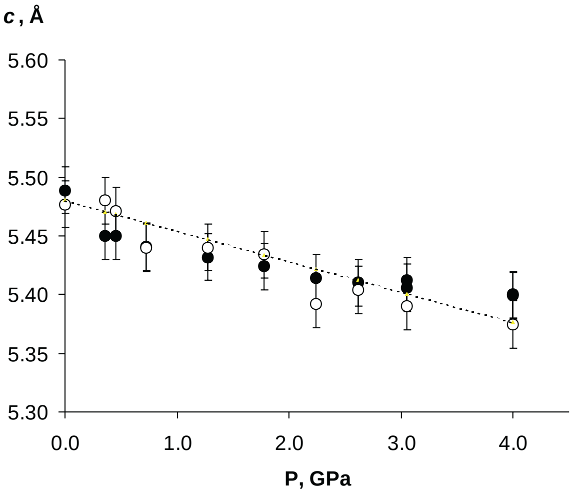

Fig. 9. Changes in the cell parameters **c** in the α- (black symbols) and in the γ-(white symbols)polymorphs of glycine versus pressure. The straight line is a least-square approximant based on the data for both polymorphs together.

Anisotropy of structural distortion with increasing pressure is not very much different from that on cooling, in contrast to some other systems, like Co(III)-nitro-pentaammine complexes [2–4]. Further single-crystal studies at high pressures will complement the results reported in the present contribution with direct data on the changes in atomic coordinates, interatomic distances, valent and torsion angles. This will allow one to interrelate shortening of intermolecular hydrogen bonds with changes in the intramolecular torsion angles and cooperative shifts of zwitter-ions with respect to each other.

In the context of a general study of the structural response of molecular crystals to high hydrostatic pressures [11] some of the results of this study are in a good agreement with data previously obtained for other systems and meet well "intuitive common-sense expectations". One could expect, for example, the structures to be more rigid in the directions, in which molecules are linked together by shorter hydrogen bonds. At the same time, some of the results were not at all obvious *a priori*. Thus, one would not expect a denser polymorph to be also a more compressible one. It was not obvious, that no polymorphic transformations take place up to 4 GPa. It was not obvious, that the maximum compression of the α-polymorph is observed in a direction in the plane of the double hydrogen-bonded layers, and not normal to these layers. It was also not obvious that there must be a direct correlation between the starting length of a hydrogen bond at ambient pressure and the compressibility of the structure in the direction of hydrogen bonds of this particular type: the longer a hydrogen bond, the larger is the compressibility of the structure in this direction. For example, in $[Co(NH_3)_5NO_2]Cl_2$ a longer NH...Cl bond *expands* with increasing pressure [4]. In the orthorhombic polymorph of paracetamol the structure compression in the directions of OH...O and NH...O bonds is the same, despite the differences in the strengths of the two types of hydrogen bonds: the orthorhombic structure contracts *isotropically* in the ($\mathbf{a} \times \mathbf{b}$)-plane under pressure, as if it were tetragonal [13]. Similarities in the anisotropy of structural distortion of the two polymorphs of glycine under pressure and on cooling are also not as obvious as one might think: for example, in $[Co(NH_3)_5NO_2]Cl_2$ the anisotropy of structural distortion is very different [4]. The amount of *experimental* data on the structural response of molecular crystals to high pressure is still so small, that any new information will be valuable for achieving a better understanding of the related phenomena and predicting directions and relative values of maximum and minimum compression/expansion, as well as possible polymorphic transitions for a selected compound. In particular, it will be interesting to compare the high-pressure behaviour of the crystals of various amino-acids $^{+}NH_3-CHR-COO^{-}$ (to see the effect of the charged, polar, or hydrophobic R-residues), as well as that of di-, tri-, etc. peptides (to study the effect of the length and flexibility of an individual zwitter-ion on the properties of the crystal as a whole).

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