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High-pressure studies on molecular crystals—relations between structure and high-pressure behavior

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Abstract

This paper summarizes attempts to understand structure–property relationships for a large class of aromatic diphenyl-1,3,4-oxadiazole molecules. Starting from the investigation of the crystal structure several common packing motifs as well as characteristic differences are derived. Many different molecules show a rather planar conformation in the solid state. A stronger intermolecular twist is only observed for compounds with substituents occupying the *ortho*-positions of the phenyl rings. Most crystal structures are characterized by the formation of stacks leading to intense π–π acceptor–donor interactions between oxadiazole and phenyl rings. High-pressure investigations result in a soft compression behavior typical for organic molecular crystals. The bulk behavior may be described by the Murnaghan equation of state with similar coefficients (bulk modulus and its pressure derivative) for nearly all investigated compounds but also for related substances. The compression shows a strong anisotropy resulting from the specific features and packing motifs of the crystal structure. This is clearly indicated by a corresponding strain analysis. Additionally to the crystal structure the Raman spectrum was also investigated under increasing pressure. The different pressure behavior of external and internal modes reflects the difference between intra- and intermolecular interactions.

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

1. Introduction

The properties of the crystalline organic solid are determined, on the one hand, by the chemical structure of the molecule and, on the other, by the three-dimensional arrangement in the crystal lattice. The intermolecular interactions between the individual building blocks, i.e. the molecules, and the resulting lattice architecture substantially determine the mechanical, electrical and optical properties of the substances. If these intermolecular interactions are modified the structure and related properties vary. This gives an insight into the structure–property relationships and implies a possible property tuning.

One method to study such structure–property relations by changing the intermolecular interactions is the modification of the chemical structure of the molecules. However, this involves a completely new molecule with different interactions

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and probably resulting in a different crystal structure. For a better study of the influences of the intermolecular interactions on the structure and properties for specific molecules without changing their structure, it is more appropriate to preserve the chemical structure. Thus, a better way is the application of high pressures. Here, the chemical structure of the molecule is maintained, only the distances between the structural units are changed and therefore the corresponding intermolecular interactions.

High-pressure investigations belong to the set of indispensable techniques in many fields of basic and applied science, ranging from solid state physics, chemistry, geophysics and geology up to materials science and even biochemical and biological problems [1–4]. Today, application areas range from the traditional synthesis of hard materials up to biochemical/biological questions like food preservation, pressure sterilization or the development of novel vaccines from pressure-treated bacteria or viruses [5]. An important field for the application of high-pressure methods to molecular crystals is found in pharmacy. Pressure may play a substantial role during several processing steps of the agents. So it is possible that irreversible phase transitions are induced during the shaping process by pressing that result in a modification of the pharmaceutical efficiency of the drug. To ensure the correct drug efficiency the only knowledge of its mechanical parameters derived from its equation of state (EOS) is insufficient. To omit probable phase transitions it is also of crucial importance to know the phase diagram, at least in the restricted area of the relevant pressure and temperature of the production process [6, 7].

Basic phenomena for the description of the evolution of structure and bonds under pressure are the occurrence of pressure-induced phase transitions or even chemical reactions, the impact on the vibrational characteristics, electronic states (for instance, metal–insulator transitions) or the appearance of new electronic or magnetic order states [3, 8].

High-pressure studies entered also the field of organic solids. Several reviews, such as for instance [6, 9–11], summarize the developments and achievements in this field. Most organic molecular crystals show high compressibility and strong anisotropy of compression. Certain features of the supramolecular arrangement, like the presence of stacks or layers, strongly determine the high-pressure response. Other influencing factors are due to the molecular structure, i.e. in the case of the discussed diphenyl-oxadiazoles, the structure of the aromatic system, the number of rings and their mutual arrangement. These characteristics determine the conformation of the molecule and thus a possible conjugation. Further influencing aspects may be differences in polarity (dipole moment) or shape anisotropy. Additionally, specific molecular structures or functional groups could cause steric influences and hindrances or could favor the formation of hydrogen bonds. The anisotropic compression due to the molecular arrangement provides insights into the action of the different forces constituting the organic molecular crystal, such as for instance π–π, van der Waals or hydrogen bond interactions.

The derivation of general trends for the high-pressure behavior and relations to the specific chemical structure requires investigations of a group of compounds that differ only in their substitutional scheme. So, for instance, biphenyl, oligophenyls or *para*-hexaphenyl were studied in [12–15], while anthracene and disubstituted anthracene derivatives were investigated in [16–18] (see also [19] for further compounds). Drugs under compression up to 4 GPa have been studied in [6, 9, 11, 20]. In particular, these studies indicated and discussed the strong anisotropic lattice response to pressure application, i.e. the lattice strain in relation to the molecular conformation, the crystal packing, the corresponding intermolecular interactions or their specific intermolecular bonds.

For our investigation we focused on a class of molecules containing the diphenyl-1,3,4-oxadiazole fragment. This group of compounds was intensively studied by our group and provides a desired variety of different examples for a profound comparison [21–32]. Aromatically substituted 1,3,4-oxadiazoles are widely used as scintillators, fluorescent and photographic materials [33, 34] and they are of interest as electron transport materials or emitting layers in electroluminescent diodes or for nonlinear optical processes. Compounds containing the 1,3,4-oxadiazole unit as a basic building block are also known as biologically active agents [35, 36].

The properties of the diphenyl-1,3,4-oxadiazole core (DPO) are varied by different substituents at the two phenyl rings adjacent to the oxadiazole ring. This involves both, the variation of the type of functional groups and changing positions at the ring. Due to modified intra- and intermolecular interactions different structures result and are therefore accompanied by a characteristic property change. The variation of the donor or acceptor strength and the substitution scheme considerably influences the electronic behavior of the compound and therefore its optical properties like absorption and fluorescence, but also the molecular dipole moment and all quantities connected with the electronic structure.

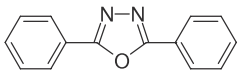
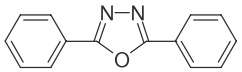
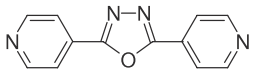
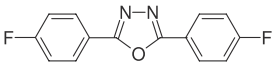
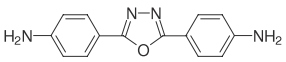
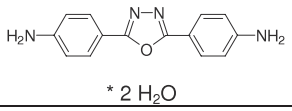
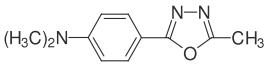
2. Structural characteristics

2.1. Molecular conformation

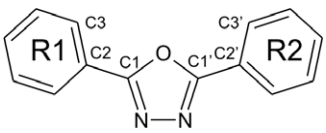
One of the basic features influencing the packing motif in the crystal structure is the conformation of the molecule. The conformation has an effect on the three-dimensional molecular arrangement as well as the electronic properties of the molecule. Characteristic parameters are the dihedral angles between the three aromatic rings and the inter-ring bond distances. In the following, the torsion angle is measured according to the numbering given in scheme 1, between the phenyl ring R1 and the oxadiazole ring using the atoms O–C1–C2–C3 and between the oxadiazole ring and phenyl ring R2 using O–C1′–C2′–C3′. The bond lengths between the phenyl rings and the oxadiazole ring are given by d(C1–C2) for R1 and d(C1′–C2′) for R2. This scheme was used to determine the corresponding values for angles and bond distances of the different compounds listed in table 1.

The individual phenyl and oxadiazole rings of all investigated compounds are almost planar. The endocyclic

Table 1. Lattice parameters for different diphenyl-1,3,4-oxadiazole compounds.

Compound Reference	Molecule (R1–Oxa–R2)	Structure space group No.	Unit cell parameters	Dihedral angle (°) R1–Oxa Oxa–R2	Inter-ring bond length (Å) R1–Oxa Oxa–R2
1a[a] [27]		Monoclinic $P2_1/c$ 14	$a = 5.188(1)$ Å $b = 18.078(2)$ Å $c = 12.144(1)$ Å $\beta = 93.19(1)°$	1.7 1.0	1.462 1.464
1b[a] [27]		Monoclinic Cc 9	$a = 24.134(4)$ Å $b = 24.099(3)$ Å $c = 12.879(2)$ Å $\beta = 110.05(1)°$	1.8–8.0 2.3–11.4 (6 molecules per asymmetric unit)	1.436–1.489 1.438–1.485
2 [32]		Monoclinic $C2/c$ 15	$a = 5.313(1)$ Å $b = 12.142(3)$ Å $c = 16.771(3)$ Å $\beta = 93.41(2)°$	3.3 3.3	1.464 1.464
3 [23]		Monoclinic $P2_1/c$ 14	$a = 10.443(2)$ Å $b = 11.444(2)$ Å $c = 10.747(2)$ Å $\beta = 116.31(9)°$	15.8 13.0	1.451 1.451
4 [23]		Orthorhombic $Pbca$ 61	$a = 13.469(5)$ Å $b = 7.968(3)$ Å $c = 22.893(8)$ Å	15.4 14.1	1.461 1.463
5 [23]		Orthorhombic $Cmcm$ 63	$a = 16.330(5)$ Å $b = 12.307(2)$ Å $c = 6.998(2)$ Å	20.6 20.6	1.450 1.450
6 [28]		Monoclinic $P2_1/c$ 14	$a = 10.300(1)$ Å $b = 6.484(1)$ Å $c = 15.812(1)$ Å $\beta = 99.48°$	1.9	1.451 1.468 (Oxa–CH_3)

[a] Different polymorphs.



Scheme 1. General molecular arrangement of aromatically substituted 1,3,4-oxadiazoles.

torsion angles remain very small. Therefore, the conformation of the molecules is determined by the dihedral angles between the phenyl rings and the oxadiazole ring. These angles are a measure of planarity of the whole molecule.

In general, the dihedral angles are mostly in the range below 15° for all molecules with symmetric *para*-substitution, indicating a rather planar conformation. Changing the position of the substituent is connected with larger deviations from planarity, as may be seen for amino-, nitro- and especially fluoro- or trifluoromethyl-substitution [21, 23]. But there is no general trend for all compounds. For instance, the trend for coplanarity increases significantly if the amino group is placed in a *meta*- or *ortho*-position [22]. The differences between *meta*- and *ortho*-substitution with respect to planarity are very small. The reasons for this behavior are still unclear. However, in the case of the amino group in the *ortho*-position intramolecular hydrogen bonds between the amino group and the nitrogen atom of the oxadiazole ring contribute to the planar arrangement of the rings.

In contrast, if the *ortho*-positions are occupied by nitro groups the torsion angle increases to 28.2° for R1 and 22.7° for the second phenyl ring R2. The same is observed for the fluorine derivative. Here, the molecule is twisted by approximately 30° [23]. Interestingly, the *meta*-compound is again more planar compared to its *para*- or *ortho*-counterparts.

A comparable trend results if the aromatic system is changed from the phenyl ring to the pyridyl ring. The molecules show a slightly decreasing planarity with the nitrogen atom positioned nearer to the oxadiazole moiety. Both polymorphs of the *ortho*-substituted molecule have two molecules per asymmetric unit and at least one ring is rotated by an angle around 10° [22]. However, this is still a value for nearly flat molecules.

Another fact should be mentioned for *meta*- and *ortho*-substitution. For fluorine substitution the bond between the phenyl ring and substituent always points in the direction towards the oxygen atom of the oxadiazole ring while nitro and

amino groups are located on the side of the nitrogen–nitrogen bond. This is also observed for the nitrogen atom in the pyridyl ring. The methyl group is an exception: for *meta*-substitution the substituents on both phenyls point in different directions, towards the oxygen atom as well as to the nitrogen atoms.

The largest deviations from planarity are found in trifluoromethyl compounds with substituents in both *ortho*-positions at one phenyl ring [21]. Here angles between 70° and 82° are found. In the case of unsymmetric substitution the ring with two *ortho*-substituents always shows a strong twist while the second unsubstituted or *meta*-substituted phenyl ring is rather coplanar with the oxadiazole ring with angles analogous to those found for *para*-substitution. Comparing *ortho*-trifluoromethyl substitution with *ortho*-methyl substitution it is obvious that the torsion angle is nearly twice as large for the fluorinated compound.

The other quantities that are important for the electronic states of the molecule are the inter-ring bond lengths responsible for the conjugation of the molecule. Most of the phenyl-oxadiazole inter-ring bonds are in the range between 1.45 and 1.47 Å bond, which corresponds well to the range for a $C(sp^2)$–$C(sp^2)$ single bond (1.48 Å [37]). Generally, no remarkable correlations between bond lengths and deviations from coplanarity were recognized. For molecules with large twist between the rings the bond between oxadiazole and phenyl rings is slightly longer than for nearly coplanar rings. For most of the compounds at least a partial conjugation of the π-system of the three rings may be assumed due to bond angles and bond lengths.

2.2. Crystal structures

A great variety of crystalline structures of substituted 2,5-diphenyl-1,3,4-oxadiazole compounds has been investigated so far [21–23, 25–32]. For a detailed structural description together with the technical background and a summary of all relevant data the reader is referred to the original papers. Table 1 summarizes characteristic crystallographic data for the examples discussed in the following. While the variations of the molecular structure remain rather restricted the real three-dimensional crystal lattice offers an extensive variability of the possible arrangements for the individual molecules. Most of the characterized structures are monoclinic or orthorhombic. The most common feature is the formation of infinite stacks due to π–π interactions between the different rings. This general principle is also found for many different crystalline aromatic substances (see, e.g., [38]). The donor–acceptor interaction induces the formation of π–π interactions, whereas the oxadiazole moiety acts as a π-acceptor and the phenyl rings of the adjacent molecules acts as a π-donor. Illustrative examples for these stacking arrangements are given in figures 1(a)–(c).

The basic 2,5-diphenyl-1,3,4-oxadiazole compound (**1**) crystallizes in a herringbone structure ([28], figures therein). Parallel molecules form stacks in the *a* direction. Molecules of adjacent stacks have opposite inclination to the stack axis with an angle of ±41°. Within the stacks, the molecules are oriented in the same direction, given by the line joining the center and the O atom of the oxadiazole ring. Neighboring stacks are translated in the *b* direction, avoiding an aligned arrangement of the oxadiazole rings along the *c* axis.

In 2,5-di(4-pyridyl)-1,3,4-oxadiazole (**2**) both phenyl rings of the diphenyl-oxadiazole unit are substituted by two pyridyl rings and a crystal structure modification results ([32], figure 1(b)). Again stacks are formed in the *a* direction by nearly planar molecules. All molecules within one stack and of neighboring stacks share the same orientation. Their molecular plane is inclined to this axis by 40°. Within a stack the oxadiazole ring is located between the two pyridyl rings of adjacent molecules, leading to π–π interactions between the rings. The stacks are linked by van der Waals interactions. While the orientation of the molecules in one stack and also for neighboring stacks is the same for both structures **1** and **2**, the relations between the stacks are different. **2** shows a highly periodic stack arrangement contrary to that of **1**, where the stacks are shifted relative to each other so that the oxadiazole rings are not aligned in the *b* direction. As a result in **1** layers of stacks overlap slightly, which is not observed in **2**. But the most obvious difference between both structures is the inclination of the molecules in a stack against the stack axis. In **2** molecules of adjacent stacks have the same inclination angle while in **1** neighboring stacks show the opposite inclination angle. So, besides common motifs like the arrangement of parallel molecules in stacks allowing intense π–π interactions between phenyl and oxadiazole rings significant differences are also found in the molecular orientation and the three-dimensional structure.

If the terminal hydrogen atoms of the phenyl rings are substituted by fluorine atoms, resulting in 2,5-bis-(4-fluorophenyl)-1,3,4-oxadiazole (**3**), the picture has to be modified ([23], figure 1(c)). The π–π electron interactions give rise to the formation of molecular layers parallel to the *a*, *c* plane in that crystal structure. The molecules within a layer are held together by two symmetry-independent intermolecular C–H···F hydrogen bonds. Together with the symmetry-related hydrogen bonds molecular chains are formed within the layers. As a common feature stacks are found oriented along the [101] direction. The molecular plane is again inclined against the stack axis with an angle similar for adjacent stacks. And, as a common motif also found for other oxadiazole compounds, the oxadiazole ring of one molecule is again located between the phenyl rings of adjacent molecules, giving rise to π–π interactions. However, in this case the arrangement within the stack is completely different. The orientation of the molecules given by the connection between the center of the oxadiazole ring and its oxygen atom changes such that neighboring molecules point in the opposite direction. An exception from the formation of π–π interactions between oxadiazole and phenyl rings is found in the case of the completely fluorinated compound. Here no π–π electron interactions were observed since the shortest distance between two rings is larger than 4.7 Å. Another reason for the lack of π–π electron interactions is probably the short repulsive interaction between the fluorine atoms of adjacent molecules [23].

In the case of amino substitution the formation of intermolecular hydrogen bonds extends the spectrum of

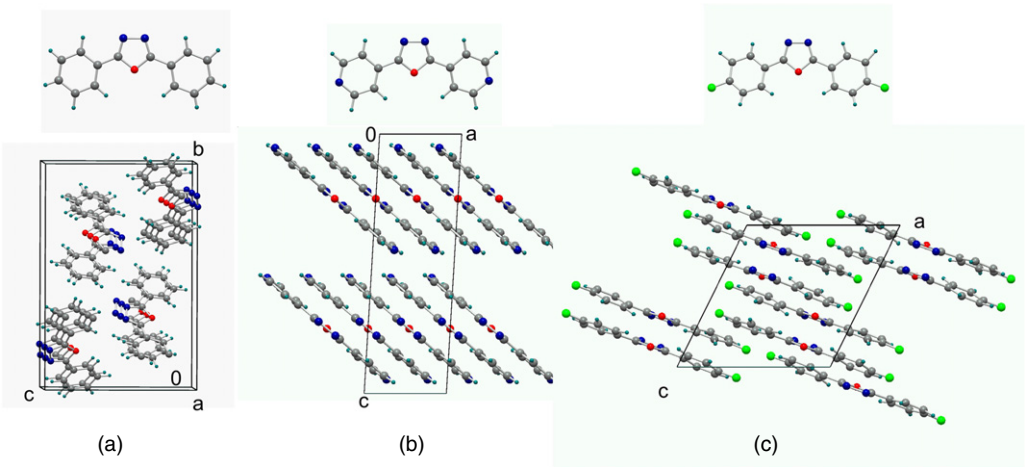


Figure 1. Crystal structures of (a) 2,5-diphenyl-1,3,4-oxadiazole (**1**), (b) 2,5-di(4-pyridyl)-1,3,4-oxadiazole (**2**) and (c) 2,5-bis-(4-fluorophenyl)-1,3,4-oxadiazole (**3**).

intermolecular interactions [22, 24]. Two symmetry-independent hydrogen bonds are formed between both nitrogen atoms of the central oxadiazole ring and the amino groups of adjacent molecules in the case of symmetric *para*-substitution. This leads to the formation of a three-dimensional intermolecular hydrogen bond network. The distances of 3.2–3.6 Å between the individual aromatic rings of different molecules accounts for π–π electron interactions between symmetry-related oxadiazole molecules.

More complex structures form if the diphenyl-oxadiazole core is substituted by more than one, and especially a more bulky, substituent, such as, for example, trifluoromethyl groups, in the *ortho*-positions of the phenyl rings. As mentioned above, this substitution leads to a strong molecular twist. These steric hindrances significantly influence the molecular packing. As a last example in this brief discussion the structure of 2-[2,6-bis(trifluoromethylphenyl)]-5-(2-trifluoromethylphenyl)-1,3,4-oxadiazole will be described [21]. This molecule contains three of these functional groups, one group on one phenyl ring and two on the other ring, all in *ortho*-positions. The bond between the phenyl ring and the single group points to the oxygen atom of the oxadiazole ring. Parallel arranged molecules are found parallel to the a, b plane. In the c direction every second molecule is rotated by approximately 120° around the center of the phenyl ring carrying the single trifluoromethyl group whereby also its orientation is inverted. This is necessary to overcome the steric hindrances, especially that the functional groups do not overlap. Therefore, by rotation and inversion the single group on the phenyl ring is in the same position only for every third molecule. An overlap between the π-systems of neighboring molecules occurs only for the ring with the single *ortho*-substitution but even here the distance between two adjacent rings is rather large at 4–4.3 Å so that the interactions will be comparatively weak. The distance between the rings with double *ortho*-substitution amounts to more than 8 Å so that no π–π interactions should be effective. The same holds for the oxadiazole rings. Due to the rotation their overlap is prevented.

Crystal polymorphism, as already found in the unsubstituted 2,5-diphenyl-1,3,4-oxadiazole [27], often has a considerable influence on the material properties. The occurrence of polymorphic modifications may lead to complications during the production process. On the other hand it may also result in novel materials with valuable properties. A multitude of factors affects the formation of the different modifications. Organic polymorphs differ only slightly in the free energy, so that these small differences are responsible for the formation of the different modifications of organic crystals. Already slight variations of the parameters pressure or temperature, but also of the solvent, the chosen cooling rate or other parameters of the crystallization process, may result in the formation of different polymorphs of organic crystals. Therefore, precise investigations of the occurrence of polymorphism in dependence on pressure, temperature and crystallization conditions are needed, particularly with regard to commercial applications of the compounds.

From the discussion of a few representative structures it is obvious that nearly every structure shows its own peculiarities although some common packing motifs exist. These are mainly the formation of stacks due to π–π interactions between aromatic rings of neighboring molecules. But the arrangement of the molecules within the stacks may vary as well as that of the respective stacks themselves in the three-dimensional architecture. However, the reasons for differences are not yet understood. Specially, the influence of the character of the substituent (donor/acceptor) or the dipole moment of the molecule is only hardly visible. As the apparent polymorphism of some compounds shows the crystallization conditions also play an important role so that different structures may be stable or at least metastable under normal conditions with a modified packing motif.

3. Diphenyl-oxadiazoles and high pressure

3.1. Experimental techniques

All structural investigations were carried out using a large-volume multi-anvil press MAX 80. Synchrotron radiation and

energy-dispersive detector equipment were used to record the diffractograms under increasing pressure. The powder sample was placed in an boron-epoxy cube serving as the sample chamber and pressure transmitting medium. Sodium chloride placed in a separate layer within the gasket cube served as an *in situ* pressure marker. The pressure was increased stepwise and at every step two diffractograms were always taken, one of the sample and another of the NaCl for the pressure determination.

The lattice parameters were evaluated from the diffractograms using the program Powder Cell. Thereby, the ambient pressure crystal structure resulting from single-crystal investigations served as the starting point. The molecular geometry is kept constant which is justified due to the much larger strength of the intramolecular interactions with respect to the intermolecular ones. The pressure is determined using the Decker equation of state. Some error sources as slight pressure gradients and stress within the sample (mostly around 0.1 GPa), reflections from the cube material or 'escape' peaks due to the detector material and the limited resolution of the energy-dispersive technique as well as the pronounced texture of the samples due to the shape of the crystallites resulting from the mostly layered crystal structure were taken into account. For details the reader is referred to, for instance, [23, 28, 39, 40].

A usual diamond anvil cell was used for the Raman investigations. The spectra were excited by an He–Ne laser (632.8 nm) and recorded by a 0.75 m triple Raman spectrometer resulting in a resolution of 1–2 cm^{-1}. In most cases Fluorinert served as the pressure medium ensuring at least quasi-hydrostatic conditions up to 10 GPa. The pressure was determined *in situ* by the usual ruby fluorescence.

3.2. Bulk behavior and equation of state

Although complexes based on diphenyl-oxadiazoles had not been investigated under compression so far, there exist high-pressure studies of several diphenyl-oxadiazole molecules that are potential ligands for such metal complexes, but also of related compounds with different substitution, mostly in the pressure range below 5 GPa [23, 24, 28, 39, 40]. The aim of these studies was to derive similarities and characteristic differences in their high-pressure behavior, to relate these to structural features of the different crystalline structures and to draw conclusions about the strength and direction of the intermolecular interactions. Such structural features are the conformation of the molecules, stack formation, the varying arrangement of the individual molecules within the stacks and the mutual positions of the different stacks. Important intermolecular interactions that considerably influence the response to the action of high pressures are π–π interactions mostly within the stacks and the formation of hydrogen bonds or van der Waals forces between the stacks. Additional information may be obtained from a comparison between results for different polymorphs of the same compound but also from pseudopolymorphs where the inclusion of solvent molecules into the structure considerably influences the interactions.

Most of the investigated oxadiazole compounds do not show phase transitions in the investigated pressure range. However, for some compounds this possibility cannot be ruled out because small but distinct changes appear in the powder diffractograms. Unfortunately the resolution of the powder patterns is not high enough to derive reliable information about the new evolving structure. Molecular modeling calculations should be performed to describe these phase transition processes. Nevertheless, all changes occurring under pressure were found to be fully reversible, even in the case of supposed phase transitions. After full pressure release all investigated compounds retain their initial structures with no remaining changes.

Usually, high-pressure investigations start with the determination of an equation of state (EOS) which describes the relation between the applied pressure and the volume of the substance. Figure 2 summarizes these relations for four potential ligand molecules of metal complexes: the diaminophenyl compound 2,5-bis-(4-aminophenyl)-1,3,4-oxadiazole (**4**) and its dihydrate pseudopolymorph (**5**), the *para*-dipyridyl compound (**2**) and the basic diphenyl-1,3,4-oxadiazole molecule (**1**). The volume of these crystals decreases strongly with increasing pressure, which indicates their high compressibility. This is in accordance with the behavior of almost all organic materials that are rather soft and characterized by a high compressibility.

A good description of the volume as a function of pressure is given by the empirical two-parameter Murnaghan EOS (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 zero pressure. K_0 is the bulk modulus and K_0' is 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 fit of this EOS to the experimental data yields results for bulk modulus K_0 and its pressure derivative K_0' with realistic precision for small compressions [41]. As was demonstrated [42, 43] the MEOS, despite its simplicity, is capable of describing experimental data for a wide variety of materials up to surprisingly high pressures of the order of $K_0/2$. For the materials discussed here this would mean pressures in the range of 3 GPa and above or compressions of about 10%–15%. However, this equation is often used in the literature to describe results also at higher pressures and larger compressions (cf. for instance the results for fluorene in [44]). An overview about different EOS types can be found, for instance, in [45, 46], while the applicability of different EOS types is discussed in [18] for the example of anthracene. The Vinet equation [45, 46]:

$$p = 3K_0(1-x)x^{-2}\exp\left[\tfrac{3}{2}(K_0'-1)(1-x)\right]$$

with

$$x = \left[\frac{V}{V_0}\right]^{1/3}$$

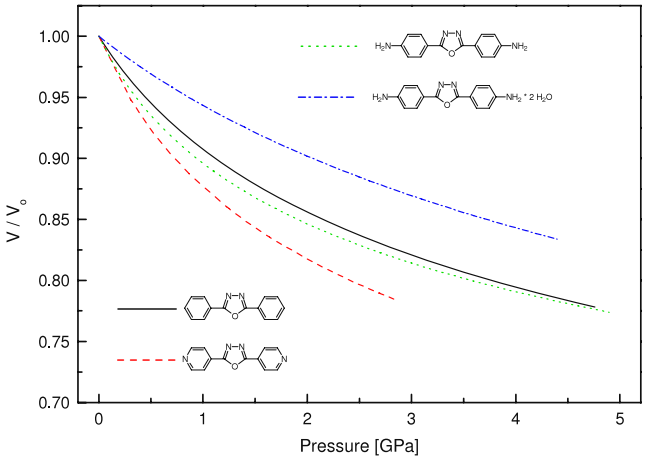


Figure 2. Equation of state for four different diphenyl-oxadiazole compounds: 2,5-diphenyl-1,3,4-oxadiazole (**1**), 2,5-di(4-aminophenyl)-1,3,4-oxadiazole (**4**) and its dihydrated pseudopolymorph (**5**), and 2,5-di(4-pyridyl)-1,3,4-oxadiazole (**2**) [23, 28, 40].

Table 2. MEOS parameters for different diphenyl-1,3,4-oxadiazole compounds. The numbers in parentheses give the standard deviations.

Compound	K_0 (GPa)	K_0'	Pressure range (GPa)	Ref.
(**1**) I[a]	7.3 (0.7)	6.7 (0.3)	0–5	[28]
(**1**) II[a]	8.6 (0.9)	7.2 (0.4)	0–5	[39]
(**2**)	4.6 (0.3)	7.4 (0.6)	0–2.5	[40]
(**3**)	6.9 (0.8)	6.2 (0.3)	0–5	[23]
(**4**)	5.6 (0.7)	8.2 (0.4)	0–5	[24]
(**5**)	14.7 (1.6)	5.1 (0.5)	0–4.5	[24]
(**6**)	6.3(2.0)	6.8 (1.0)	0–4	[28]
(**7**)[b]	6.6 (2.3)	6.3 (1.2)	0–2	[23]
(**8**)[c]	5.1 (0.6)	9.1 (0.4)	0–5	[23]
(**9**)[d]	5.2 (0.6)	11.2 (0.5)	0–2.5	[23]
Diphenyl	5.1	8.1	0–4.5	[19]
Terphenyl	5.8	8.4	0–4.5	[19]

[a] Different polymorphs.
[b] (**7**): 2,5-bis(3-fluorophenyl)-1,3,4-oxadiazole.
[c] (**8**): 2,5-bis(2-fluorophenyl)-1-3-4-oxadiazole.
[d] (**9**): 2,5-bis(pentafluorophenyl)-1,3,4-oxadiazole.

should be more appropriate for compressions above 10% to include a larger pressure interval, but the evaluation of our experimental data results in comparable values with only small deviations compared to those determined with the MEOS so that the latter is preferred. The comparison of the volume at $p = 0$ GPa determined using the MEOS with that obtained from the single-crystal structure analysis provides a good test for the fit quality. In general, both values show very good agreement which ensures the applicability of the MEOS.

Table 2 clearly shows that all studied oxadiazoles have very low values of the bulk modulus K_0 and higher values of its pressure derivative K_0'. Similar parameters have already been found for other organic compounds (not necessarily aromatic), which have quite different molecular and crystal structures. Literature data of diphenyl and terphenyl, which have a comparable aromatic structure, are added for comparison. The values of K_0 and K_0' determined for the oxadiazole compounds are also in good agreement with data on solid benzene derived from the Vinet equation [47]. The results of figure 2 and table 2 indicate that the bulk behavior is rather independent of the individual molecular structure and the specific molecular arrangement. The crystal structure is different for most of the compounds despite some common motifs which lead to different intermolecular interactions between the diverse building blocks. It is interesting to note that polymorphic compounds such as (**1**) I and II show nearly the same behavior as also found for further organic polymorphs [48] (note that in figure 2 the results are only given for the polymorphic structure I). The pseudopolymorphic dihydrate form of (**4**), (**5**), makes the only exception [23]. This structure is less compressible due to the hydrogen bond network between the oxadiazole and the incorporated water molecules.

The rather similar bulk behavior as described by the EOS does not allow conclusions about the structural pressure response, i.e. the deformation of the specific crystal structure. However, all compounds experience a pronounced anisotropic lattice response that considerably varies with the structure and that can be related to the different intermolecular interactions. The study of this anisotropy including the strain analysis gives a deeper insight into the basic interactions. Such strain analysis is essential for the interpretation of high-pressure data to derive information about the intermolecular interactions. The results of the strain analysis allow the comparison between different compounds having different crystallographic structures but probably similar structural features or elements. It is obvious that the individual packing motif gives rise to the anisotropy of the intermolecular interactions and is responsible for the observed compression behavior. The EOS only gives information about the bulk behavior. The strain analysis relates structural features, intermolecular interactions and the resulting high-pressure behavior.

The structural peculiarities and the complex interaction network within the crystal, which determine the anisotropic lattice compression, shall be discussed for the example of (**1**) in its first polymorphic form [28]. The structure of (**1**) is monoclinic. Three nearly coplanar rings form the almost flat diphenyl-oxadiazole molecules (figure 4). The molecules are arranged parallel in stacks along the a direction and all share the same orientation with respect to the oxadiazole moiety. Intense π–π interactions between phenyl and oxadiazole rings connect neighboring molecules. The molecular plane is tilted by $\pm 41°$ against the stack axis with an opposite sign for neighboring stacks, thus forming a herringbone arrangement. Adjacent stacks in the c direction are shifted along the b axis by half a molecule (figure 4). Adjacent stacks are linked by van der Waals interactions.

This arrangement gives rise to the anisotropic compression shown in figure 3a. The a axis is the least compressible one while the highest compression is found in the b direction. The monoclinic angle β is nearly constant.

The other investigated compounds show a similar behavior. However, the lineal compression of the different axes depends considerably on the specific structure and the relation to the individual intermolecular interactions. The relative

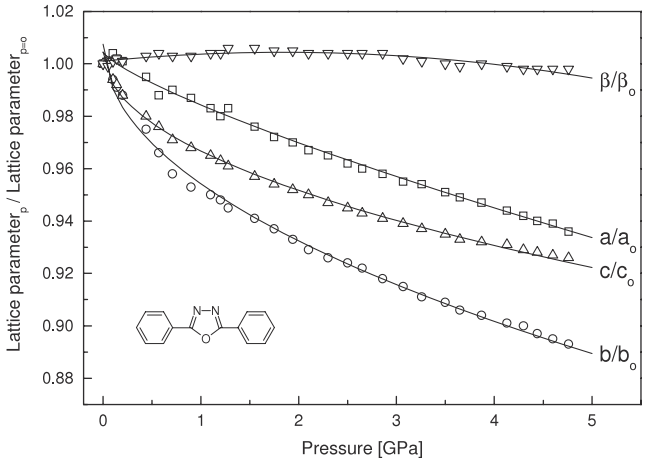


Figure 3a. Lattice parameters of (**1**) as a function of pressure [28].

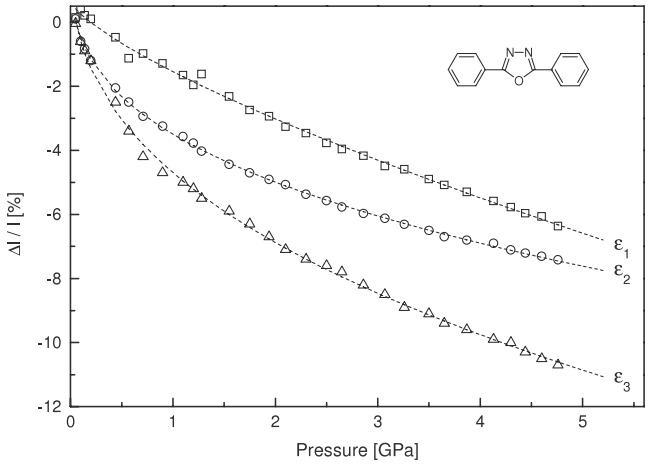


Figure 3b. Components of the strain tensor as a function of pressure for (**1**) using the results illustrated in figure 3a.

changes of the lattice parameters give therefore insight into the strength and direction of the relevant intermolecular packing forces. In the pressure range up to 5 GPa the most compressible axis may be shortened by approximately or slightly more than 10% such as, for instance, in the case of (**1**) (polymorph I: b axis: $b/b_0 = 0.89$; polymorph II: b axis: $b/b_0 = 0.91$). The complex arrangements of molecules in the architecture of polymorph II (six different stacks are arranged in layers perpendicular to c) results in smaller lineal compressions in the a and c directions of approximately 4% and 6%, respectively. For compounds (**3**) ($c/c_0 = 0.88$), the fluorine-substituted 2,5-bis(2-fluorophenyl)-1-3-4-oxadiazole (**8**) ($c/c_0 = 0.88$) or the two-ring compound (**6**) ($c/c_0 = 0.87$) the largest compression up to 5 GPa is in the same range as observed for (**1**). The other two axes are less compressed up to values around 0.93–0.96. However, in the case of (**3**) both other axes are less compressible with nearly the same relative value of approximately 0.93 at 5 GPa due to hydrogen bonds between C–H and F formed in the a, b plane.

A very small compression is found for the a axis of the dihydrate (**5**). This axis is nearly incompressible due to the hydrogen bonds between the water molecules and the NH_2 groups of the oxadiazole molecule (at 4 GPa: $a/a_0 = 0.99$). The highest compressibility is found in the c direction perpendicular to the layers ($c/c_0 = 0.90$). A very small, though slightly increased, compressibility compared to the a axis of (**5**) is also observed for the a axis of (**8**) ($a/a_0 = 0.98$ at 5 GPa) [23]. Interestingly, in the range up to 2.5 GPa all axes of the *meta*-fluorine-substituted compound 2,5-bis(3-fluorophenyl)-1,3,4-oxadiazole (**7**) and the *per*-fluorinated analog of (**1**)—2,5-bis(pentafluorophenyl)-1,3,4-oxadiazole (**9**) show nearly the same compression behavior. These axes are compressed by approximately 5%. Figure 3c gives two additional examples for compounds (**3**) and (**5**). For comparison the data for the linear compression of the different axes at a pressure of 2.5 GPa have been compiled in table 3 for all investigated compounds.

However, the lattice constants reflect more the geometric constraints from the determination of the unit cell dimensions. Therefore every compound has to be analyzed individually and it would be necessary to compare related axes to derive conclusions about the different intermolecular interactions. That is why a different way is chosen to gain more insight into the reasons for the anisotropic compression behavior.

To relate the differences in the compression of the lattice parameters a, b and c to the structural details and to quantify the anisotropic lattice distortion a strain analysis has to be carried out. The strain gives an idea about the strength of the intermolecular interactions along the different directions. This analysis may be done evaluating the strain tensor from the unit cell data under pressure compared to those at ambient pressure [49]. Here, the lengths of the principal axes of the strain ellipsoid result (ε_1 denoting the smallest strain and ε_3 the largest, respectively) together with the orientation of this ellipsoid in relation to the given crystal structure. Thus in the following figures 4–6 this ellipsoid will be projected onto the specific lattice planes. Figure 3b (obtained from the data of (**1**) given in figure 3a) illustrates the strain evolution in the direction of the three principal axes of the strain tensor. Sections through the strain tensor ellipsoid together with the corresponding projections of the crystal structure allow drawing conclusions about the influence of the packing motifs and the related intermolecular interactions in the different directions. Figure 4 summarizes the results for (**1**) at 0.6 GPa. The relations between neighboring stacks are given by the section of the strain ellipsoid in the b, c plane (figure 4, below). The strain in the b and c directions, i.e. in directions perpendicular to the stack axis, is comparable, thus indicating nearly equivalent intermolecular interactions. The herringbone motif with the opposite orientation of the molecular plane in neighboring stacks prevents that the largest strain appears more or less perpendicular to the molecular plane of the molecules as observed, for instance, in layered structures. The largest strain, ε_3, is found along the b axis, i.e. in the [010] direction (figure 4 above). So it makes an angle of approximately $\pm 41°$ with the normal to the molecular plane of the differently oriented molecules in adjacent stacks. Although the most intense π–π interactions between oxadiazole (π-acceptor) and phenyl (π-donor) rings are expected in the direction normal to the plane

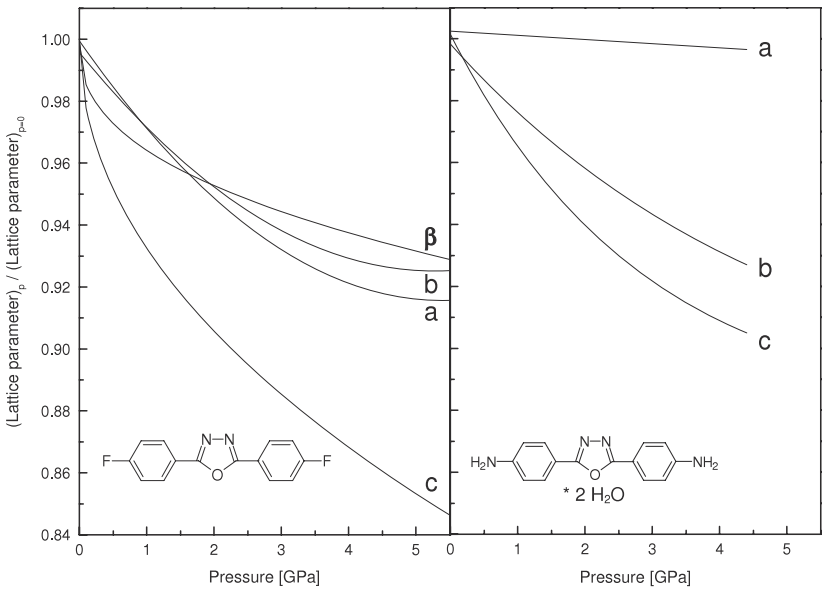


Figure 3c. Lattice parameters of (**3**) (left) and (**5**) (right) as a function of pressure [23, 24].

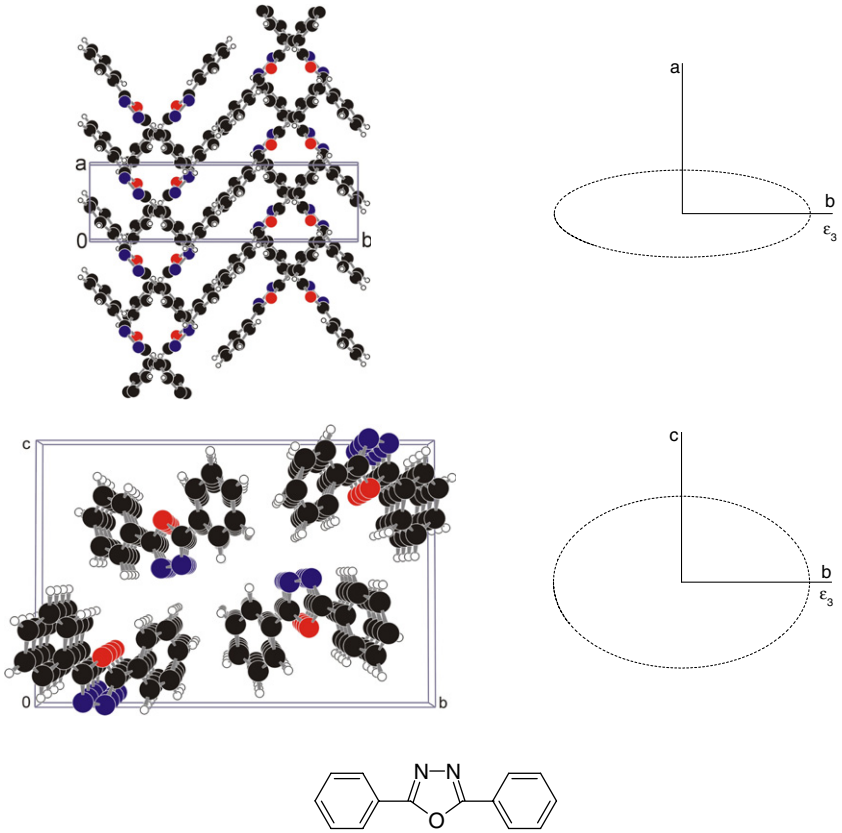


Figure 4. Structure of (**1**) with corresponding sections of the strain ellipsoid at 0.6 GPa according to the data given in figures 3a and 3b. Projection in the [001] (top) and [100] directions (bottom) illustrating the stack arrangement [40].

of the nearly coplanar rings ε_3 is still found in a direction with π donor–acceptor interactions between molecules within a stack. The inclination of the molecular planes against the stack axis also slightly influences the compression in the [001] direction.

The situation becomes clearer for layered structures. Figure 5 illustrates the results for three different compounds: (**2**) containing two pyridyl rings instead of the phenyl rings of (**1**), at 0.3 GPa; the *para*-difluorinated compound (**3**) at 0.4 GPa; and an example for a two-ring molecule, *N*, *N*-dimethyl-*N*-[4-(5-methyl-1,3,4-oxadiazol-2-yl)phenyl]amine (**6**). Besides this layer motif a stack-like arrangement is also found for all three compounds (see [23, 28, 32] for the specific arrangement). Here, the strongest compression ε_3 is found nearly nor-

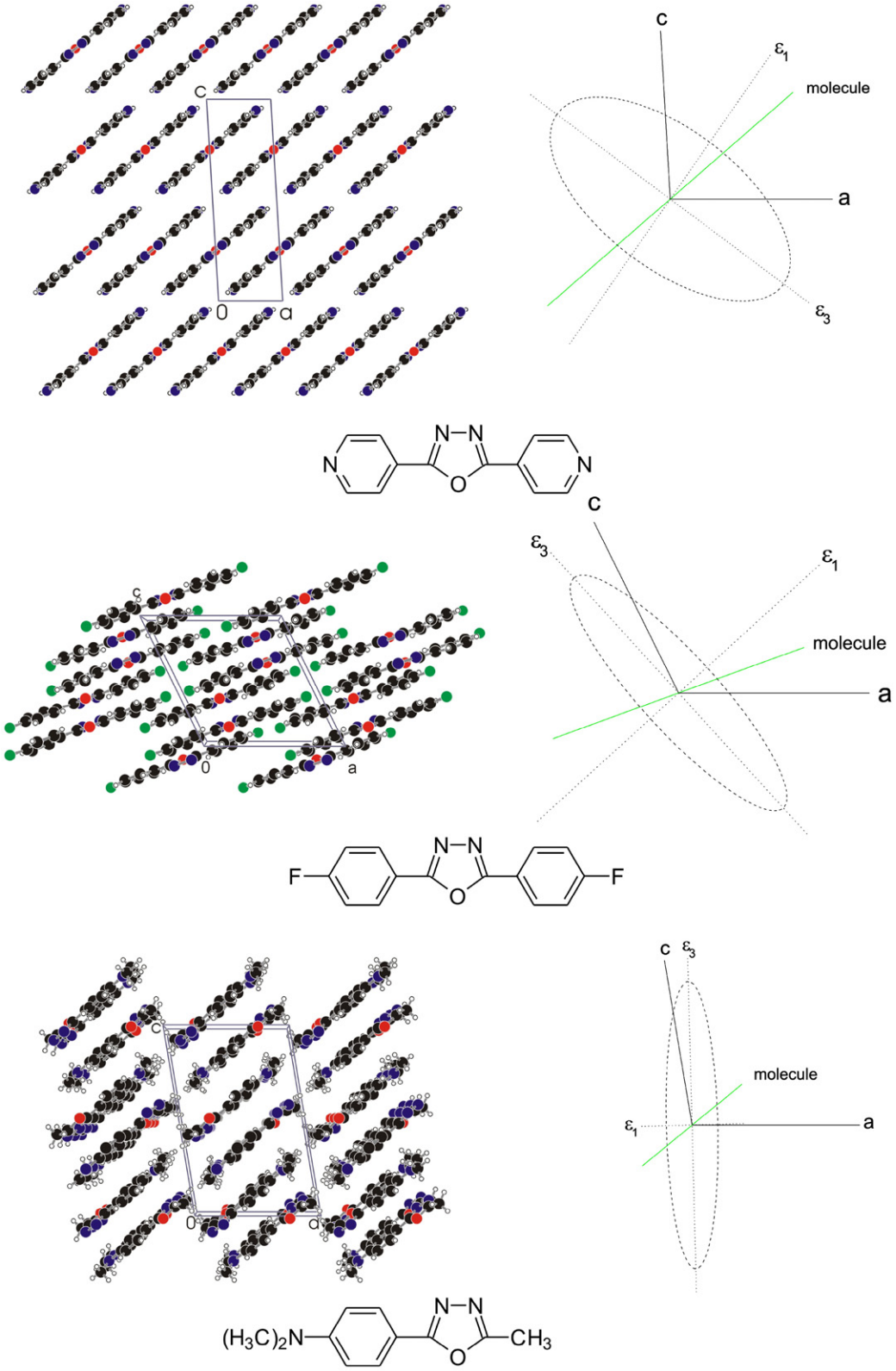


Figure 5. Structure and related strain ellipsoid for some layered structures: (**2**) at 0.3 GPa (above, [40]), the fluorine-substituted diphenyl-oxadiazole compound (**3**) at 0.4 GPa (middle, data from [23]) and the two-ring compound (**6**) at 0.9 GPa (below, data from [28]).

mal to the molecular layers, that is, in the direction of the π interactions. This behavior is expected in layered structures. For instance, paracetamol or benzoquinone show a similar compression [6, 48, 50]. In these cases, the largest strain is 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, contrary to the ex-

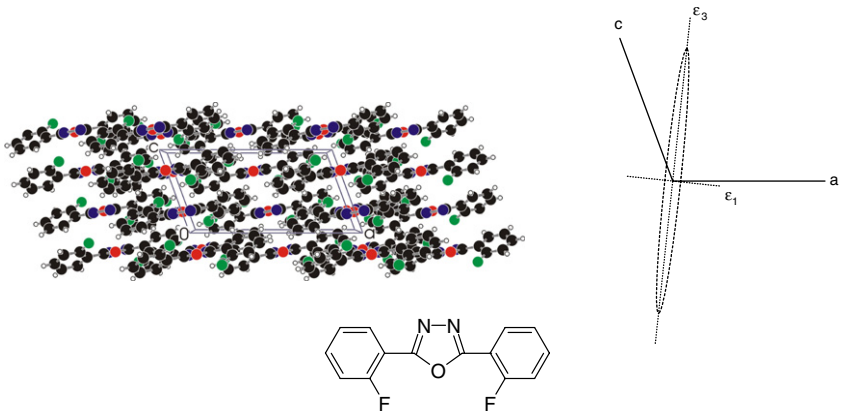


Figure 6. Strain distribution in 2,5-bis(2-fluorophenyl)-1-3-4-oxadiazole (**8**) at 2.6 GPa.

Table 3. Relative lattice parameters for the oxadiazole compounds at 2.5 GPa determined by a fit to the experimental data.

Compound	a/a_0	b/b_0	c/c_0	β/β_0
(**1**) I[a]	0.963	0.925	0.946	1.005
(**1**) II[a]	0.974	0.941	0.968	1.043
(**2**)	0.916	0.933	0.942	0.957
(**3**)	0.958	0.947	0.895	0.948
(**4**)	0.941	0.914	0.959	
(**5**)	0.988	0.939	0.921	
(**6**)	0.976	0.936	0.901	0.971
(**7**)[b]	0.922	0.929	0.942	1.020
(**8**)[c]	0.994	0.943	0.911	1.027
(**9**)[d]	0.957	0.938	0.936	0.983

[a] Different polymorphs.
[b] (**7**): 2,5-bis(3-fluorophenyl)-1,3,4-oxadiazole.
[c] (**8**): 2,5-bis(2-fluorophenyl)-1-3-4-oxadiazole.
[d] (**9**): 2,5-bis(pentafluorophenyl)-1,3,4-oxadiazole.

amples discussed here with oxadiazole and phenyl rings leading to additional acceptor–donor interactions between the layers.

Other compounds show different architectural features. For instance, in 2,5-bis(2-fluorophenyl)-1-3-4-oxadiazole (**8**) a layered arrangement is observed for the a, b plane but the molecular plane is inclined against this plane and the orientation of the molecules in different layers is opposite as given by the line connecting the oxygen atom and the middle of the N–N bond of the oxadiazole ring. The stacks extend in the c direction but only the central oxadiazole rings give rise to π–π interactions. This is well reflected in the compression behavior as illustrated in figure 6. The largest strain appears inclined against the c-(stack-)axis and therefore also against the molecular plane by approximately 26°. The small compressibility of the a axis, i.e. the low strain in this direction, is explained by F–F contacts. Therefore, this compound also shows a comparable strain distribution as those compounds with a clear arrangement of layers with parallel molecular planes.

The compression behavior of 2,5-bis(pentafluorophenyl)-1,3,4-oxadiazole (**9**) is clearly dominated by intense F–F interactions that prevent close contacts between the different molecules. Although the molecular arrangement resembles those of the other compounds, no stack formation occurs; the distances are too large for such interactions. Due to this arrangement, the largest strain occurs in the a, c plane according to the large distances between the molecular while in the b, c plane both strains are nearly equal due to the complex fluorine interactions (cf figure 7).

In most cases where a stack formation is found the strain in directions perpendicular to the stacks is comparable. Its magnitude is nearly equal and much smaller than in the stack direction. Some characteristic differences occur due to the specific intermolecular interactions, such as, for example, van der Waals interactions, hydrogen bonds or bond networks, C–H$\cdots$ halogen interactions or close halogen–halogen contacts. An example is given by the dihydrate pseudopolymorph of the p-diaminophenyl compound (**5**). The strong hydrogen bond network between the included water molecules and the amino groups of the substituted diphenyl-1,3,4-oxadiazole molecule in the b, c plane [23] prevents a large strain in the [010] direction (cf figure 8).

Summarizing the results for the different investigated compounds it is obvious that the largest strain is mainly observed nearly perpendicular or slightly inclined to the molecular plane, especially in layered structures. This is also the direction of the π interactions between neighboring molecules, specifically between oxadiazole and phenyl rings as acceptors and donors. The behavior between stacks perpendicular to their axes is clearly different. It is dominated by different intermolecular interactions such as van der Waals forces, hydrogen bonds, etc. Additionally, specific structural features such as the herringbone motif may slightly modify this picture. However, it is possible to derive conclusions about the different intermolecular interactions based on the anisotropy of the pressure response.

3.3. Raman investigations

Another important contribution for the understanding of the high-pressure behavior is derived from the evolution of the vibration spectrum during the compression. This results in the determination of the mode Grüneisen parameters, which together with the data of the EOS may serve as input for the construction of a thermodynamic equation of

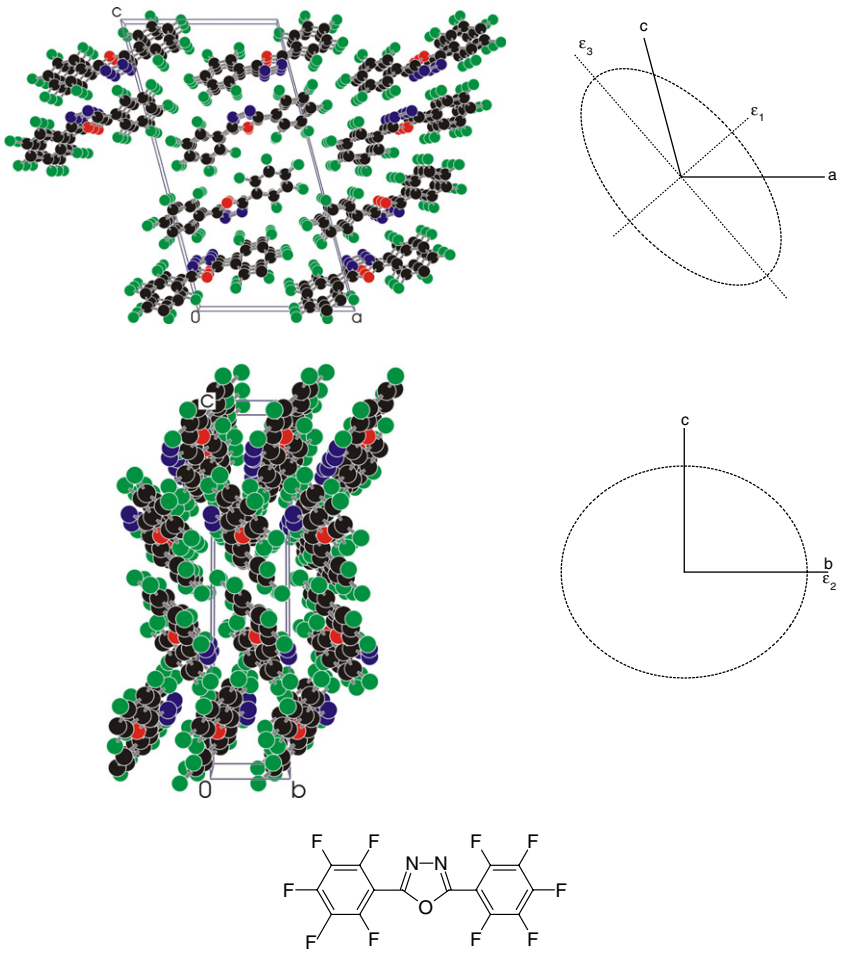


Figure 7. Strain ellipsoid for 2,5-bis(pentafluorophenyl)-1,3,4-oxadiazole (**9**) at 0.8 GPa.

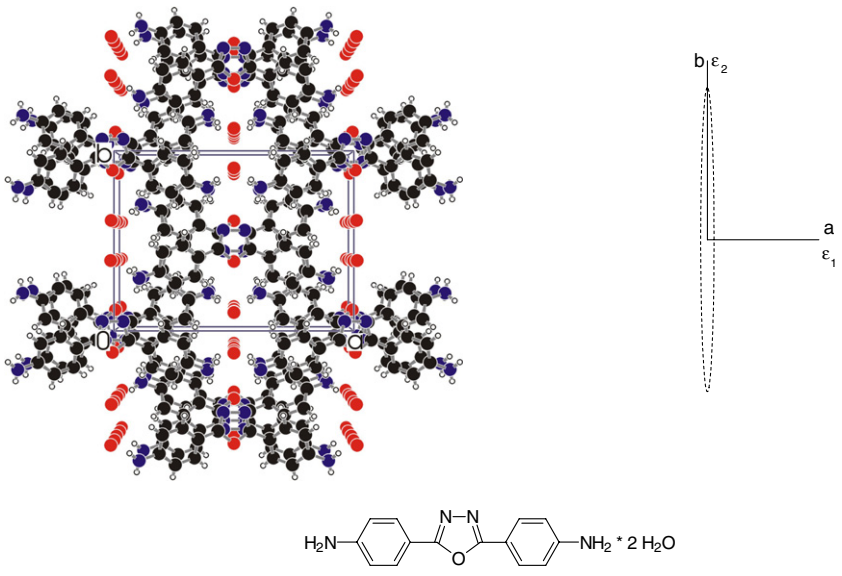


Figure 8. Strain distribution in the structure of the dihydrate pseudopolymorph (**5**) at 3.9 GPa (data from [23]).

state (for instance, in the framework of the extended Debye model [51–54]). However, here the complete vibration spectrum including the IR modes has to be considered to cover all vibrational degrees of freedom.

Figure 9 shows a typical Raman spectrum of 2,5-di(4-aminophenyl)-1,3,4-oxadiazole $*$ $2H_2O$ (**5**) at ambient pressure in the fingerprint region below 2000 cm^{-1}. Three different regions may clearly be distinguished: the region of

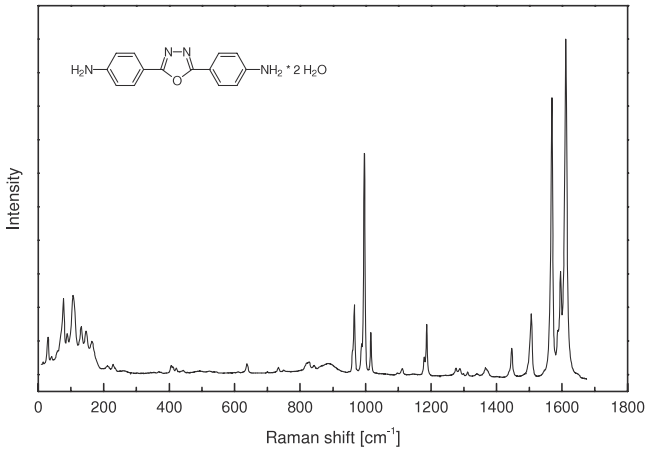


Figure 9. Raman spectrum of (**5**) at ambient pressure [55].

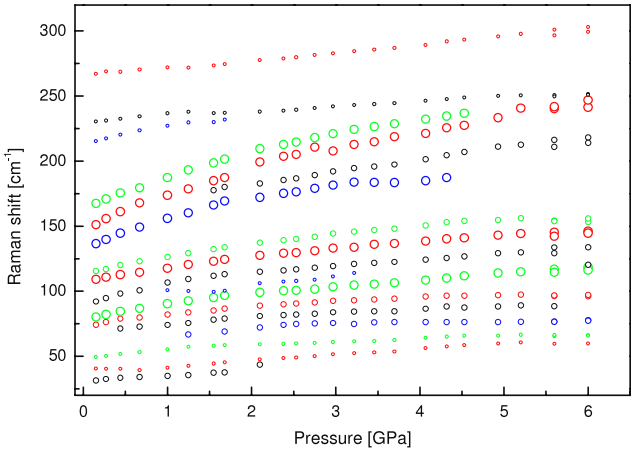


Figure 10. Pressure shift for selected Raman bands of (**5**) in the region below 400 cm^{-1} [55]. The symbol size shall give an idea of the intensity of the respective bands.

the external modes below 200 cm^{-1} and two groups with strong vibrations around 1000 and 1600 cm^{-1}. These strong lines result from ring vibrations of the oxadiazole and phenyl rings, respectively. Under pressure these modes continuously shift to higher wavenumbers. No phase transitions occur for this compound as well as for most other compounds. The spectrum does not show substantial modifications in the region of the lattice modes as shown in figure 10 for the region below 400 cm^{-1} (in the figure the symbol size corresponds to the intensity of the individual vibration). This would be characteristic for a structural transition due to the change of the space group. It is worth noting that differences in the external modes can also be used for the discrimination between different polymorphic forms (without using extensive x-ray techniques) as has been shown for the examples of (**1**) [27] and (**4**). The shift of the modes with pressure is due to the anharmonicity of the vibrations. The behavior for low pressures is slightly nonlinear while it changes to rather linear at higher pressures. A general trend found for all investigated compounds is a gradual decrease of the intensity of the spectra due to an increased amorphous portion within the sample. However, this effect as well as the shift is completely reversible, indicating that no irreversible modifications originate under pressure.

It should be mentioned that the derivative $\mathrm{d}\nu/\mathrm{d}p$ is of the same order of magnitude for all different oxadiazole compounds studied. This leads to the derivation of the mode Grüneisen parameters γ_i taking into account the results from the determination of the bulk modulus:

$$\gamma_i = -\left[\frac{\partial \ln \nu_i}{\partial \ln V}\right]_{V(p)} = \frac{K(p)}{\nu_i(p)}\left[\frac{\partial \nu_i}{\partial p}\right]_p .$$

The pressure shift $\mathrm{d}\nu/\mathrm{d}p$ of the lattice modes is nearly one order larger than that of the intramolecular vibrations. Therefore, the variation of γ_i reflects the higher compressibility of the intermolecular distances compared to the intramolecular bonds [56, 57]. This gives rise to the characteristic behavior illustrated in figure 11. The Grüneisen parameter varies strongly with the mode frequency due to the highly anisotropic solid as usually observed for layered or molecular crystals.

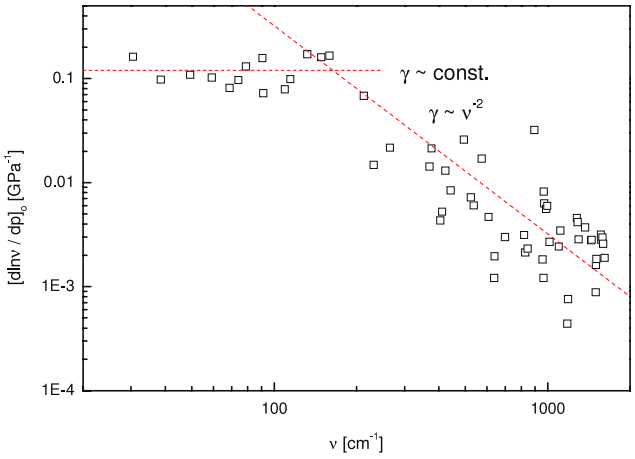


Figure 11. Mode Grüneisen parameters as a function of pressure (divided by K) for the vibration modes of (**5**) together with the proposed functional dependence (see text).

Here, the points for the external modes fall on a line, i.e. $\gamma_i \sim$ const of the order of magnitude 1, but in the region of the internal vibrations γ_i strongly decreases. If weak intermolecular interactions are present together with strong intramolecular bonds, i.e. van der Waals and covalent forces act simultaneously, the Grüneisen parameters become frequency-dependent. In a model that may account for this dependence the different strengths of intra- and intermolecular forces have to be considered. Following a proposal by Zallen [58, 59] this leads to a specific scaling relationship with approximate inverse-square dependence $\gamma_i \sim \nu^{-2}$. The results for all different oxadiazole compounds verify this, although for some of them smaller deviations occur and a slightly better description is given by a fit with $\gamma_i \sim \nu^{-1.5}$ dependence. Nevertheless, these results support the ideas outlined in [59] to explain the Raman spectra of molecular solids (see also, for instance, the results of Hochheimer *et al* [56] for the investigation of quasi-one-dimensional crystals).

Summarizing, the behavior of the investigated diphenyl-oxadiazoles under high pressures resembles that of many other

organic compounds. In particular, the bulk behavior is nearly independent on the individual molecular and crystal structures; only the analysis of the strain that develops during pressure application gives detailed information about the strength and direction of the different intermolecular interactions. The observation of the Raman spectrum under pressure with the derived mode Grüneisen parameters is a first contribution for the derivation of a thermodynamic equation of state. These results also form the basis for studies of related metal–organic compounds in the future.

4. Concluding remarks

Modern materials research aims to develop innovative materials with optimized properties for new or improved applications. This requires knowledge about the structure–property relationships and their variation with the change of the molecular and supramolecular structures for specific molecules. Theoretical simulations and computations often form the starting point for these considerations. Therefore structural input parameters for analogous or related molecules are required to obtain highly reliable results to minimize experimental efforts.

However, as could be shown for several examples of differently substituted diphenyl-1,3,4-oxadiazole molecules it is difficult to derive general packing principles or data about the molecular conformation that are independent of the specific chemical structure of the molecules. Although some comprehensive features exist like the prevailing occurrence of stack architectures of rather flat molecules the individual arrangements of the molecules within the stacks or the relation of the different stacks are different from molecule to molecule as well as the molecular conformation depending on the structure of the individual molecules, especially on the position of the functional groups. Despite the study of a large class of different molecules therefore it is still difficult to predict the real three-dimensional supramolecular architecture only based on the molecular structure as intended by the ideas of crystal engineering.

This specific crystalline arrangement with the different intermolecular interactions influences the high-pressure behavior. Interestingly, here it resulted that the bulk behavior as described by the equation of state is nearly independent of the specific crystal structure and rather similar for the different compounds investigated and comparable to other organic molecular crystals. However, the variation of the packing motifs and the resulting special intermolecular interactions manifest in the strain analysis. Due to the different intermolecular interactions the compression is different in the different directions within the crystal lattice. As a general trend it results that the compression is largest in those directions with π–π donor–acceptor interactions, i.e. in the direction of the stack axis and smaller perpendicular to it, determined mostly by van der Waals forces.

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