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Characterization of a new non-centrosymmetric polymorph of diphenyl-1,3,4-oxadiazole

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Abstract

Diphenyl-1,3,4-oxadiazole (DPO) crystallization experiments from solutions clearly reveal the polymorphism of the substance. Besides the formerly known centrosymmetric monoclinic structure with space group $P_{2_1/c}$ (DPO I) a new monoclinic structure with the non-centrosymmetric space group Cc is found (DPO II): a = 2.4134(4) nm, b = 2.4099(3) nm, c = 1.2879(2) nm, $\beta = 110.048(3)^\circ$, and V = 7.0363(17) nm³. The asymmetric unit contains six independent molecules in a complex packing motif. A re-determination of the crystal structure of DPO I at room temperature gives lattice parameters a = 0.51885(6) nm, b = 1.8078(2) nm, c = 1.21435(14) nm, $\beta = 93.193(3)^\circ$, and V = 1.1373(2) nm³. X-ray measurements at 363 K show a significant increase of the unit cell volume by 1.6%. Differences between both structures concerning morphology and characteristic Raman bands are outlined in detail. DSC investigations show an irreversible transition from DPO I to DPO II at 97 °C. DPO II does not show any transition in the temperature range up to the melting point at 141 °C. The non-centrosymmetric DPO II structure shows triboluminescence.

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1. Introduction

The rapid technological development requires the search for advanced materials with tailor-made properties. Organic substances may easily be modified by chemical syntheses thus tuning the properties and therefore have attracted increasing attention as high performance materials for instance in sensoric applications, optical and display techniques, new electronic devices, batteries etc. [1,2]. But, tailoring of the properties requires the exact knowledge of the relationship between structures and properties of the materials and their mutual dependence. Based on a model where complex structures are built from small and relatively simple units like the synthonic approach [3-5] it is assumed that some of the properties of a basic unit are preserved in the final product while others may change in a systematic manner. Therefore, the knowledge of structure and properties of more or less simple starting materials is

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required to determine an effective and successful combination procedure. Structural investigations of crystalline organic compounds are the starting point for several different other research topics. Many efforts are directed to the understanding of the relations between molecular structure and supermolecular arrangement.

Especially organic molecules tend to show a distinct polymorphism that complicates all assertions about the crystal structure resulting under real conditions and therefore the properties what is of special importance [6-9]. This polymorphism is due to very small differences in the free energy between the different polymorphic structures, usually in the range of approximately 4-8 kJ/mol. The crystallization process is influenced by a variety of different factors like pressure and temperature, kind of solvents, cooling rates, mechanical treatment, impurities etc. and their complicated interplay. Thus, a way to obtain the desired supermolecular architecture for molecules with already optimized functional structure could also be possible by the application of various crystal growth techniques and conditions before changing the chemical structure again.

Compounds containing the 1,3,4-oxadiazole ring as a basic building block are known as scintillator materials or as biologically active agents. Modifications of their chemical structures open up possibilities for new technical applications for instance as potential electroluminescent materials or as active sensoric substances. Also other optical properties like possibilities for non-linear processes should be taken into account.

First results of structural investigations on different compounds containing the diphenyl-1,3,4-oxadiazole (DPO) moiety as central building block have been published recently [10-12] (or see the Cambridge Structural Database). The structures found up to now for the differently in para-position substituted DPO basic units were mostly monoclinic or orthorhombic but always centrosymmetric. In the following we discuss the polymorphism of the basic DPO unit with a newly determined crystal structure (DPO II). These results may serve as starting point for investigations of a family of DPO with different substitution scheme.

A previous structure solution for DPO was presented by Kuznetsov et al. [13]. The structure is

monoclinic (space group $P2_1/c$) with cell parameters a = 0.52032 nm, b = 1.81436 nm, c = 1.21844 nmand $\beta = 93.243^{\circ}$ (DPO I). The packing motif shows infinite stacks and a herring bone configuration, a general principle known from many different organic materials, where the solid is formed by $\pi - \pi$ interactions and van der Waals contacts between the different molecules (cf. for instance [14]). The nearly planar molecules of adjacent stacks show opposite orientation given by the O-atom and the center of the oxadiazole ring and also an opposite inclination against the stack axis a by $\pm 41^{\circ}$ ([13], see also Ref. [12], where the high pressure behavior of this DPO structure is discussed in detail, for a structure description). A re-determination of the crystal structure of DPO I gave very similar structural parameters. Additionally, structural investigations at higher temperatures were carried out. In order to ensure a better comparison between structural parameters obtained at different temperatures the newly obtained data for DPO I will be presented additionally.

But, during the preparation of the starting DPO material for the high pressure investigations [12] using solution crystallization crystals with different morphology were found. The careful analysis by X-ray and Raman techniques showed that DPO crystallizes at least in two different polymorphic forms from solution. So, in the following we will describe the newly found second DPO crystal structure and discuss the main differences and structural relations.

2. Sample preparation and experimental setup

Synthesis and crystallization. 2,5-Di(phenyl)-1,3,4-oxadiazole was synthesized by direct condensation of benzoic acid with hydrazine hydrate in polyphosphoric acid [15]. 2.38 grams (0.02 mol) benzoic acid and 0.55 g (0.011 mol) hydrazine hydrate were stirred in 50 g polyphosphoric acid (84.6% P₂O₅) at 160 °C for 3 h. After cooling the clear solution was poured into water, filtered and the product was dried in vacuum. The product was recrystallized three times from ethanol. Melting point: 139 °C (determined by melting point microscope, lit. 138-140 °C [26]).Solid-¹³C-NMR: O-C=N: 163 ppm. Yield: 95 wt%.

To investigate the crystallization behavior of DPO and to determine the appropriate conditions for the precipitation of a single phase, either DPO I or DPO II, several different experiments have been carried out carefully. The synthesized DPO was recrystallized from different solvents like petrolether or ethanol with varying dilution at ambient or decreased temperature. Additionally, the products resulting from a distinct solvent were dissolved in the other solvent and recrystallized again. The resulting crystals were first microscopically inspected for their morphology and in such cases were only ill crystallized material resulted by Raman spectroscopy to determine the phase content of the sample. But, in most cases the visual inspection of well crystallized samples is sufficient to differentiate between both structures having a unique habit (needle, plate) as could be concluded from extensive Raman investigations (see below).

In general, it has to be stated that it was rather impossible to obtain a fully crystallized sample containing only one single unique DPO phase from the solution experiments. Always both phases were present in different ratios at least in traces like small admixtures, especially few needles of phase I (preferentially grown at impurities) in larger amounts of phase II or very small crystallites grown on the surface of larger crystals. This is mainly observed if phase I crystallizes in excess. Then some needles with very small crystallites of phase II on their surface are found. In the latter two cases the admixtures are well below the X-ray detection limit and may best be detected visually. Therefore, it is concluded, that the final structure is independent on the DPO synthesis route as could be the case for instance by the existence of very small and nearly inextractable traces of synthesis residues or molecular fragments. So, only the influence of the solvent and the ambient conditions have to be taken into account.

The same holds also for sublimated DPO. The product predominately consists of DPO I needles that are stronger agglomerated but also contains smaller admixtures of DPO II stuck together in polycrystalline grains. Smaller crystallites of the second structure are also found on the surface of the needles.

X-ray structure analysis. The X-ray data of DPO I were collected on a SIEMENS SMART diffractometer at 293 and 353 K using Mo K α radiation ($\lambda = 0.71073$ Å) monochromatized by a graphite crystal.

For the high temperature measurement a heated air stream was directed onto the same crystal also used for the room temperature measurement. The data of DPO II were recorded at 293 K. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELX-97 [16]. All hydrogen atoms of both DPO I structures were located by difference Fourier syntheses and refined isotropically. In the case of DPO II only small single crystals with relatively weak diffraction power were available. Therefore, the atomic coordinates were refined using restraints demanding nearly equal lengths for corresponding bonds of the six symmetry independent molecules. The existence of the space group Cc instead of C2/c was confirmed by the results of the structure analysis. A careful inspection of the molecular packing using CELLGRAF [29] indicated that there are no twofold axes in the crystal structure. The hydrogen atoms of DPO II were calculated according to their geometrical conditions and included in the structure refinement using the riding model. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition number CCDC 190263 (DPO I at 293 K), CCDC 190264 (DPO I at 353 K), and CCDC 160022 (DPO II).

Crystal data of DPO I (at 293 K). A colorless needle shaped crystal with dimensions $1.00 \times 0.075 \times 0.070 \text{ mm}^3$ was used for data collection. Crystal system: monoclinic, space group $P2_1/c$ (No 14), a = 0.51885(6) nm, b = 1.8078(2) nm, c =1.21435(14) nm, $\beta = 93.193(3)^\circ$, $V = 1.1373(2) \text{ nm}^3$, Z = 4, d(calc.) = 1.298 Mg/m^3 , linear absorption coefficient $\mu = 0.083 \text{ mm}^{-1}$, and Fw = 222.24 for C₁₄H₁₀N₂O, F(000) = 464. The total number of reflections in the range $4.0^\circ < 2\Theta < 46.6^\circ$ was 10468, 1595 independent, 1154 observed [$I > 2\sigma(I)$]. The number of refined parameters was 195. Final R (on F) = 0.0486.

Crystal data of DPO I (at 353 K). The same crystal described above was used for data collection. Crystal system: monoclinic, space group $P2_1/c$ (No 14), a = 0.52131(12) nm, b = 1.8116(5) nm, c = 1.2155(3) nm, $\beta = 92.933(9)^\circ$, V = 1.1464(5) nm³, Z = 4, d(calc.) = 1.288 Mg/m³, linear absorption coefficient $\mu = 0.083$ mm⁻¹, and Fw = 222.24 for C₁₄H₁₀N₂O, F(000) = 464. The total number of reflections in the range $4.0^\circ < 2\Theta < 46.6^\circ$ was 10685, 1580

independent, 1110 observed $[I > 2\sigma(I)]$. The number of refined parameters was 195. Final *R* (on *F*) = 0.0500.

Crystal data of DPO II (at 293 K). A colorless plate shaped crystal with dimensions $0.23 \times 0.12 \times 0.03 \text{ mm}^3$ was used for data collection. Crystal system: monoclinic, space group Cc (No 9), a = 2.4134(4) nm, b = 2.4099(3) nm, c = 1.2879(2) nm, $\beta = 110.048(3)^\circ$, $V = 7.0363(17) \text{ nm}^3$, Z = 24 (6 symmetry independent molecules having different conformations), d(calc.) = 1.259 Mg/m³, linear absorption coefficient $\mu = 0.083 \text{ mm}^{-1}$, and Fw = 222.24 for C₁₄H₁₀N₂O, F(000) = 2784. The total number of reflections in the range $2.4^\circ < 2\Theta < 40.0^\circ$ was 9639, 4254 independent, 3007 observed $[I > 2\sigma(I)]$. The number of refined parameters was 920. Final *R* (on *F*) = 0.0630.

Raman investigations. A Raman triple spectrograph 'T64000' (INSTRUMENTS S.A.) with a liquid nitrogen cooled CCD detector the was applied for the recording procedure. The resolution of the system is about 1 cm⁻¹. The Raman spectra were excited by a He–Ne laser (632.8 nm) focussed to a spot of 10 μ m with a reduced power output of less than 4 mW to avoid thermal heating effects of the sample. All spectra were calibrated using the spectral lines of Ne from a pen ray calibration lamp.

The selected crystals were mounted on usual micro slides either as single crystals or as powder to avoid orientational effects. An additional camera system allowed the visual inspection of the sample and the precise localization of the laser spot on the sample.

DSC. The DSC studies were performed applying a DSC 7 device (PERKIN–ELMER). The sample mass

was always around of 5 mg. Closed aluminum crucibles were used. The system was calibrated using the usual calibration substances like indium or zinc. Heating rates of 10 °C/min were chosen. An experimental error of 1 °C for the determination of the phase transition temperatures (peak value) resulted.

3. Results and discussion

3.1. DPO—new polymorphic structure DPO II and comparison to DPO I

From the solution crystallization experiments two morphologically different forms of DPO crystals resulted. In general, both forms consist of white colorless opaque to slightly transparent crystals. One form shows a needle-like habit (Fig. 1(a)) with a length up to several millimeters for the long needle axis. The width may amount to maximum 1 mm while the thickness is much smaller. The second polymorphic form exhibits plate-like up to prismatic shapes (Fig. 1(b)) with all dimensions usually smaller than 0.5-1 mm. Depending on the crystallization conditions both crystal types form larger aggregates, in the case of the needles this are fan-shaped polycrystals while the second polymorph forms larger clusters of impinged grains.

For the structure determination well grown crystals of both polymorphs were selected. The structure determined for the needle like crystals—DPO I corresponds at room temperature to that published by Kuznetsov et al. [13]. The monoclinic unit cell $(P2_1/c)$



Fig. 1. Example for the morphology of DPO I (a) and DPO II (b).



Fig. 2. Molecular packing of DPO I (a) and DPO II (b).

contains four DPO molecules (one symmetry independent). DPO I crystallizes in a herringbone structure, characterized by stacks of parallel molecules (see Fig. 2(a)). The molecules of adjacent stacks have opposite inclination to the stack axis, in this case the *a*-axis. 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 *b*-direction, avoiding an aligned arrangement of the oxadiazole rings along the c-axis. The molecules of adjacent stacks show an inclination angle of $\pm 41^{\circ}$ to the stack axis, respectively. The most intense inter-molecular interactions in DPO I occur along a stack between the π systems of the oxadiazole unit of one molecule and the phenyl groups of the adjacent molecules (Fig. 3). The strong electron acceptor character of the oxadiazole moiety induces the formation of π -complexes resulting from the interaction between one π -donor (phenyl ring) and a π -acceptor (oxadiazole ring) [8]. Therefore, a sandwich arrangement along the stacks, where the oxadiazole ring of one molecule is located between two phenyl rings of the neighboring molecules, is the result of the optimization of the $\pi - \pi$ interactions between π -donors and π -acceptors. In this way, the oxadiazole group of every molecule interacts with two phenyl rings of the adjacent molecules and the phenyl ring of a molecule interacts with one oxadiazole ring of the adjacent molecule. The distance between the molecular planes of a π -complex amounts to 0.3352(2) nm, a usual spacing for such complexes [8]. The forces between different stacks are described by van der Waals interactions.

The structure determined for polymorph DPO II forming plates or small prisms is different to that published by Kuznetsov et al. [13]. It is also monoclinic, space group *Cc* but with a rather complex packing motif compared to DPO I. The structure of DPO II contains six symmetry independent molecules (A, B, C, D, E, F). A DPO molecule from this structure together with the average bond distances is depicted in Fig. 4. The conformations of the six symmetry independent molecules are different as indicated by the dihedral angles between the central oxadiazole ring and the phenyl rings. These angles are listed in Table 1. The molecular arrangement of DPO II is illustrated in Fig. 2(b). The crystal packing is



Fig. 3. Molecular pair in the crystal structure of DPO I. (The e.s.d. is 0.0002 nm).



Fig. 4. DPO molecule. Average bond distances are given for the six symmetry independent molecules of DPO II. The standard deviations are between 0.0010 and 0.0016 nm.

characterized by layers parallel to the *ab*-plane These layers are built by stacks of molecules, where the molecular planes are perpendicular to the layer plane. Inside a layer, alternating stacks of parallel molecules produce a zig-zag arrangement. The molecules of adjacent stacks are oriented nearly perpendicular to each other. Along a stack parallel molecules are placed in such a way that the oxadiazole unit of a molecule is sandwiched between the phenyl rings of the adjacent molecules, leading to the formation of π complexes. In contrast to the first polymorph every third molecule in these stacks is oriented in opposite direction in relation to its neighbors. Therefore, the formation of perfect stacks is prevented and two principally different kinds of π -complexes are formed, one between molecules with the same orientation and another between those with opposite orientation. All occurring stacks are depicted in Fig. 5. The spacing between averaged molecular planes range from 0.342(1) to 0.353(1) nm.

Table 1

Dihedral angles in DPO II, DPO I (at 293 K), and DPO I (at 353 K) (signs of angle values were taken from pertinent torsion angles)

Polymorph	P1(O1,C2,N3, N4,C5,C6,C12)– P2(C5,C6,C7,C8, C9,C10,C11)	P1(01,C2,N3,N4, C5,C6,C12)- P3(C2,C12,C13,C14, C15,C16,C17)
DPO II molecule A Molecule B Molecule C Molecule D Molecule E Molecule F DPO I (at 293 K) DPO I (at 353 K)	-2.37(13) -3.74(14) 5.03(19) -5.31(14) -4.68(15) 11.46(18) 2.01(8) 2.17(9)	$\begin{array}{r} -6.83(18) \\ -3.15(14) \\ 9.45(16) \\ 3.75(12) \\ -8.51(16) \\ 3.37(12) \\ -1.82(9) \\ -1.76(10) \end{array}$

Analyzing a layer the shortest spacing between adjacent stacks of the same layer occurs between C atoms of phenyl rings and amounts to 0.383(2) nm. The relatively large value of this distance together with the perpendicular orientation between molecules of different stacks leads to the conclusion that the interactions between stacks are almost van der Waals interactions. Additionally, between different layers weak hydrogen bonds could exist because the shortest distance between layers is found between one of the phenyl ring C atoms of a molecule and a nitrogen atom of the oxadiazole ring of other molecule. The C-N spacing amounts to 0.345(1) nm, well in the range 0.3–0.4 nm expected for weak hydrogen bonds [17] and also the angle between the three involved atoms corresponds to this assumption with 143° (range $100 - 180^{\circ}$).

Although the molecules of both polymorphs are almost planar the conformation shows small but significant differences. In DPO I the three rings are perfectly planar with endocyclic torsion angles lower than 1°. The deviation of the phenyl groups from the molecular plane, defined by the oxadiazole unit, amounts to 2.0 and -1.8° . Both phenyl rings are inclined in the same direction. The molecular conformation of DPO II is not as planar as in the first polymorph. The rings themselves are nearly planar again with endocyclic torsion angles up to 3° , they do not lie in the same plane. The amount of the dihedral angles between the rings varies among the six molecules constituting the asymmetric unit with a maximum angle of $11.5(2)^{\circ}$ and a mean value of 6° . Except in molecule D the phenyl rings are rotated in opposite directions to the oxadiazole group. A detailed comparison of the conformations is given in Table 1.

For both polymorphs the high planarity induces at least a partial conjugation of the π system along the whole molecule confirmed by the shortness of the inter-ring bonds. In both polymorphs the mean value amounts to 0.146 nm and is shorter than 0.154 nm, expected for a C–C single bond and such bond shortening is usually considered to result in a partial conjugation of a single bond (for instance Ref. [18]). Especially for DPO II these values also indicate that the deviation of the phenyl rings from the molecular plane is not large enough to prevent a partial conjugation within the molecule.



Fig. 5. Molecular pairs in the crystal structure of DPO II. (The e.s.d's are between 0.001 and 0.002 nm).

3.2. Raman spectroscopic investigations of DPO I and DPO II

Fig. 6(a) shows the Raman spectra of both phases DPO I and DPO II, respectively, in the finger print region between 15 and 1700 cm^{-1} . The spectra are characterized by well resolved internal modes and the external lattice vibrations below 200 cm^{-1} . The internal modes are dominated by two groups, one around 1000 cm^{-1} and a second between approximately 1500 and 1600 cm^{-1} . Several smaller bands may be found between these two groups but these shall not be discussed here in detail. Looking at these two groups separately it is obvious that there exist no remarkable differences between DPO I and DPO II in the first region within the resolution limits of the system $(\pm 1 \text{ cm}^{-1})$. In the region around 1000 cm^{-1} the main band at 992 cm⁻¹ is approximately twice broader for DPO II compared to DPO I while the smaller surrounding lines are more intense in DPO II. The broadening may be explained by the presence of several independent molecules with slightly different geometry in the unit cell. The assignment of the different modes is done tentatively using literature data for other organic compounds, especially those containing phenyl and 1,3,4-oxadiazole rings (a general review is found in Refs. [19,20]). Additional data for 1,3,4-oxadiazoles are taken from Refs. [21–23] as well as from Raman investigations of different diphenyl-1,3,4-oxadiazoles with varying functional groups and different chain length up to the phenyloxadiazole polymer [6]. This assignment may be compared with molecular modeling calculations using GAUSSIAN 94 where a first attempt showed rather good agreement.

The bands result from both building blocks, the two monosubstituted phenyl rings and a diaryl substituted 1,3,4-oxadiazole ring. The most prominent internal vibrations at 1607 and 992 cm⁻¹ are attributed to ring vibrations of the phenyl rings, while the oxadiazole ring marks at 1554 cm^{-1} .



Fig. 6. Raman spectra of DPO I and II in the complete finger print region (a) and in the region of the external modes below 400 cm⁻¹ (b).

The literature reports three oxadiazole ring modes in the region around 1500 cm^{-1} : 1542, 1479, and 1456 cm⁻¹, so that the first vibration may be identified with the experimental value. The other two bands may also be found in the spectra but with lower intensity. The phenyl band at 1607 cm^{-1} and an additional smaller line around 1580 cm^{-1} result from the splitting of the quadrant stretch mode that is degenerated for the pure benzene ring due to the substitution. The phenyl semicircle stretch bands are not identified with security, but these bands are always weak in Raman. The strong mode at 992 cm^{-1} should be due to the diaryl substituted oxadiazole having two additional characteristic frequencies at 1115 and 1022 cm^{-1} according to Ref. [24]. This is also concluded from the comparison with Raman spectra of other diphenyl oxadiazoles [25] and from first rough molecular modeling results. Monosubstituted phenyl rings should exhibit a band usually showing high Raman intensities in the range between 990 and 1010 cm^{-1} resulting from the in-plane ring deformation or ring breathing vibration. A ring stretching vibration should occur below 1000 cm^{-1} . Both modes may interact and mix due to the same symmetry species [19] giving rise to an intense Raman band around $1000 \pm 5 \text{ cm}^{-1}$. The slightly asymmetric shape of the bands with a shoulder at lower wavelengths may indicate a convolution of both bands resulting either from the oxadiazole and the monosubstituted phenyl rings. The other lines with minor intensities found in the spectra may

also be assigned to ring vibrations mainly of the phenyl rings. Generally, it has to be mentioned, that the combination of different building blocks with known Raman frequencies may lead to larger deviations due to superposition and interaction of different ring vibrations and possibly with C-H motions. So, frequency shift or mode splitting may occur, some lines may be missing or new ones appear so that the assignment for the resulting compound's spectrum not necessarily must be unique. Several experimental data in literature were also obtained in solution. But here the molecules are investigated in the solid crystalline state and therefore the interaction with neighbored molecules within the crystal has to be taken into account.

Remarkable differences in the Raman spectra are found in the region of the external modes. Both phases clearly may be distinguished by their spectra below approximately 400 cm^{-1} as illustrated in Fig. 6(b). While DPO I shows at least four well resolved bands below 50 cm⁻¹ DPO II has only three but rather broad lines in that region. Nevertheless, it is expected that the bands consist of superimposed vibrations and not of a single one. Adjacent to this for DPO II a very broad shoulderlike structure is found also consisting of a superposition of several lines seen in several slight maxima. These could only be resolved by a deconvolution procedure for an appropriate number of bands. This structure is stronger orientation dependent than the lines at lower wave numbers.

Compared to this DPO I is characterized by two broad but separate bands between 50 and 100 cm^{-1} . Another remarkable difference is a band found at 164 cm⁻¹ for DPO I while it is shifted to about 154 cm⁻¹ in DPO II. Also minor lines around 250 and 340 cm^{-1} show some smaller shifts. These smaller variations are indicated by arrows in the figure. Summarizing it has to be stated that it is of crucial importance to investigate the low frequency Raman modes to investigate the phase behavior of DPO because the internal modes are not sufficient to discriminate between the different structures at least under ambient pressure (the high pressure behavior and the resulting differences for both structures will be discussed elsewhere [26]). But as also may be concluded micro Raman spectroscopy turns out to be a valuable tool for the distinction between different crystal structures due to lower requirements for the crystal perfection compared to single crystal X-ray investigations and to the faster procedure. In the different crystallization attempts Raman spectroscopy was successfully applied to determine the phase content.

3.3. Thermal investigations and phase transition from DPO I to DPO II

The thermal behavior of DPO was characterized using the usual DSC technique. For the DSC study three successive heating and cooling cycles were performed. During the first heating, DPO I shows an endothermic peak at 97 °C (value at peak maximum) with an enthalpy increment of $\Delta H = 2.7$ kJ/mol. Further heating induces the melting of the crystal at 141 °C ($\Delta H = 24$ kJ/mol). The melting point is in accordance with Ref. [27]. By cooling, the liquid recrystallizes at 115 °C ($\Delta H = -20$ kJ/mol). The subsequent heating and cooling cycles show only the peak corresponding to the solid-liquid phase transition, no indications for further processes within the sample are found (see Fig. 7). Therefore it may be concluded that the first peak describes an irreversible phase transition.

The DSC analysis of DPO II indicates that this crystal does not undergo any solid-solid phase transitions. The melting temperature found for the three heating cycles was 141 °C also corresponding to the DPO melting temperature [27] ($\Delta H = 24$ kJ/mol).



Fig. 7. DSC study of the transition of DPO I into DPO II. The inserts show the Raman spectra in the region of the lattice modes for the identification of the phase content.

Thus both compounds show the same melting temperature and heat of fusion. The substance shows the analogous recrystallization behavior like DPO I (temperature: 113-114 °C, $\Delta H = -20 \text{ kJ/mol}$).

To investigate the nature of the solid-solid transition in DPO I an additional DSC run with DPO I was stopped at temperatures slightly above the transition. Here, also during cooling of the sample no peaks appear. All recovered DSC samples were then investigated by means of Raman spectroscopy. All samples, those that recrystallized from the melt after three measuring cycles as well as that from the stopped DSC run showed clearly the Raman characteristics of DPO II. So, due to missing hints on further transitions it is concluded that DPO I converts to DPO II with increasing temperature in a solid-solid phase transition. This structure also recrystallizes from the melt under normal conditions. Accompanying powder X-ray investigations under increasing temperature also confirmed the transition process although the limited precision of the temperature determination prevented a detailed insight into the transition process i.e. if there exist possibly intermediate stages and structures or if it proceeds directly from one to the other structure.

Fig. 2 shows the packing of molecules in the corresponding unit cells of both polymorphs. The lattice of DPO II can nearly be obtained from that of DPO I by the following matrix: $(3\ 1\ 0)\ (-3\ 1\ 0)\ (-0.5\ 0\ 1)$. To obtain some further insights into a possible topotactic transition mechanism X-ray single crystal investigations at higher temperatures were carried out. Table 2 lists the lattice parameters of DPO I obtained by measurements between 293 and 363 K. The cell volume significantly increases up to 1.6%. The relatively largest increase was observed for

 Table 2

 Lattice parameters of DPO I at different temperatures

the *a*-axis. This corresponds to a change of the stacking interactions in DPO I.

An intensity data collection for a complete structure determination could be carried out at 353 K. But none significant deviations of corresponding molecular parameters were observed. Only the spacing within the molecular stacking pairs increased from 0.3352(2) to 0.3375(2) nm (Fig. 3). An attempt to determine the complete crystal structure at 363 K failed because the single crystal was destroyed by sublimation. Before this destruction the formerly clear crystal became turbid.

Because of the weak diffraction power of the available crystals high temperature X-ray measurement for DPO II gave no very significant results. But nevertheless it was found that the volume of the unit cell increased at 363 K by 0.8% and at 393 K by 1.4% compared with that at the room temperature.

Although some relations between crystallographic axes exist there is no greater evidence for a topotactic reaction between both phases. Appropriate relations between the individual molecules and therefore possible motions that could lead from structure I to II could not be found. This mechanism would require larger molecular motions and especially the change to an opposite orientation of every third molecule within the solid state.

From the temperature treatment only DPO II results as final product. No back transformation to DPO I could be detected. Additional high pressure X-ray and Raman investigations showed that neither DPO I nor DPO II exhibit any pressure induced transition in the pressure range up to 7 GPa (for an equation of state for DPO I see Ref. [12], that for DPO II is found together with extensive Raman

T (K)	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	α (°)	eta (°)	γ (°)	$V(\mathrm{nm}^3)$
296	0.51885(14)	1.80883(42)	1.21435(29)	90.000(24)	93.193(34)	90.003(28)	1.13728(53)
303	0.51947(16)	1.80946(45)	1.21509(27)	90.026(27)	93.129(36)	90.015(39)	1.14043(55)
313	0.51979(18)	1.80975(46)	1.21481(32)	89.991(27)	93.098(36)	90.025(31)	1.14108(57)
323	0.52049(17)	1.81178(46)	1.21650(35)	90.042(28)	93.006(38)	90.034(33)	1.14561(56)
353	0.52108(16)	1.81205(50)	1.21639(34)	90.020(31)	93.019(35)	90.000(33)	1.14695(59)
363	0.52382(19)	1.80898(68)	1.22081(46)	90.265(31)	92.712(46)	90.115(43)	1.15552(91)

investigations of both structures in Ref. [26]). That means that no way was found to transform DPO II into DPO I. Consequently, DPO II could be the thermodynamically stable phase but it generally cannot be fully ruled out, that the transformation is only kinetically hindered.

Concluding it shall be stated that the free energy of both structures is nearly the same as expected from several examples of organic polymorphism and indicated by the low energy barrier to induce the transition of DPO I into DPO II. Only a small energy of 2.7 kJ/mol is necessary. The inter-molecular interactions in both crystals are nearly similar. In both cases, they are principally strong $\pi - \pi$ interactions along the infinite π -complexes, van der Waals forces between nearly perpendicular phenyl rings and weak H-bonds between one N atom of the oxadiazole unit and the C–H group of the phenyl ring of a nearly perpendicular molecule.

4. Conclusion

For a rather simple molecule, the 2,5-diphenyl-1,3,4-oxadiazole molecule as a root molecule for a huge class of differently substituted compounds with many different potential applications it could be shown that at least two different polymorphs exist. These two forms already differ by their morphology, having either needle-like or plate-like habit. Although both structures are monoclinic the packing motif is completely different. Nevertheless, some features of the molecular arrangement like stacks of molecules connected by van der Waals interactions or by the formation of π -complexes within the stack are encountered for DPO I as well as for DPO II. This leads to similarities of the intermolecular interactions. The simpler structure DPO I transforms into the more complex structure II under heating with low transition enthalpy as expected. To distinguish between both structures extensive X-ray investigations are not always required, it could be shown, that Raman spectroscopy offers a fast and easy-to-use tool for discrimination between different polymorphs due to characteristic differences of the lattice modes. Additionally, at least in this case already the careful investigation of the varying morphology is sufficient for this purpose.

As in general polymorphism is a common phenomenon especially for organic molecular crystals thermodynamic and kinetic aspects shall not be discussed here. It should only be remarked that summarizing all observations the crystallization process of DPO from the solution should be an example for Ostwald's law of stages. DPO I mostly forms first from the solution (if it is not prevented due to the specific conditions) due to the faster kinetics (lower nucleation activation energy, higher growth rate). This structure remains metastable. The crystallization of DPO II sets in later and seems to be slower. But, generally a deeper insight into the whole processes resulting either in DPO I or DPO II or their mixture is still missing due to the complex interactions and influences of the variety of different thermodynamic and kinetic factors.

The newly discovered structure of DPO is a noncentrosymmetric one thus offering possibilities for non-linear optical effects. Additionally, it is worth noting that the crystals of DPO II show a blue triboluminescence signal if they are mechanically treated or crushed while the DPO I crystals do not exhibit such features. As known from other triboluminescent materials it is always a non-centrosymmetric structure that is active in contrast to centrosymmetric polymorphs [28]. Therefore it was concluded that a piezoelectric charge may be responsible for this effect. The non-centrosymmetric space group Cc belonging to the crystal class m offers the possibilities for both, piezo-and pyroelectricity. In a first rough experiment both coefficients were measured at a compacted non-oriented powder sample of DPO II. A piezocoefficient of $d_{33} = 3$ pC/N and a pyroelectric coefficient of $p_3 = 0.01 \text{ nC/Kcm}^2$ resulted. The pyroelectric measurements showed a stronger hysteresis. Compared to other substances especially like polymers these parameters are rather small but the results give further evidence for the importance piezoelectric charges of in triboluminescence.

So the experiences obtained with this molecule may serve as starting points for future investigations of differently substituted DPO molecules with the aim of a higher perfection of the grown crystals and possibly new application fields for this group of compounds. Additionally these investigations substantially contribute to the understanding of structure-property relationships, particularly in connection with high pressure experiments that may give a deeper insight into the different molecular interactions.

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