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High pressure structural investigations of 2,5-di(4-pyridyl)-1,3,4-oxadiazole—importance of strain studies for the description of intermolecular interactions

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Abstract

Results of a high pressure x-ray study of 2,5-di(4-pyridyl)-1,3,4-oxadiazole up to 2.5 GPa are presented and discussed. Parameters for the Murnaghan equation of state are derived. The bulk modulus amounts to $K_0 = 4.6 \pm 0.3$ GPa and its pressure derivative to $K_0' = 7.4 \pm 0.6$. These values are comparable to values of other diphenyl-1,3,4-oxadiazoles. The anisotropy of the compression is analysed using the strain tensor and discussed based on the anisotropy of the intermolecular interactions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The state and the properties of matter mainly depend on two thermodynamic parameters: pressure and temperature. Relationships between structure and properties for organic compounds may be derived from temperature investigations and high pressure studies. The latter is now a well developed field that further attracts increasing importance [1, 2].

Pressure influences the intra- and intermolecular interactions by reducing the distances between the individual building units. Therefore, molecular properties like conformation and supramolecular arrangement may be modified by pressure. Consequently, the dependence of the resulting material properties upon fundamental interactions and structural parameters may

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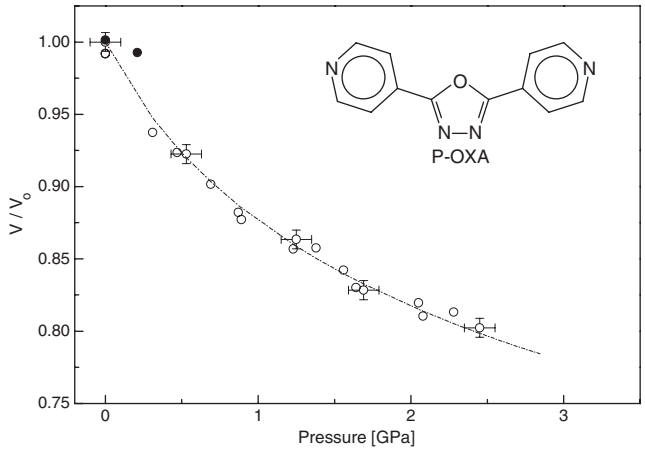

Figure 1. Equation of state for P-OXA. Full symbols: data after pressure release.

be studied without changing the chemical structure. Studies of intermolecular interactions give important information for the design of supramolecular structures or for crystal engineering.

High pressure experiments on a series of related organic molecular crystals lead to the question of whether some general rules for high pressure behaviour exist. Such rules may either be rather independent of the individual molecular structure or, on the contrary, may be determined by the individual structure and, therefore, the specific intermolecular interactions. For instance, the structure of an aromatic system, the conformation of the molecule, its planarity and thus a possible conjugation along the whole molecule, shape anisotropy, differences in polarity or dipole moment, and the impact of these molecular properties on the crystal structure by the formation of hydrogen bonds or other intermolecular interactions may influence the compression. The different interactions and their complicated interplay result in a specific pressure response that is usually anisotropic and may be described by the strain tensor. To derive some more general conclusions, it is necessary to investigate a broad variety of different compounds with slightly changed molecular structure, which may be obtained by a modified substitution. Here, our previous work on di(phenyl)-1,3,4-oxadiazoles [3–6] is continued with a related compound, 2,5-di(4-pyridyl)-1,3,4-oxadiazole (P-OXA; see the inset in figure 1 for the molecular structure).

At ambient pressure P-OXA has a monoclinic structure, with lattice parameters $a = 5.313$ Å, $b = 12.142$ Å, $c = 16.771$ Å, $\beta = 93.41°$, and space group $C2/c$ (15), that was determined from single crystal studies [7]. The structure is characterized by the presence of molecular stacks in the a-direction (see figure 3). The main interactions are of π–π type and occur perpendicular to the molecular plane between the oxadiazole ring and the pyridyl rings of the two adjacent molecules as also found for similar oxadiazole crystals [8].

2. Experimental set-up

2.1. Sample synthesis

The investigated 2,5-di(pyridyl)-1,3,4-oxadiazole compound was synthesized by direct condensation of isonicotinic acid with hydrazine hydrate in polyphosphoric acid [9]. The isonicotinic acid and hydrazine hydrate were stirred in polyphosphoric acid (84.6% P_2O_5) at 180 °C for 10 h. After cooling, the clear solution was poured into water and filtered, and the

product was dried in vacuum. The product was recrystallized three times from water. Melting point: 188 °C (lit. 185–186 °C [9]).

2.2. High pressure investigations

The high pressure structure studies were carried out in the multi-anvil press MAX-80 [10] using synchrotron radiation at HASYLAB, DESY Hamburg, and energy dispersive techniques. The general set-up has been described elsewhere together with a discussion of some disadvantages that have to be considered in the evaluation procedure, for instance additional reflections from the epoxy cube, which serves as gasket and sample chamber, or the occurrence of 'escape' peaks due to the detector material [3].

The pressure is determined *in situ* according to the Decker equation of state for NaCl [11]. Slight pressure gradients around 0.1 GPa may be present within the sample.

For the subsequent evaluation of the diffractograms and the determination of the lattice parameters the program Powder Cell 2.3 [12] is applied. The theoretical pattern that resulted from single crystal investigations at ambient pressure is fitted to experimental patterns obtained under pressure. The program enables this procedure independently of texture influences upon the intensity of the peaks. Every peak is treated separately. This procedure gives information about the variation of the lattice parameters but not on the crystal symmetry or the individual atomic positions. The conformation of the molecule is kept unaltered, which is justified since the molecules are rather rigid due to their delocalized π-systems. Actually, the molecules are nearly planar at ambient pressure with a dihedral angle of the different rings against each other of $\pm 3.3°$, resulting in an at least partial conjugation of the molecule. Thus, the tendency for further planarization under compression is limited. This approximation is suitable for aromatic compounds with a partially delocalized π system such as the oxadiazoles. A deeper analysis to determine the molecular conformation is not possible due to the limited resolution of the energy-dispersive diffractograms compared to angle-dispersive ones. Nevertheless, the pattern is sensitive to changes of the orientation and rotations of the individual molecules, i.e. to variations of the relative positions. These would result in modifications of the powder pattern.

The relative error of the fit procedure to determine the lattice parameters using Powder Cell is estimated to be 0.003 for the b- and c-axis lengths and slightly larger (0.005) for both the a-axis and the monoclinic angle. Of course, the resulting error also depends on the quality of the experimental energy dispersive pattern.

3. Results and discussion

Figure 1 shows the evolution of the unit cell volume with pressure in the range below 2.5 GPa. The volume data are fitted applying the usual two parameter Murnaghan equation of state (MEOS):

$$p = \frac{K_0}{K_0'}\left[\left(\frac{V_0}{V}\right)^{K_0'} - 1\right].$$

Here, p denotes the pressure and V the volume. The index '0' refers to the initial state at ambient pressure. K_0 is the bulk modulus and K_0' its pressure derivative, both evaluated at $p = 0$ GPa, i.e.

$$K_0 = -\left(\frac{\mathrm{d}p}{\mathrm{d}\ln V}\right)_{p=0}, \qquad \text{and} \qquad K_0' = \left(\frac{\mathrm{d}K}{\mathrm{d}p}\right)_{p=0}.$$

The MEOS yields results for bulk modulus K_0 and its pressure derivative K_0' with realistic precision for small compressions [13]. An overview about possible EOS forms may be found

in [14], while the applicability of different EOS types is discussed in [15] for the example of anthracene. A fit of the data to the MEOS in the pressure region below 2.5 GPa gives $K_0 = 4.6 \pm 0.3$ GPa and $K_0' = 7.4 \pm 0.6$. This characterizes P-OXA as very soft material, which is also found for many other organic crystals, which show a high compressibility and a strong anisotropy. It should be noted that the volume at $p = 0$ GPa determined from the equation of state (1075.8 $\pm$ 2.6 Å^3) is in very good agreement with that determined from the single crystal structure analysis (1080.0(4) Å^3, [7]).

The values obtained for K_0 and K_0' may be compared to data for other compounds containing the oxadiazole ring like 2,5-di(phenyl)-1,3,4-oxadiazole (DPO I) [3], where the pyridyl rings are replaced by phenyl rings, or to 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (F-OXA) [5]. Here, in relation to DPO the terminal hydrogen atom of the phenyl ring is substituted by fluorine in the *para*-position. The aromatic system and the molecular conformation are similar for all three compounds. All molecules are nearly flat and the rings are almost coplanar. The crystal structures are different despite some common motifs. The main common motif is the occurrence of stacks of parallel arranged molecules in a certain crystal direction (c for F-OXA and a for DPO I). This gives rise to π–π interactions between phenyl and oxadiazole rings of neighbouring molecules. Usually, the molecular axis is tilted against the stack axis. Structural differences result from a possible change of the orientation of the molecules within a stack and/or in adjacent stacks or from the relations between the individual stacks (see also [7]). However, the behaviour of the volume under pressure is quite similar, the EOS parameters are nearly equivalent: $K_0 = 7.3 \pm 0.7$ GPa, $K_0' = 6.7 \pm 0.3$ [3], and $K_0 = 6.9 \pm 0.8$ GPa, $K_0' = 6.2 \pm 0.3$ [5] for DPO I and F-OXA, respectively. Similar parameters have already been found for other fluorine containing diphenyl-1,3,4-oxadiazoles [5] and also for various, not necessarily aromatic, compounds, which have quite different molecular and crystal structures [2]. Terphenyl, a comparable aromatic compound, which contains a phenylene ring instead of the central oxadiazole ring, has a bulk modulus of 5.8 $\pm$ 0.2 GPa and a pressure derivative K_0' of 8.4 $\pm$ 0.2 (estimated from literature data [17]). Paracetamol [16] and DPO I and II [3, 8] are examples of polymorphic compounds where the polymorphs have nearly the same bulk compressibility. In general, besides small differences, these compounds show a rather consistent high pressure bulk behaviour independent of their structure. However, the anisotropic lattice response varies considerably in these cases, which is related to the different intermolecular interactions. Only the analysis of this anisotropy studying the strain may give a deeper insight.

The structural peculiarities and the complex interaction network within the crystal result in an anisotropic lattice distortion under pressure. Figure 2 shows the behaviour of the lattice parameters as function of pressure. The differences in the compression of the lattice parameters a, b, and c may be explained taking into account the intermolecular interactions acting in their directions. The main features of the packing motif [7] are illustrated in figures 4(a) and (b), that give the (010) and (100) projections, respectively. Stacks along the a-direction are formed by nearly planar and parallel molecules. The molecular plane is tilted against the stack axis by 40°. All molecules share the same orientation with respect to the oxadiazole moiety. Within a given stack, the oxadiazole ring is located between two pyridyl rings of adjacent molecules, giving rise to π–π interactions between the rings. Therefore, these interactions are oriented in the a, c-plane. Van der Waals interactions act between the stacks. The a-axis is the most compressible one while the lattice parameter c shows the smallest compression. It is remarkable that the stack axis shows the largest compression in the investigated pressure range, in contrast to other oxadiazole compounds, for instance DPO I [3]. Despite their small molecular differences and some common packing motifs mentioned above (like coplanar rings or the occurrence

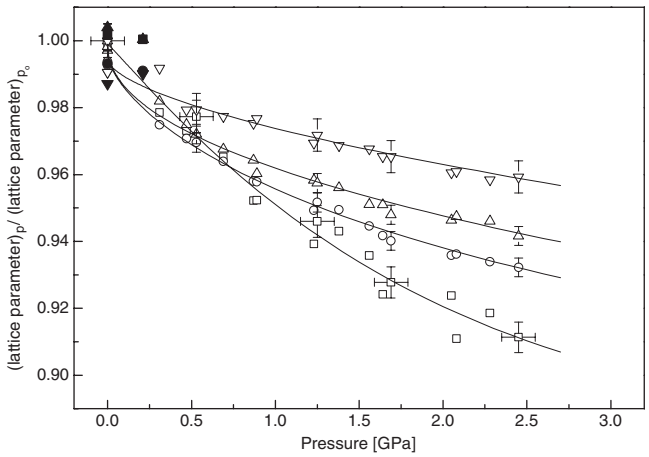

Figure 2. Variation of the lattice parameters with pressure. □, a; ○, b; △, c; ▽, β; full symbols, data after pressure release (for clarity, error bars are not given for every pressure step in the figures).

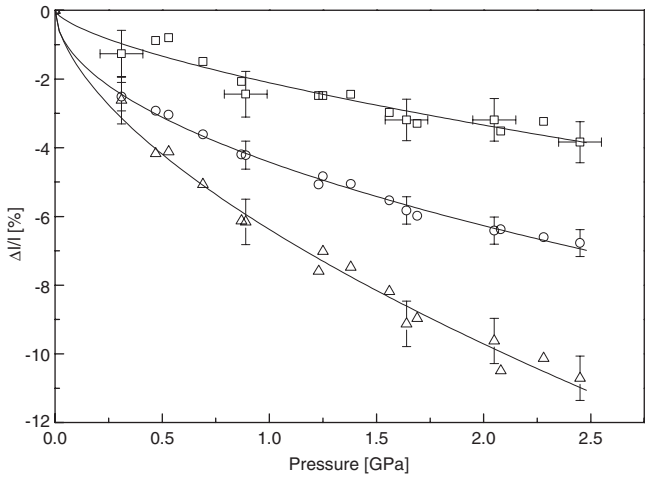

Figure 3. Linear strain along the principal axes of the strain ellipsoid. □, ε_1, ○, ε_2, △, ε_3.

of stacks), both compounds P-OXA and DPO I show deviations in their three-dimensional structure. Their stack arrangement is different: in P-OXA the stacks are related by a translation along the b-axis while in DPO I the stacks are shifted against each other in the b-direction so that the oxadiazole rings are not aligned along the c-axis (the analogue to the b-axis of P-OXA; compare figures 4(b) and 6). The inclination of the molecular plane against the stack axis is the same for all stacks in P-OXA, resulting in the arrangement of the molecules in planes parallel to $(\bar{1}04)$, which leads to a layered structure. In contrast, in DPO I the tilt angle changes its sign for neighbouring stacks ($\pm 41°$). However, though the aromatic π-system is modified from phenyl (DPO I) to pyridyl (P-OXA), the motif for the π–π interactions within the stacks is nearly the same. The π-systems are not oriented parallel but inclined to the cell axes (in the a, c-plane for P-OXA and in the a, b-plane for DPO I). This influences the compression behaviour of the corresponding lattice parameters.

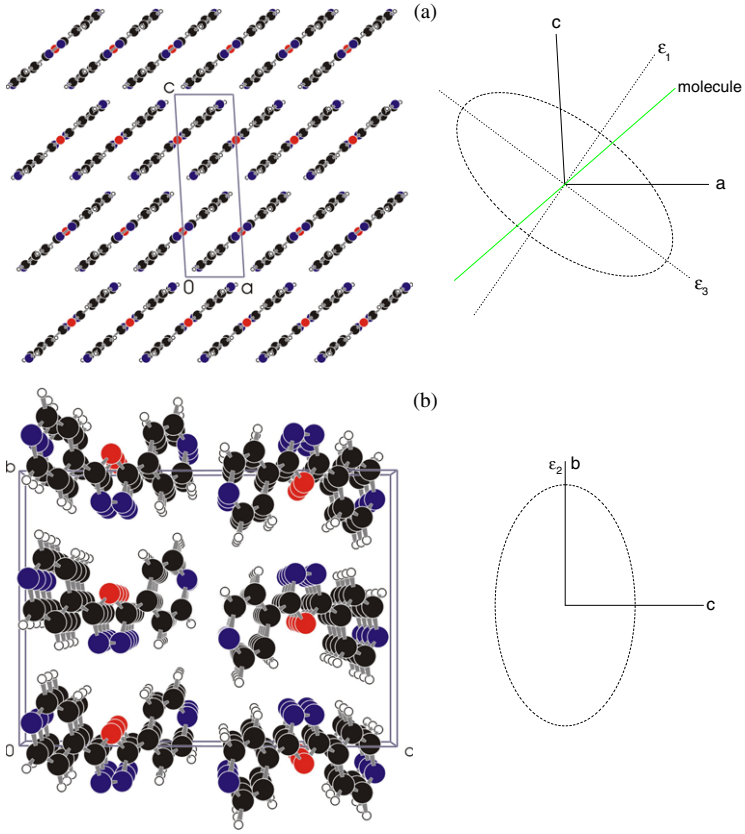

Figure 4. (a) [010] projection of the P-OXA structure (left) showing the stack arrangement and the corresponding strain ellipsoid at 0.3 GPa (right). (b) Projection of the P-OXA structure onto the b, c-plane (left) and the corresponding section of the strain ellipsoid at 0.3 GPa (right).

To quantify the anisotropic lattice distortion, the strain tensor was evaluated from the unit cell data using the STRAIN program by OHASHI [18]. The strain gives an idea about the strength of the intermolecular interactions along different directions. Figure 3 illustrates the evolution of the linear strain along the main axes of the strain ellipsoids for P-OXA. A section through the strain ellipsoid in the a, c-plane, i.e. perpendicular to the ε_2-direction, which corresponds to the [010] direction of the crystal structure, is given in figure 4(a) for a pressure of 0.3 GPa using the linear strain data of figure 3. Figure 4(b) gives the corresponding section in the b, c-plane. The strongest compression is found along ε_3, that is, nearly normal to the molecular layers as usually expected in layered structures. This direction is inclined by about 12° against the normal of the molecular plane. Thus, the interactions between π-acceptor (oxadiazole) and π-donor (pyridyl) with an initial distance of approximately 3.7 Å measured at the ring centroids are enhanced during the compression process. Other compounds with a layered structure (for instance paracetamol or benzoquinone) show a similar compression [2, 16, 19]. In these cases, the largest linear strain was observed in the direction perpendicular or nearly normal to the layers. However, these molecules contain only one aromatic ring type (phenylene) and the layers are mainly linked by van der Waals interactions or hydrogen bonds. In the case of P-OXA the additional acceptor–donor interactions occur between the layers.

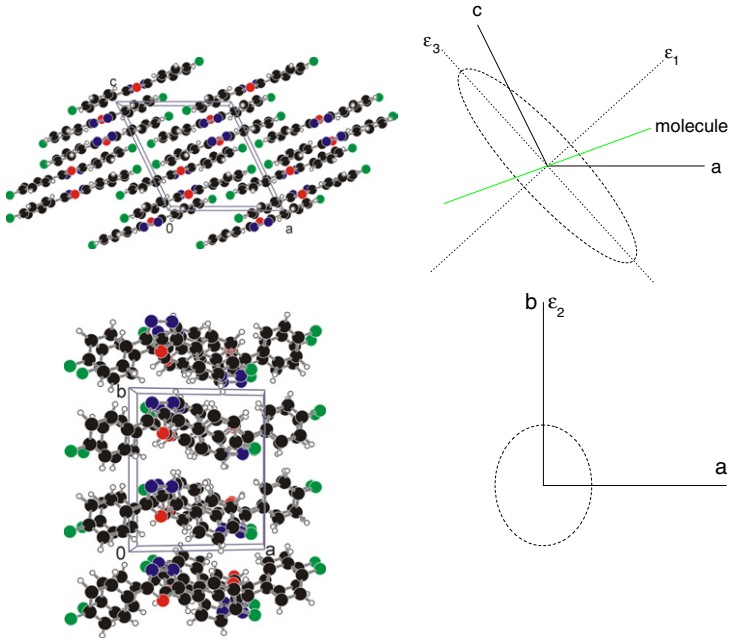

Figure 5. F-OXA structure with the corresponding sections of the strain ellipsoid at 0.4 GPa (data from [5]). Top, a, c-plane; bottom, a, b-plane illustrating the stack arrangement.

In the direction of the long molecular axis, that connects both pyridyl nitrogen atoms, a considerably lower compression is observed, mainly given by the ε_1 component of the strain tensor (cf figure 3). This results from the initially short distances between C and N (approximately 3.5 Å) or C and C (3.4 Å) of adjacent molecules from neighboured stacks (of the same layer). It is possible that here a C–H $\cdots$ N hydrogen bond is formed with increasing pressure. This could contribute to the low compression along the c-axis. Figure 4(b) shows the (100) projection of the structure, i.e. the b, c-plane, and the corresponding section of the strain ellipsoid. The b-direction, which corresponds to the ε_2 tensor axis, shows an intermediate compressibility. There exist short distances between the nitrogen atoms of the oxadiazole ring and C atoms of adjacent pyridyl rings (approximately 3.5 Å). So it may be concluded that the packing motif that gives rise to the anisotropy of the intermolecular interactions is responsible for the observed compression behaviour.

To underline the importance of the strain analysis for the description of intermolecular interactions, some previously published high pressure data of different oxadiazole derivatives have been re-evaluated. The first compound is F-OXA [5]. It shares several common structural features with P-OXA. Its monoclinic structure ($P2_1/n$) is characterized by stacks in the c-direction and an arrangement of nearly flat molecules in planes approximately parallel to the $(10\bar{3})$ plane. If the strain tensor is evaluated for a pressure of 0.4 GPa a similar picture as for P-OXA arises (figure 5). Again, the highest strain ε_3 is observed only slightly tilted to the normal of the molecular plane, i.e. in direction of the π interactions, while in directions perpendicular to the stacks the strain is nearly equal and much smaller. The smallest strain, ε_1, nearly parallel to the molecular plane, may be due to two symmetry independent intermolecular C–H $\cdots$ F bonds that lead to the formation of molecular chains within the layers, preferentially in the a-direction. Also in this case, the compression anisotropy induced by the different intermolecular interactions and the molecular arrangement is clearly visible.

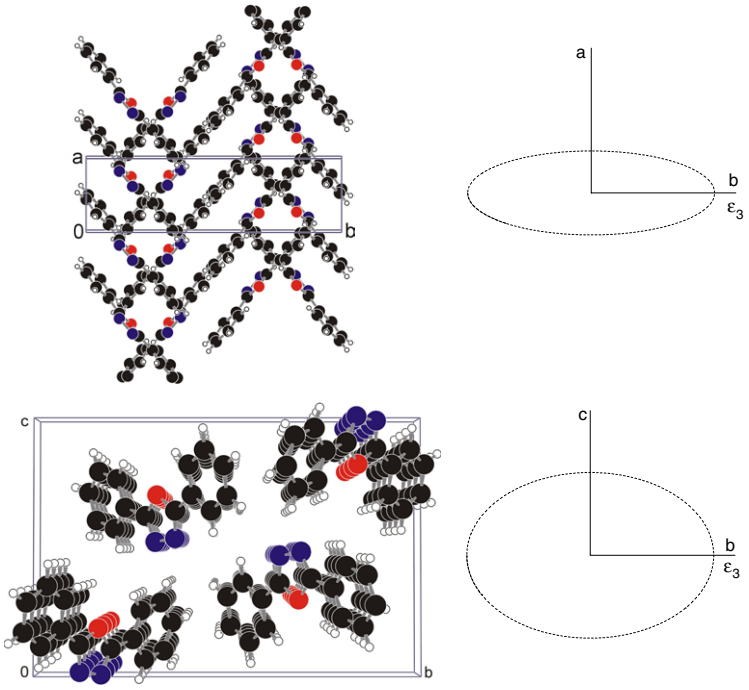

Figure 6. DPO structure with the corresponding sections of the strain ellipsoid at 0.6 GPa (data from [3]). Top, (001) projection; bottom, (100) projection showing the stack arrangement.

The high pressure behaviour of the basic compound DPO I was investigated in [3, 20]. Typical views of the crystal structure and the corresponding strain ellipsoid for a pressure of 0.6 GPa are illustrated in figure 6. Compared to P-OXA and F-OXA the result of the strain analysis is a little bit different due to the structural features, especially the herring-bone motif. The largest strain is observed in the *b*-direction, i.e. inclined to the molecular plane by 49°. The herring-bone arrangement prevents the largest strain from appearing more or less perpendicular to this plane, as found for the layered structures P-OXA and F-OXA. However, it is still in the direction of π interactions between the different rings. The behaviour between the stacks is comparable to that of both other compounds, although the lateral shift in the *b*-direction modifies it slightly. The strain in the shift direction (ε_3) is approximately 1.5 times as large as perpendicular to this direction.

As a third additional example the high pressure behaviour of another oxadiazole derivative, 2,5-di-(4-aminophenyl)-1,3,4-oxadiazole (A-OXA) [4], is analysed briefly. A-OXA has an orthorhombic structure (*Pbca*). Due to both *para* amino-groups a complex three-dimensional hydrogen bond network is formed. Additionally, stacks are also formed in the *b*-direction [6]. Figure 7 gives an impression of the crystal arrangement and the corresponding strain ellipsoid at 0.6 GPa [4]. Again, the correspondence between structural features is obvious. The largest strain, ε_3, is observed in directions with π interactions. The strain in directions perpendicular to the stacks, i.e. ε_1 and ε_2, is nearly the same.

Summarizing, the results clearly underline the importance of the strain analysis to relate structural features, intermolecular interactions and the resulting high pressure behaviour. This can be seen most clearly for layered structures like P-OXA or F-OXA. The largest strain is observed nearly perpendicular to the molecular plane. This is also the direction of

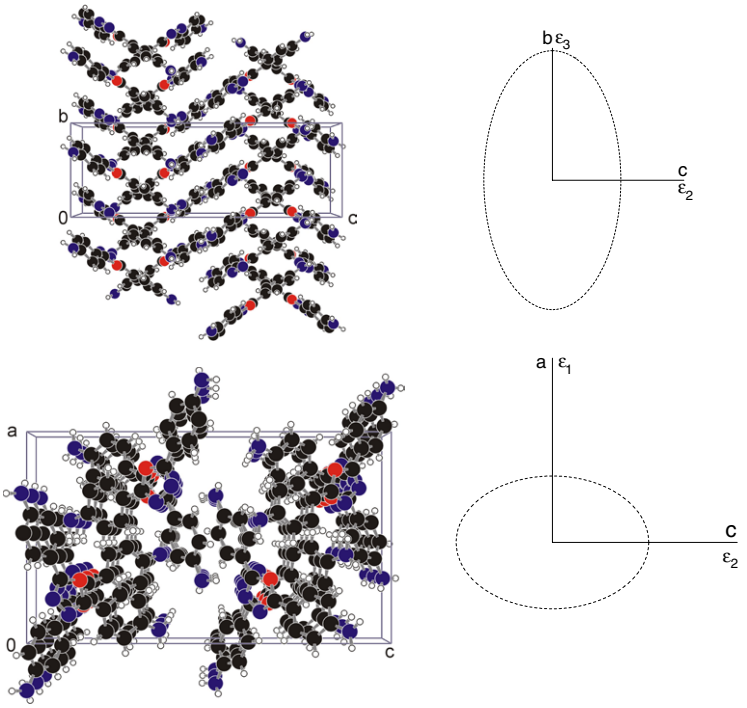

Figure 7. Crystal structure of A-OXA together with the corresponding sections of the strain ellipsoid at 0.6 GPa (data from [4]). Top, (100) projection; bottom, (010) projection.

π interactions between neighbouring molecules, specifically between oxadiazole and phenyl rings. The behaviour between stacks perpendicular to their axes, dominated by different intermolecular interactions such as van der Waals forces, is clearly different. However, this picture has to be modified slightly if, for instance, hydrogen bonds or specific structural features such as the herring-bone motif influence the behaviour.

4. Conclusion

High pressure investigations give an idea about the complex intermolecular interactions in a molecular solid and their relation to structural features. Characteristic structural elements for P-OXA and many comparable oxadiazole compounds are the occurrence of stacks of planar molecules and the formation of molecular layers. The crystal structure is characterized by a complex three-dimensional interaction network. In P-OXA the main forces are π–π interactions between the π-systems of oxadiazole and pyridyl rings, i.e. π–π donor–acceptor interactions between the different aromatic rings, and van der Waals forces.

The bulk behaviour of P-OXA under high pressure as given by the equation of state and the corresponding bulk modulus and its pressure derivative resembles that of other diphenyl-1,3,4-oxadiazole containing compounds and, more generally, that of many other aromatic compounds. Using the strain tensor analysis, it could be shown for the example of different oxadiazole compounds that the behaviour between molecular stacks, that is mainly determined by van der Waals interactions, is different from that within a stack or more or less perpendicular to the molecular plane, i.e. in the direction of the π–π interactions between acceptors and donors.

The results of the strain analysis allow the comparison between different compounds having different crystallographic structures but probably similar structural features or elements as mentioned. It is possible to derive conclusions about the different intermolecular interactions based on the anisotropy of the pressure response. Thus, the strain analysis is essential for the interpretation of high pressure data to derive information about the intermolecular interactions.

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