High pressure and supramolecular systems*

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The present review summarizes the results of studies of supramolecular systems under high hydrostatic pressure. The possibilities of using high pressure for the preparation of new supramolecular structures, investigation of intermolecular interactions in these structures, and control over the physical and chemical properties of supramolecular assemblies are considered.

Key words: high pressures, supramolecular chemistry, X-ray diffraction, vibrational spectroscopy, polymorphism, diamond anvil cells, phase transitions.

Introduction

Supramolecular chemistry is an interdisciplinary field of science, which has been particularly rapidly developed since the late 20th century.[1,2]

According to J.-M. Lehn, who is one of the founders of this field of science, supramolecular chemistry is a sort of "molecular sociology"[1] dealing with molecules involved in "various collectives," the so-called supramolecular assemblies (examples of supramolecular assemblies are presented in Fig. 1).[2] Supramolecular chemistry is concerned, in particular, with the following problems: the controlled synthesis of new supramolecular assemblies with desired structures and properties; elucidation of the reasons for the formation of particular structures under particular conditions; investigations of the nature and detailed characteristics of intermolecular interactions; elucidation of the structure—property relationships for supramolecular assemblies; study of the influence of supramolecular assemblies on the structure, properties, and chemical reactions of the constituent molecules; the design of supramolecular devices and simulation of biochemical processes.[1,2]

High-pressure studies can help in solving all these various problems as applied to diverse supramolecular systems. The present review considers examples of both supramolecular assemblies, *viz.*, molecular crystals (paracetamol and glycine), and models of supramolecular systems, *viz.*, ionic molecular crystals (cobalt complexes and sodium oxalate). In the latter crystals, structurally complex aspherical fragments, which retain their individuality in the crystals and in which both the geometric parameters (including conformations) and the relative orientation can be changed, are present along with simple ions.

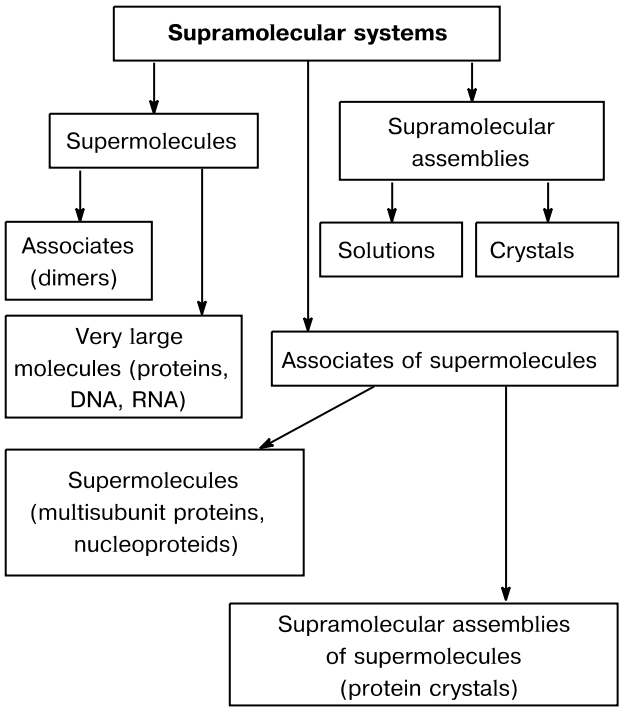

Fig. 1. Examples of supramolecular systems.

Most attention is concentrated on the following questions:

How does the pressure affect the structure of a supramolecular assembly as a whole?

How does the pressure affect the structures of the individual molecules forming this supramolecular assembly?

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What is the relationship between the changes in the structure of the supramolecular assembly as a whole and the structures of individual molecules?

Whether it is possible to use high pressure for the construction of supramolecular assemblies, whose structures differ radically from the structures of the supramolecular assemblies formed by the same molecules in other conditions (for example at atmospheric pressure and low temperature)?

Whether the same supramolecular assemblies respond identically to two scalar effects, such as a decrease in the temperature and an increase in the pressure?

Whether it is possible to use experiments with molecular crystals for obtaining information important for an understanding of more complex biochemical systems?

The notion of "structural changes" includes changes in the bond lengths and bond angles, changes in the conformation (of molecules) and even in the electronic structure (of molecules and crystals) up to valence isomerization (of molecules) as well as polymorphic transformations (of crystals) or isomerization (of molecules). The pressure can induce all these changes. The present review considers the effect of pressure on the geometric parameters of molecules (without radical changes in the electronic structure or isomerization) as well as on the crystal structures both upon anisotropic compression within the same polymorph and in the course of polymorphic transformations.

The possibilities of using high pressure in studies of supramolecular systems have been discussed in more detail in the publications.[3—5]

Experimental procedures

Pioneering studies of compounds under high pressure, which were begun early in the 20th century, required sophisticated and bulky equipment based on the use of hydraulic presses.[6—8] In spite of large sizes of these presses, the pressures, which could be generated with these devices, were by today's standards very modest (10000—30000 atm or several gigapascals; 1 GPa = 10000 atm). In the late 1940s, a radically different device, *viz.*, a tiny diamond anvil cell, was constructed for generating high pressures. This device has revolutionized studies:[9,10] it became possible not only to substantially increase (by several orders of magnitude) pressures in experiments but also to combine the generation of high pressure with *in situ* investigation of substances by various physicochemical methods, such as optical microscopy, vibrational (IR or Raman) spectroscopy, X-ray or neutron diffraction, Mössbauer spectroscopy, NMR spectroscopy, calorimetry, conductivity measurements, magnetic properties measurements, *etc.*[10,*]

* See also http://www.diacellproducts.com and http://www.tau.ac.il/ramot/danvils

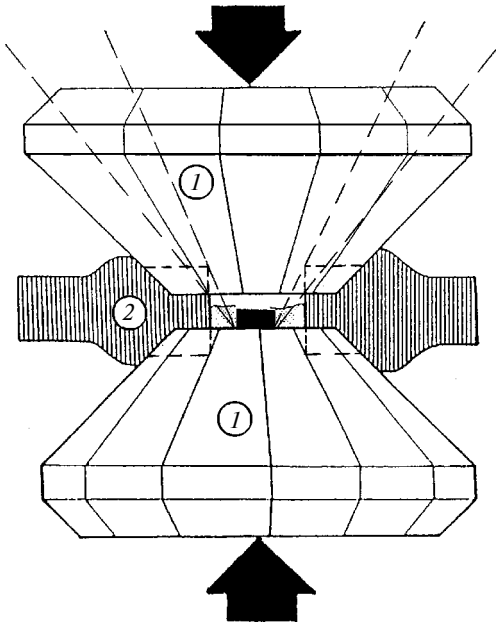

Fig. 2. Scheme of a diamond anvil cell: *1*, diamonds; *2*, a metallic gasket.

State-of-the-art diamond anvil cells generate pressures up to 500 GPa (5000000 atm) and allow one to vary the temperature from very low (5 K) to extremely high (3000 K).* The following principle is used for generating pressure in a diamond anvil cell (Fig. 2): a metallic gasket with a hole is placed between the parallel faces of two diamonds, and the hole is filled with a sample and a hydrostatic pressure medium (liquid or gas). The diamonds are brought into contact with the metallic gasket, the gasket applies pressure to a liquid or gas, and the latter exerts pressure on the sample. The smaller the diamond faces, the higher pressure that can be generated as the diamonds are brought together, but at a sacrifice in the sample size.

To measure the pressure, special reference calibrants are added to a cell containing the sample under study. The pressure dependences of the properties of such reference calibrants are well known. For ruby, which is most commonly used for this purpose, the shift of the luminescence band is known to depend on the pressure.[11,12] If the changes in the unit cell parameters of compounds depend noticeably on the pressure, such compounds (for example, quartz, NaCl, or $AlPO_4$) can also be used as calibrants.[10,13—16] It is also possible to use compounds, for which the pressure dependence of the positions of the vibrational frequencies in the IR spectra is known.[17]

Experimental techniques using diamond anvil cells were described in more detail elsewhere.[10,13—16] Let us only note that significant and interesting effects can be observed for supramolecular systems even at relatively moderate pressures (up to 10 GPa), and this allows one to study rather large samples (diameter of the diamond faces and, correspondingly, the holes in the metallic

gasket are about 1—0.5 mm). This, in turn, enables one to obtain reliable structural parameters even for molecular crystals, which have low space group symmetry and contain only light atoms (N, O, C, H) as constituents. For example, the crystal structure of the monoclinic modification of paracetamol at 4 GPa was solved and refined anisotropically (for all nonhydrogen atoms) to the R factor of 3% (111 parameters were refined, 20 atoms per asymmetric unit cell, 2600 measured reflections, of which about 600 reflections are independent) based on single-crystal X-ray diffraction data obtained with the use of a diamond anvil cell. The bond lengths in the molecules were measured[18] with an accuracy of 0.0003 nm. The results of similar quality were obtained for $[Co(NH_3)_5NO_2]Cl_2$,[19,20] quadratic acid,[21] 2-methylcyclopentane-1,3-dione,[22] pentaerythrite,[23] and dimedone.[24]

Effect of pressure on structures of supramolecular assemblies

Pressure can exert different effects on the structures of supramolecular assemblies.

1. Continuous changes in the structural parameters, which are not related to polymorphic transformations or other phase transitions but result from reversible elastic compression of the same phase. In the general case, contraction occurs anisotropically, and the structure can even expand along particular directions despite a decrease in the volume with increasing pressure, *i.e.*, the linear strain along these directions is positive.[25]

2. Phase transitions, including pressure-induced polymorphic transformations. Transitions can occur either reversibly or irreversibly, with or without changes in space group symmetry, and with or without a sharp change in the volume.[5,15,16,26,27] As applied to biopolymers, the terms "changes in the secondary and tertiary structure" or "population of conformational states" rather than "phase transitions" are commonly used.[3—5]

3. High-pressure formation of supramolecular structures, which qualitatively differ from the structures formed through self-association of the same structural fragments in other conditions, for example, on cooling.[28—31]

Let us give several examples.

Effect of pressure on the crystal structure of $[Co(NH_3)_5NO_2]Cl_2$. The cell parameters of

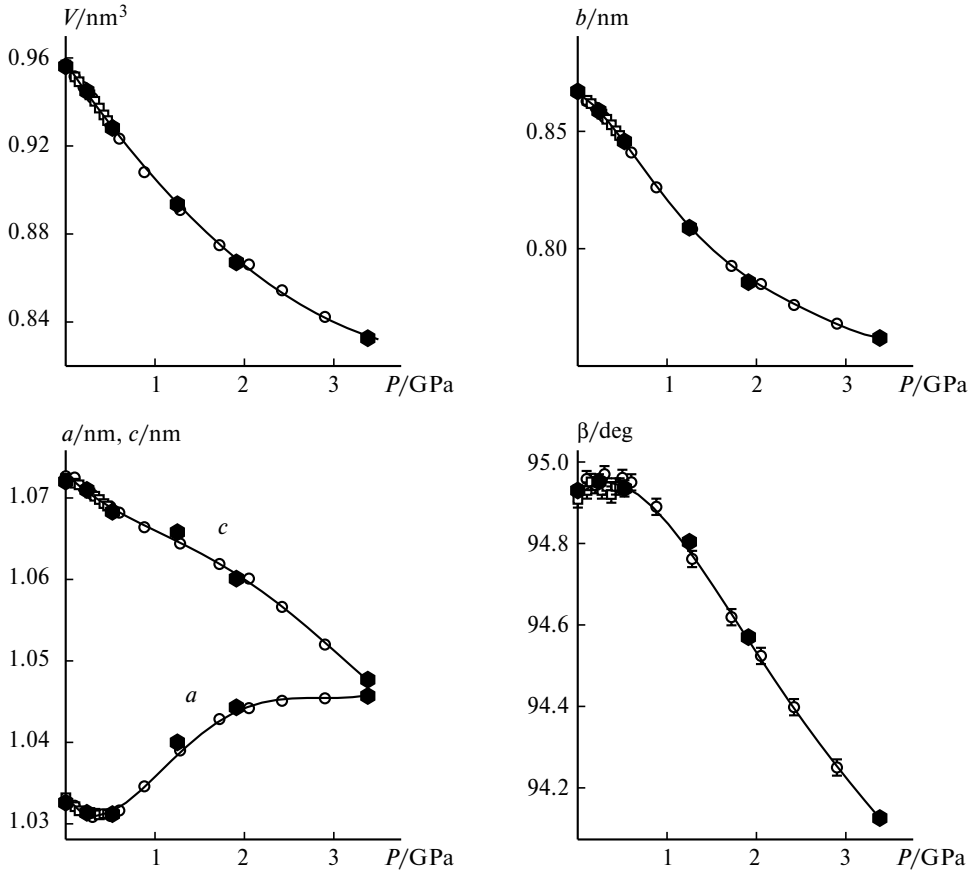

Fig. 3. Plots of the volume (V) and the cell parameters (a, b, c, β) of $[Co(NH_3)_5NO_2]Cl_2$ *vs.* the hydrostatic pressure. The solid hexagons correspond to the pressures at which the crystal structure was refined.[19,20]

$[Co(NH_3)_5NO_2]Cl_2$ change nonmonotonically with increasing pressure. However, the plot of the volume *vs.* the pressure shows clearly that no phase transition occurs and only anisotropic compression of the structure takes place (Fig. 3). This conclusion is additionally confirmed by calculations of the pressure-induced linear strain of the structure along the principal axes of the strain tensor of the structure (which changes monotonically) as well as by the results of structure refinement at all pressures in the same space group ($C2/c$).[19,20] The anisotropic compression of the structure results from shortening of some intermolecular hydrogen bonds (NH...O, NH...Cl^-) and elongation of other bonds (NH...Cl^-) in the structure (Fig. 4) as well as from rotation of the complex cations relative to each other.[20] This process is accompanied by distortion of the geometry of the complex cations, *e.g.*, the bond lengths and bond angles are changed and the nitro ligands rotate with respect to the line between the NH_3 ligands.[20] The pressure-induced compression of the structure is qualitatively different from the compression of the same structure induced by decreasing temperature. The changes in the cell parameters are radically different even in the case of equal changes in the volume (Fig. 5). The changes in the interatomic distances and bond angles are also qualitatively different.[20]

Effect of pressure on the crystal structures of the polymorphs of paracetamol. Hydrostatic pressure induces only anisotropic compression of the structures of the monoclinic ($P2_1/n$) and orthorhombic ($Pbca$) polymorphs of paracetamol.[18,32] In spite of substantial differences in the structures of two polymorphs, they have the same bulk compressibility (Fig. 6, *a*), whereas the anisotropy of lattice strain is substantially different (see Fig. 6, *b*). As could be expected, the maximum compression of the structures of both polymorphs was observed along the direction normal to the molecular layers, which are linked to each other only by weak van der Waals interactions. Deformation of the molecular layers induced by increasing pressure is accompanied by shortening of the intermolecular OH...O and NH...O hydrogen bonds within the layers and changes both in the molecular shape (molecules become more planar) and the angle between the planes of the adjacent molecules in the layer (Fig. 7).[18] Distortions of the structures of two modifications differ depending on whether these distortions are induced by increasing pressure[18] or decreasing temperature.[33,34] Cooling of two polymorphs leads to different relative changes in the cell volume (Fig. 8, *a*). The anisotropy of compression is also different (see Fig. 8, *b*). In the case of the pressure-induced compression of both the monoclinic and orthorhombic polymorphs of paracetamol, the weaker NH...O hydrogen bonds are shortened to a smaller degree than the stronger OH...O hydrogen bonds. In the course of cooling of the same structures, the weaker NH...O hydrogen bonds are, on the contrary, more contractable.[18,33,34]

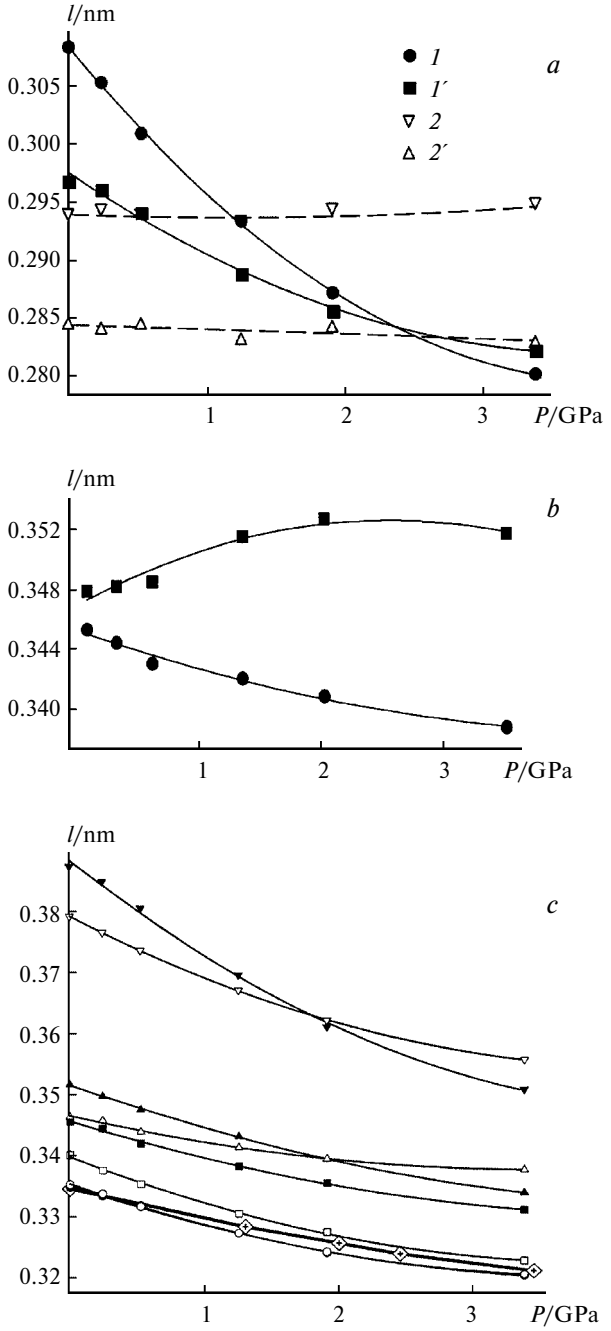

Fig. 4. Shortening of the distances (l) between the nonhydrogen atoms in the hydrogen bonds in the $[Co(NH_3)_5NO_2]Cl_2$ structure with increasing hydrostatic pressure: *a*, the NH...O distance between the *cis*-NH_3 and NO_2 ligands; *1* and *1′*, intermolecular hydrogen bonds; *2* and *2′*, intramolecular contacts; *b*, the NH...Cl distances between the *trans*-NH_3 ligands and the Cl^- anions; *c*, the NH...Cl distances between the *cis*-NH_3 ligands and the Cl^- anions.[19,20]

Effect of pressure on the crystal structure of sodium oxalate. Sodium oxalate provides an example of how an increase in the pressure can induce the rearrangement of the crystal structure classified as the phase transition (poly-

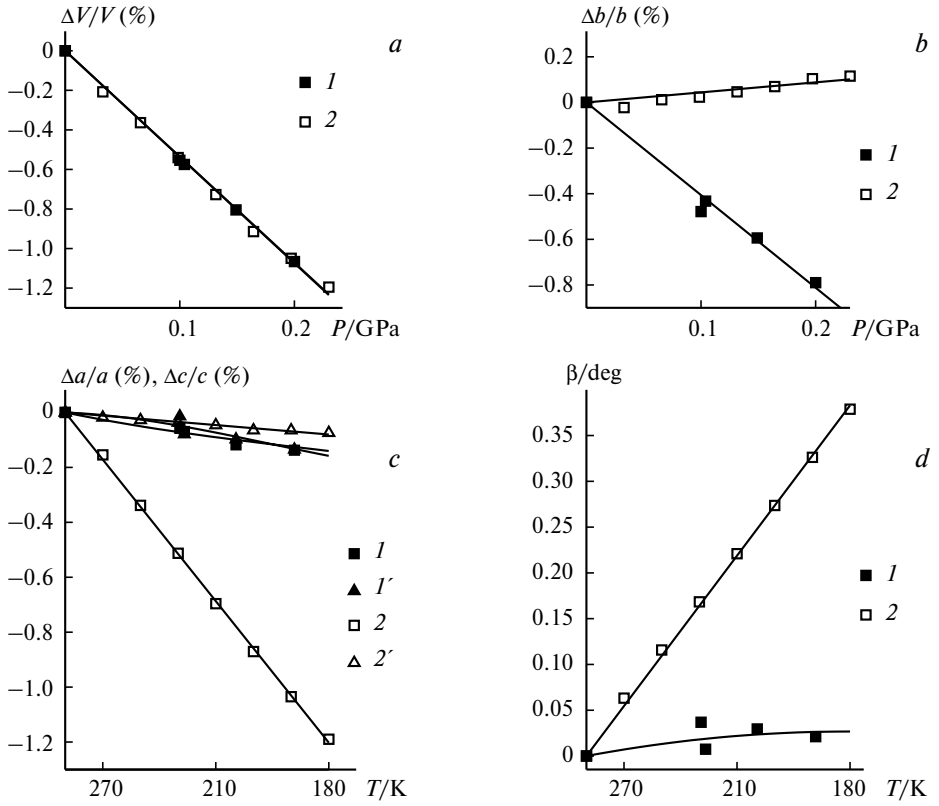

Fig. 5. Comparison of the relative changes in the cell parameters (*a*, *b*, *c*, β) of the $[Co(NH_3)_5NO_2]Cl_2$ complex corresponding to the same change in the cell volume with increasing hydrostatic pressure (*1*, *1′*) and decreasing temperature (*2*, *2′*);[20] *c*, $\Delta a/a$ (*1*, *2*); $\Delta c/c$ (*1′*, *2′*).

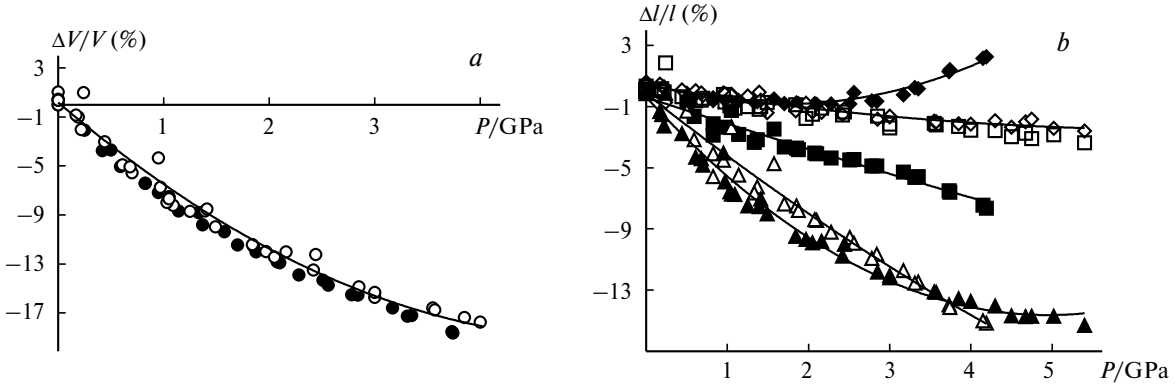

Fig. 6. Relative changes in the volume (*a*) and linear strain along the principal axes of the strain ellipsoid (*b*) under pressure applied to the monoclinic (solid symbols) and orthorhombic (open symbols) polymorphs of paracetamol.[18,32]

morphic transformation). At the transition point (at a pressure of about 3.8 GPa), the interface, which rapidly passes throughout the crystal from one face to another, is observed with an optical microscope. The volume and the cell parameters as well as the vibrational frequencies in the Raman spectra change jumpwise.[35] At the same time, the space group of the crystal structure ($P2_1/c$) is preserved. Hence, the polymorphic transformation belongs to isosymmetric transitions. The structure of the high-pressure phase was solved and the structures of the low- and high-pressure phases at several pressures (varying from atmospheric pressure to 8 GPa) were refined by full-profile analysis of high-resolution X-ray powder diffraction patterns, which were obtained with the use of synchrotron radiation. The results of this investigation demonstrated that the single-layer packing of oxalate ions in the structure remains, in principle, unchanged (positions of the centroids of these ions are considered), but a

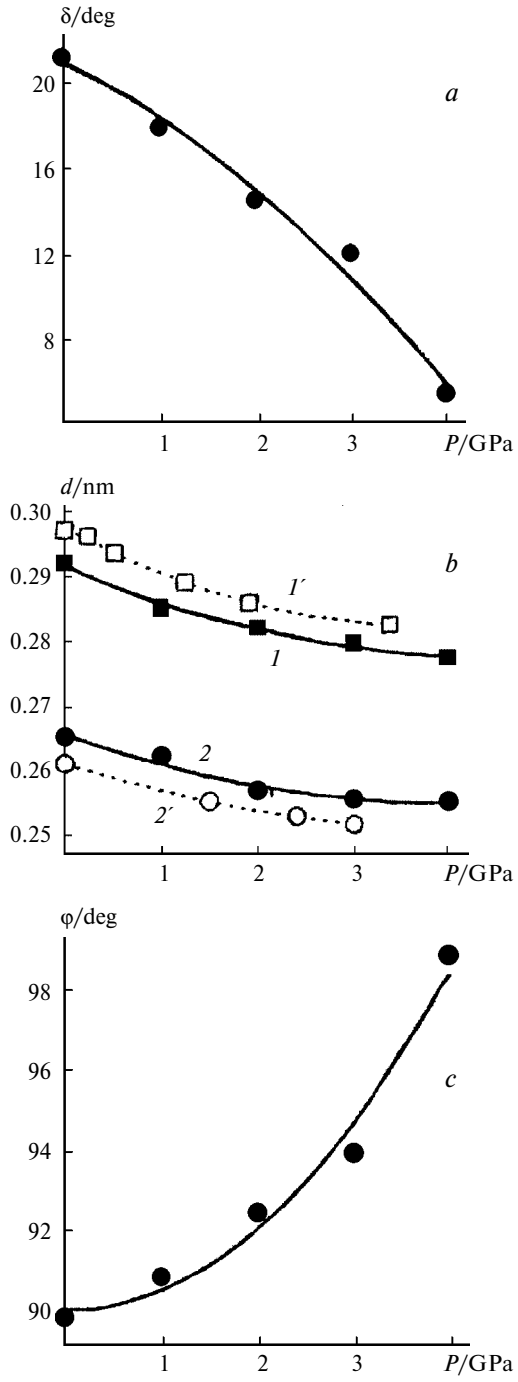

Fig. 7. Intra- and intermolecular structural distortions in the monoclinic modification of paracetamol with increasing pressure: *a*, a decrease in the dihedral angle between the planes of the phenyl ring and the acetamide group in the molecule; *b*, shortening of the distances between the non-hydrogen atoms involved in the intermolecular NH...O (*1*) and OH...O (*2*) hydrogen bonds; the corresponding values for $[Co(NH_3)_5NO_2]Cl_2$ [19,20] (*1′*) and 2-methylcyclopentane-1,3-dione[22] (*2′*) are given for comparison; *c*, an increase in the angle between the planes of the phenyl rings of the adjacent molecules.[18]

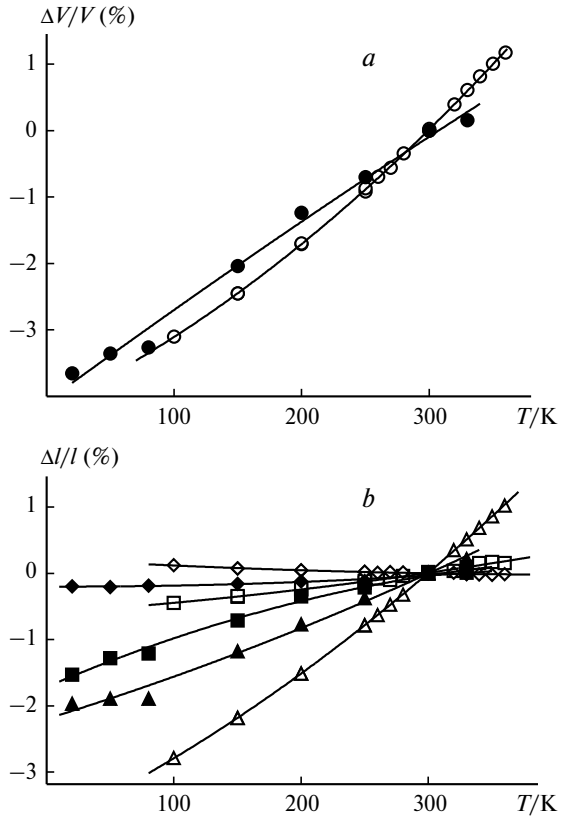

Fig. 8. Relative changes in the volume (*a*) and linear strain along the principal axes of the strain ellipsoid (*b*) on cooling of the monoclinic (solid symbols) and orthorhombic (open symbols) polymorphs of paracetamol.[33,34]

jumpwise rotation of the oxalate ions takes place so that the dihedral angle between their planes increases by almost 20° (from 32 to 52°). This process is accompanied by a jumpwise change in the coordination of the sodium atoms by the oxygen atoms of the oxalate ions (coordination number increases from 8 to 10), which is most clearly demonstrated by calculating the corresponding Voronoi polyhedra (Fig. 9).[26]

Effect of pressure on the crystal structures of the polymorphs of glycine. The polymorphic transition in sodium oxalate is completely reversible and even can occur without destruction of the crystal.[35] The pressure-induced polymorphic transformation in glycine, which was also studied by our research group, provides an example of another type.

Under normal conditions, glycine can exist as three polymorphs, the so-called α ($P2_1/n$), β ($P2_1$), and γ ($P3_1$) polymorphs. Two of them (α and γ) can be preserved for an indefinitely long period of time at ambient conditions, and their relative thermodynamic stability has been reliably established only recently by precision calorimetric measurements.[36,37] An increase in the pressure leads only to anisotropic compression of the α modification,[38,39]

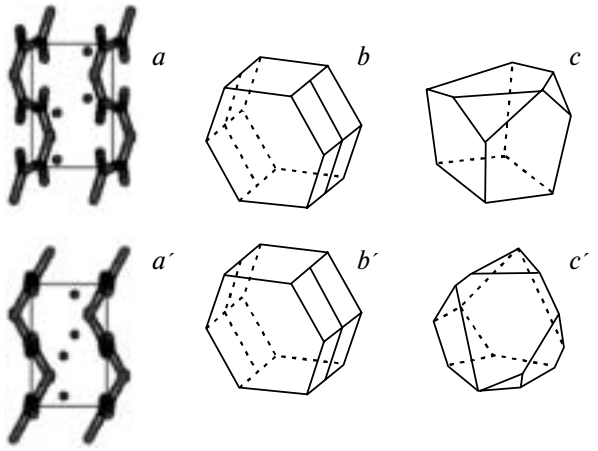

Fig. 9. Changes in the crystal structure of sodium oxalate in going from the low-pressure phase (*a*, *b*, *c*) to the high-pressure phase (*a´*, *b´*, *c´*): *a*, *a´*, packing of the oxalate anions and sodium cations; *b*, *b´*, Voronoi polyhedra for the centroids of the oxalate ions; *c*, *c´*, Voronoi polyhedra for the coordination environment of the sodium ions by the oxygen atoms.[26]

whereas the β and γ modifications undergo pressure-induced phase transitions.[38,40,41] Under high pressure, the γ modification of glycine is transformed into a new polymorph (δ), whose structure is described by the space group *Pn*, the phase transition occurring incompletely and being only partially reversible.[41] At high pressure, the starting γ modification and the high-pressure phase coexist in a broad pressure range.[41] First evidence of the δ phase appears already at 1.6 GPa. However, the sample contain an impurity of the starting γ phase up to ~8 GPa, after 4.2 GPa the δ phase becomes undoubtedly the major one. On decompression, the δ phase persists down to atmospheric pressure, a mixture of the γ phase, the δ phase, and an unidentifiable third phase being observed. In the δ phase, the zwitterions are linked *via* hydrogen bonds to form layers, whose structure is similar to those present in the α and β phases (Fig. 10), but the δ phase differs in the stacking of the layers. It is noteworthy that the δ phase of glycine is formed under high pressure only starting from the γ phase, in which the chains of the zwitterions are linked to each other to form triple helices, whereas the

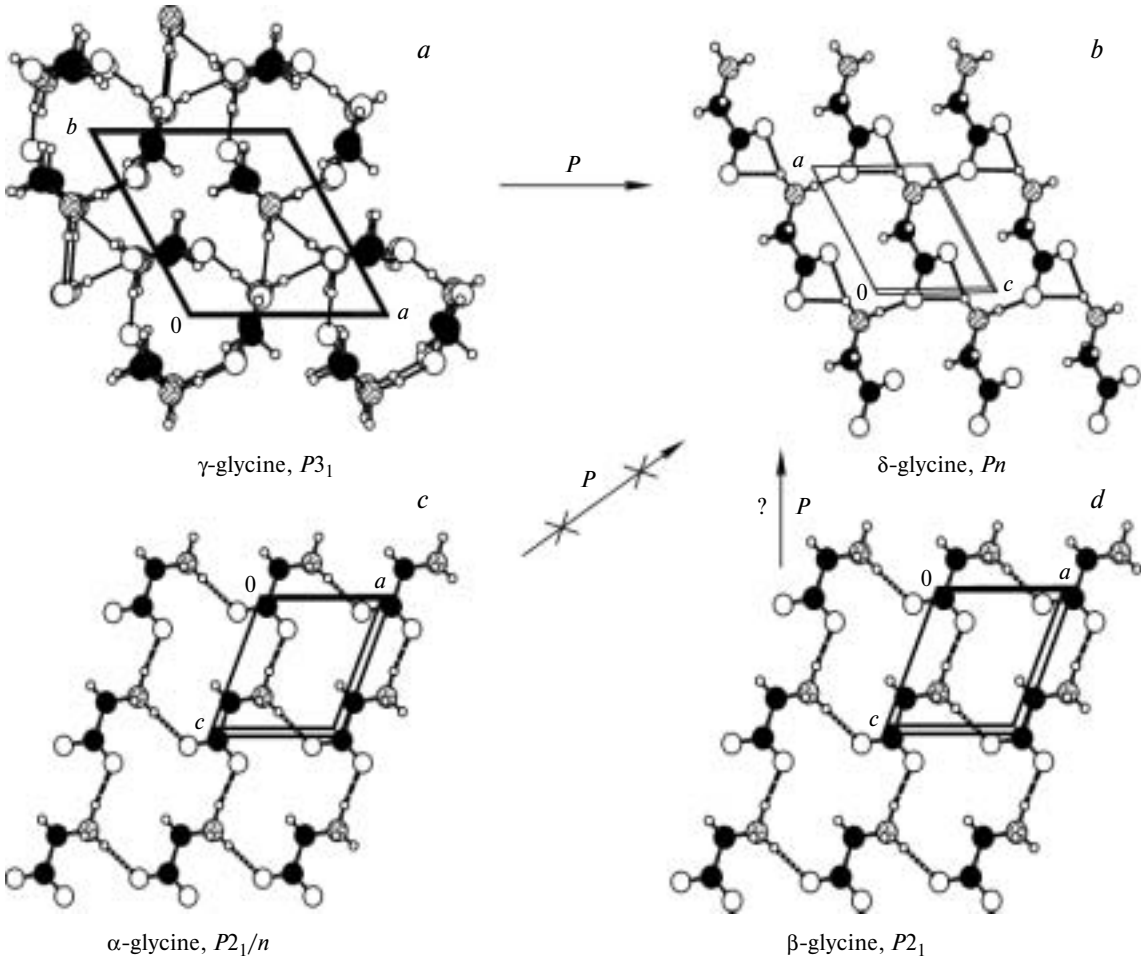

Fig. 10. Fragments of the crystal structures of the α, β, and γ polymorphs of glycine and the high-pressure δ phase.[41]

α modification, in which the zwitterions are linked in the layers very similar to those present in the δ phase, undergoes only pressure-induced anisotropic compression and does not transform into the δ modification.

The phase transition of the γ modification of glycine to the δ modification is the first example of the pressure-induced polymorphic transition observed for the crystals of amino acids. This transition is not only of interest by itself but also from the viewpoint of understanding the effect of pressure on the secondary and tertiary structures of biopolymers.[3—5] The pressure-induced polymorphic transformation from the γ modification into the new phase can be related to a change in the secondary structure of the biopolymer resulting in the formation of sheets instead of helices.[41]

Effect of pressure on the structures of biopolymers. The pressure effect on the structures of biopolymers has attracted attention from the very beginning of high-pressure investigations of substances. Denaturation of lysozyme at pressures of 0.5—0.7 GPa has been described already in the first experiments performed by Bridgman.[42] Later on, the effect of pressure on proteins and other biopolymers was extensively studied by different methods. An increase in the pressure causes a change in the secondary structures of proteins up to their denaturation.[3—5,43—47] An increase in the pressure results in conformational changes in nucleic acids, the water present in the system playing an important role in this process.[48] The effect of pressure on the structures of biopolymers is of great importance for the life of organisms under high pressures, for example, in depths of the world's ocean,[49] and finds application in food industry[43,44] and medicine.[45—47] Conformational changes in myoglobin and hemoglobin make an additional contribution to a change in the rate of binding of oxygen by these proteins under high pressure. The kinetics of this reaction is strongly nonexponential, because the pressure not only affects the rate of an elementary event of binding of the ligand to the protein but also changes the populations of the conformational states of the protein, which differ in the kinetics of binding of oxygen.[50] Studies of the effect of pressure on the cell membrane permeability are also remarkable. These studies are not only of importance from the fundamental point of view but are also of interest, in particular, for understanding the effect of pressure on neurons and anesthetic action.[51] The pressure can affect the membrane permeability by changing both the structure of the membrane and the conformations of the molecules, which are inserted into the membrane and serve as channels.[52—54]

Investigation of the pressure effect on the structures of biopolymers based on studies of molecular crystals. Experimental studies of the pressure effect on biopolymers present considerable difficulties. One could hardly expect detailed information on pressure-induced changes in intermolecular bond lengths and angles to be obtained, although it is these intermolecular interactions and relatively small changes in intermolecular contacts that are responsible for changes in the secondary structures of biopolymers.

Main effects of pressure on biochemical specimens result finally in changes in the interatomic distances (as in the case of molecular crystals of small molecules). The changes in the interatomic distances can, in turn, be responsible for elastic deformation or conformational changes of the molecules (in terms used for biomolecules, changes in the secondary, tertiary, and ternary structures). Changes in the structures of biomolecules can occur as continuous anisotropic elastic deformation within the stability limits of the same phase. Since these pressure-induced changes can also be very sharp, they are similar to polymorphic transformations or irreversible plastic deformation and amorphization of crystals composed of small molecules. Similar to molecular crystals, where the pressure can cause shortening of the bonds, changes in the bond angles, torsion angles, and dihedral angles between the planes of the molecules and molecular fragments, electron density redistribution, charge transfer, dimerization, and polymerization, biomolecules can undergo pressure-induced ionization, aggregation, and dissociation.[3—5]

Thoroughly selected molecular crystals, which have intermolecular bonds and interactions analogous to those present in biopolymers (OH...O, NH...O, NH...N, and CH...O hydrogen bonds, carbonyl—carbonyl interactions CO...CO, *etc.*), can be used as imitation models for biological systems (biomimetics). Data on the effect of pressure on hydrogen bonds of different types similar to those obtained in our studies of modifications of glycine, paracetamol, cobalt complexes, and benzoquinone[18,20,25,26,38,40,41] or in studies of several research groups devoted to other organic compounds[3—8,15,16,21—24,27—32] may help in analyzing the effect of pressure on analogous bonds in biopolymers.[3—5]

As mentioned above, studies of pressure-induced polymorphic transformations in the crystals of glycine are of importance for understanding the effect of pressure on the secondary structures of proteins. Carbonyl—carbonyl interactions, which are responsible for the structures of β strands and α helices in proteins provide another example.[55] Analysis of the structures available in the Cambridge Structural Database revealed three main types of the relative arrangement of the carbonyl groups in the structures of molecular crystals, *viz.*, antiparallel, perpendicular, and sheared parallel motifs (Fig. 11).[56] Studies of the crystal structures of the polymorphs of acetone formed upon cooling or under high pressure made it possible not only to observe the formation of all three types of CO...CO contacts in reality but also to reveal the differences in the effect of the temperature and pressure on their relative energies.[28] These data obtained for the crystals of small molecules (acetone) are useful also for the prediction of

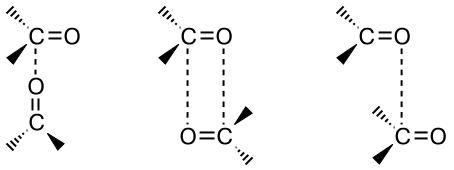

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Fig. 11. Three main types of the relative arrangement of the carbonyl groups in the structures of molecular crystals.[56]

the response of the CO...CO interactions in biomolecules to temperature and pressure.

Conclusions

Although geochemistry, experimental mineralogy, physics, and materials science are "traditional consumers" of the results of high-pressure studies, the pressure is also of considerable interest as an efficient tool for influencing relatively weak intermolecular interactions and conformations of molecules in supramolecular assemblies of different types resulting in both reversible elastic anisotropic structural distortions and irreversible plastic deformation, phase transitions, and amorphization—denaturation. Studies of these phenomena will provide a better understanding of the nature and properties of intermolecular interactions in supramolecular assemblies and allow one to learn how to control the formation of the structure and the properties of the latter. Crystals of small molecules can be used as imitation models in studies of more complex supramolecular systems, in particular, of biopolymers.

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