Compressibility of Oxadiazole Crystals

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To study the different intermolecular interactions and their dependence upon structural parameters differently substituted diphenyl-1,3,4-oxadiazole (DPO) compounds serve as model substances for organic crystals. Especially the determination of an equation of state (EOS) is of crucial importance for such parameters depending on the distance between the individual molecules. The different DPO molecules offer a variety of different crystal structures (mostly monoclinic or orthorhombic) and packing motifs like layers or stacks. But most of the structures show a common feature of the arrangement between oxadiazole and phenylene rings. The nearly flat molecules are placed in such a way that the oxadiazole ring (π-acceptor) of one molecule is sandwiched between phenyl rings (π-donor) of the adjacent molecules above and below. At least two molecules form pairs with an analogous arrangement. A detailed structure description may be found in [1,2]. In general, an anisotropic compression is expected due to the complicated interaction network consisting of π-π, van der Waals or possibly hydrogen bond interactions and their different strengths [3].

The high pressure X-ray diffraction experiments were carried out using the MAX-80 equipment in the pressure range up to 4 GPa. For the subsequent evaluation of the powder diffractograms and the determination of the lattice parameters the program POWDER CELL 2.3 [4] was applied.

The results are described using the two parameter MURNAGHAN EOS

$$p = \frac{K_o}{K_o'}\left[\left(\frac{V_o}{V}\right)^{K_o'}\right] - 1$$

The pressure is denoted by p and the volume by V. The index 'o' refers to the initial state at ambient pressure. K_o is the bulk modulus and K_o' its pressure derivative. Table 1 summarizes the results and Fig. 1 shows some examples for the volume compressibility of the basic DPO molecule with its two polymorphs and of additional compounds, where only the substitution in para position is modified.

In general, besides small differences all compounds show a rather consistent high pressure bulk behavior The EOS parameters are in the same range that is also typical for organic molecular crystals (see Fig. 1 for comparison). These characterize the materials as rather soft and well compressible. Nevertheless, the molecular as well as the supramolecular structure of the oxadiazole compounds have a small but distinct influence on the compressional behavior. This influence is expressed in the compressional behavior of the individual axes. The comparison of the structural and packing features gives some ideas about the intermolecular interactions. Figure 2 clearly shows the anisotropy of the compression for the two unsubstituted polymorphs DPO I and II. While DPO I shows a stack arrangement the motif for DPO II is rather complex with molecules forming layers [5]. It is obvious that the individual pressure response strongly depends on the structure and therefore on the different intermolecular interactions like π-π or van der Waals interactions, hydrogen bonds etc. acting in the different directions. From structural considerations it may be concluded that the compressibility is significantly lower in those directions with intense π-π interactions, i. e. preferentially in stack direction or in such directions with a layered arrangement of parallel molecules and therefore interacting oxadiazole and phenylene rings. In other directions where only van der Waals interactions are found as between adjacent stacks this compressibility may be enhanced. An intense discussion of the compression behavior of DPO I is found in [1] or [6]. The strength of the π-π interactions between adjacent molecules in stacks or different layers and the specific arrangement of most of the DPO compounds prevents a stronger destruction of the donor – acceptor system. Thus the varying crystal structure and the resulting evolution of a complex three-dimensional interaction network from π-π, van der Waals and other interactions lead to the anisotropy of the compression but, nevertheless, all compounds show a rather similar bulk behavior under pressure as expressed by K_o and K_o'. These results correspond well to those found for different organic compounds [3].

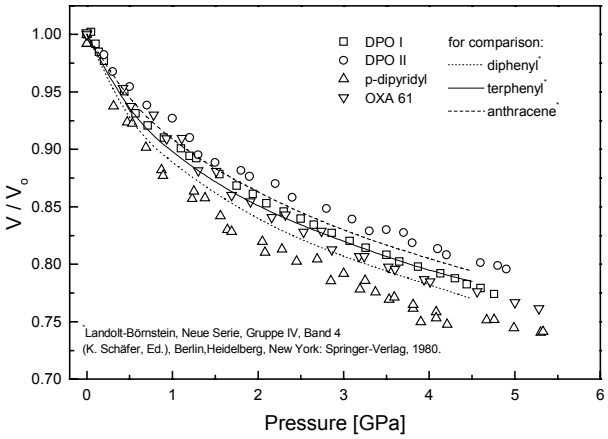


Fig. 1: Bulk compressibility of DPO compounds.

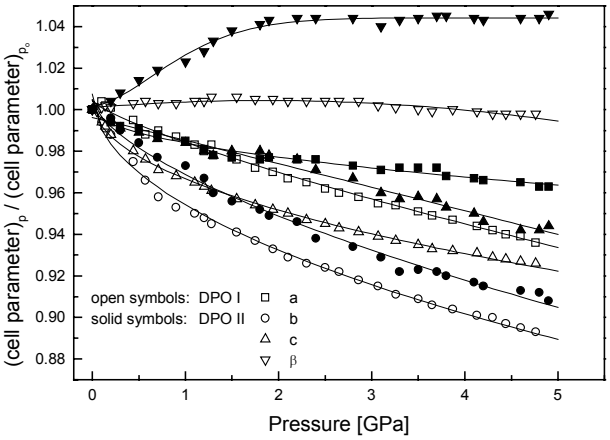
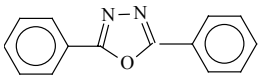
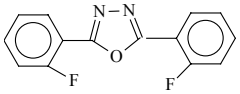
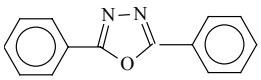
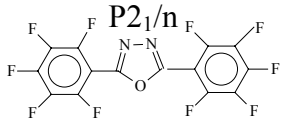
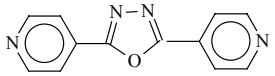
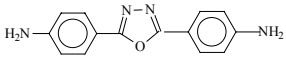
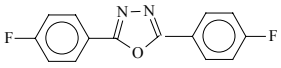
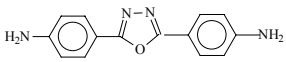


Fig. 2: Unit cell axes of DPO I and DPO II vs. pressure.

Table 1: EOS parameters for oxadiazole compounds (*:V_o from single crystal structure analysis)

Compound	Molecule / Structure	K_o [GPa] K' V_o [Å^3]*	Compound	Molecule / Structure	K_o [GPa] K' V_o [Å^3]*
DPO I	monoclinic $P2_1/c$ 	7.3 6.7 1137.3	OXA 63	monoclinic C2/c 	5.1 9.1 1141.3
DPO II	monoclinic Cc 	8.6 7.2 7036.3	OXA 64	monoclinic $P2_1/n$ 	5.2 11.2 1323.5
OXA 26	monoclinic C2/c 	4.3 7.6 1080.0	DAPO I	orthorhombic Pbca 	5.6 8.2 2457.0
OXA 61	monoclinic $P2_1/n$ 	7.0 6.2 1151.3	DAPO II	orthorhombic Cmcm  * 2 H_2O	14.7 5.1 1406.4

References

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