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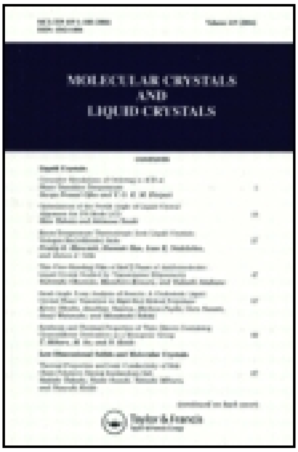

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Crystal Structure of 2,5-Di(4-Methoxycarbonyl-Phenyl)-1,3,4-Oxadiazole Charactrized by AFM and IR-Spectroscopy

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CRYSTAL STRUCTURE OF 2,5-DI(4-METHOXYCARBONYL-PHENYL)-1,3,4-OXADIAZOLE CHARACTRIZED BY AFM AND IR-SPECTROSCOPY

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Abstract Low molecular aromatic 1,3,4-oxadiazoles are of interest for scientists dealing with biologically active or photochemically active materials. They are also of interest as model compounds for thermostable polymers. Here, for the first time the characterization of the crystal structure of 2,5-di(4-methoxycarbonyl-phenyl)-1,3,4-oxadiazole by Atomic Force Microscopy (AFM) and IR-spectroscopy is presented. Additionally, the experimental data are interpreted by molecular modelling results. The crystallographic data known from X-ray investigations can be determined from the molecular resolved AFM pictures too. The molecular parameters of the organic crystal were also calculated by molecular modelling and agree with all experimental results. The modelling was carried out without any assumptions about the molecular or crystal structure of the oxadiazole molecule. The oxadiazole crystal was also characterized by FTIR-spectroscopy using polarized radiation. A distinct dichroism was observed for several bands as well as of the oxadiazole ring, the phenylene group and the carboxylic group. On the contrary the dichroism for the methylene bands is lower. All IR-data support the crystal structure deduced from AFM, X-ray investigations and molecular modelling.

INTRODUCTION

1,3,4-Oxadiazoles are of great interest for medicine and drug synthesis with antimicrobial activity, for polymer synthesis, for dye preparation and application in photography, light screening agents and as scintillators. Especially, the structure of low molecular aromatic 1,3,4-oxadiazoles is of interest as model compounds for thermostable polymers.

Only litle is known about the crystal structure of such compounds. Therefore, the characterization as well as of the molecular and crystal structure of 2,5-di(4-

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methoxycarbonyl-phenyl)-1,3,4-oxadiazole (DMPO) by AFM and IR-spectroscopy is presented. The crystallographic data of this compound are known from X-ray investigations [1]. Together with other oxadiazole DMPO was modelled without any assumptions about its molecular or crystal structure. All calculated and experimental results will be compared.

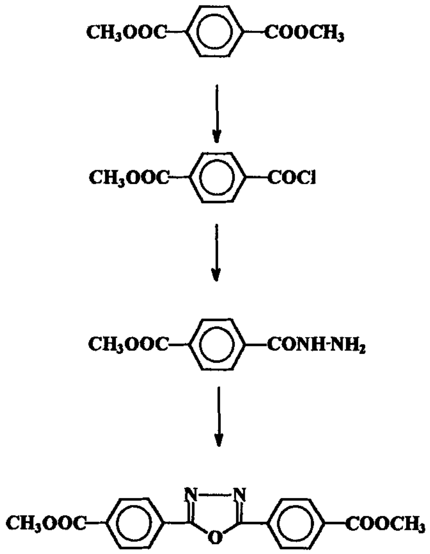
EXPERIMENTS

DMPO was synthesized as shown in the scheme. It was recrystallized from ethanol. The crystal dimension were $1\times1\times10$ mm^3. [2]

The STM/AFM equipment SA1/BD2 from Park Scientific Instr. S.A. (USA) was used under the following conditions : air; 20°C; 55%rh. The AFM has an optical system (beam-deflection) to measure the repulsive forces between tip and cantilever ($F\approx10^{-8}$N) in contact mode. A 2.5μm scanner and a soft cantilever (200μm; k=0.032N/m) were used.

Transmission-IR-spectra were registered with a NICOLET-MAGNA-550-FTIR spectrometer. Main parameters for data-collection were: resolution 4cm^{-1}; number of scans 300; apodization HAPP-GENZEL.

DMPO was modelled with POLYGRAF using the DREIDING II force field and simultaniously optimizing atom positions and cell parameters.



Reaction Scheme

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RESULTS AND DISCUSSION

Atomic Force Microscopy

Different places at various crystal samples of DMPO were measured without any special crystal preparation. At each measuring point a reproducible molecular resolution was obtained. It is assumed, that applying a normal measuring force some molecular layers were removed. In such a way pictures (Figure I) with a characteristic double row structure were observed. The molecular resolution were received in both the constant heigh and in the constant force mode. The measured distances between the double rows are 15.6±1.3Å and inside the rows are 4.8±1.1Å .
By comparing these data with the data from molecular modelling it can be seen, that the obtained values are not pure molecular crystal data but secondary periodicity's. In bigger scale (1 x 1 μm) typical monomoleculare steps were visible. The measured step height is ≈ 9Å (Figure II).
The dimensions determined by AFM pictures agree well with those calculated by molecular modelling.

Molecular Modelling

Using the DREIDING II force field calculations with simultaneously optimizing atom positions and cell parameters the calculated crystal data are: $a= 7.8$ Å, $b= 6.5$ Å, $c= 21.5$ Å, $\alpha= 102^{\circ}$, $\beta= 51°$, $\gamma= 105^{\circ}$. Two DMPO molecules per unit cell placed with the oxadiazole rings in antiparallel positions are the main feature of this structure (Figure III). Simulated X-ray data using CERIUS correspond positively to these results.[1]
By modelling oxadiazoles it soon becomes clear from general behaviour that their structure is determined to a great part by phenyl rings. They tend to reach a mutual position similar to that acquired in the most stable configuration for benzene dimers[3]. This PD-shape of dimers is characterized by the phenylene rings laying on two parallel planes distanced 3.85 Å from each other. The line connecting the centres of both benzene molecules inclines 65° to the ring planes. For DMPO a parallel distance of 3.5 Å and a displacement angle of 63° were calculated.

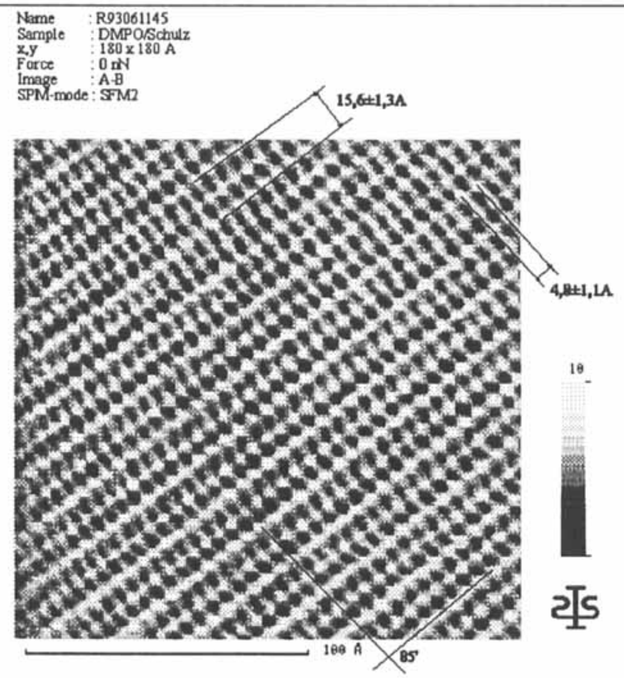

FIGURE I: Molecular resolution of DMPO

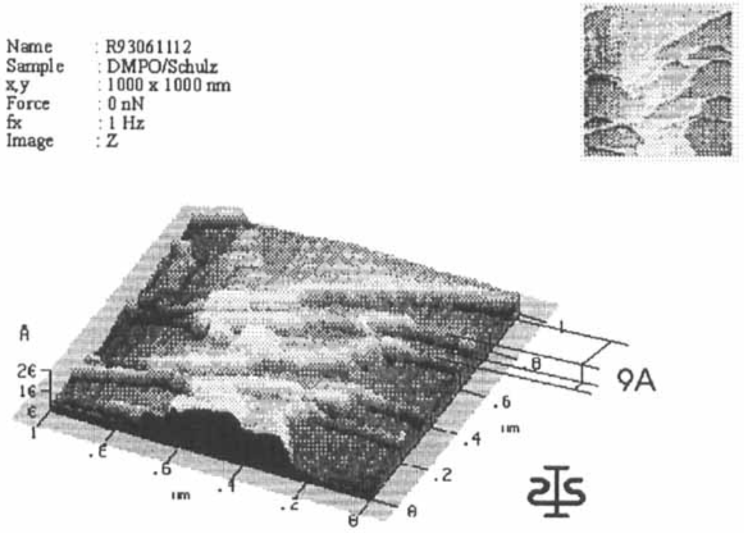

FIGURE II: Molecular steps

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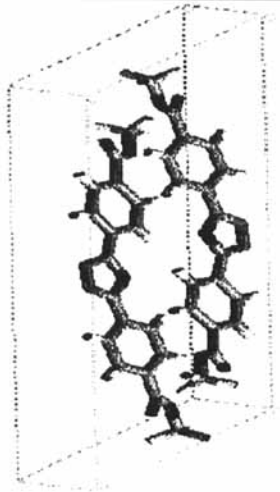

FIGURE III: Unit cell of DMPO

FIGURE IV: Z - clipping along the (010) direction

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All phenyl rings in the DMPO crystal are almost parallel due to the great freedom to arrange resulting from the nonphenylic parts of the molecule. In solid benzene there are strings of perpendicular situated rings ^{4}. This is experimentally excluded for DMPO by IR-specroscopy.The two phenyl rings of DMPO show a deviation of 2.8° each from their common average plane.

The surface of the crystal and especially the series of z-clipping shots (Figure IV) from this surface show great similarities to AFM pictures. This two dimensional array is characterized by distances of 7.7Å and 17.3Å as well as an angle of 82.4°, which is in good agreement to the experiment.

Infrared spectroscopy

Due to the anisotropy of the investigated crystals dichroic transmission spectra were observed by IR-spectroscopy with polarized radiation (Figure V). As an example the C=O overtone vibration at 3416 cm^{-1} is shown in Figure VI for different polarizer positions.

After a first assignment of several absorption bands to characteristic groups their intensities were registered depending on different polarizer positions (see table).

Deg.	C=O-group 3416 cm-1	Phenyl-ring 3057 cm-1	Phenyl-ring 3045 cm-1	Phenyl-ring 3018 cm-1	Methyl-group 2962 cm-1	Phenyl-ring 1585 cm-1	Oxadiazol-ring 1552 cm-1	Oxadiazol-ring 967 cm-1
0	0,06	0,34	0,17	0,81	0,18	0,17	0,16	0,22
30	0,12	0,20	0,22	0,45	0,23	0,32	0,32	0,39
45	0,18	0,13	0,26	0,32	0,28	0,49	0,50	0,48
60	0,22	0,08	0,31	0,23	0,34	0,74	0,74	0,70
90	0,22	0,08	0,31	0,23	0,33	0,73	0,74	0,70
120	0,12	0,21	0,23	0,46	0,24	0,32	0,33	0,34
135	0,08	0,29	0,20	0,63	0,21	0,22	0,22	0,30
150	0,05	0,34	0,18	0,81	0,19	0,17	0,16	0,22

At least two groups of vibrations are distinguishable. Absorption bands of the oxadiazole ring at 1552 cm^{-1} and at 967 cm^{-1}, some bands of the phenyl ring at 3045 cm^{-1} and 1585 cm^{-1}, the overtone vibration of the C=O-group at 3416 cm^{-1} and the stretching vibration of the CH_3-group at 2962 cm^{-1} belong to the first group.

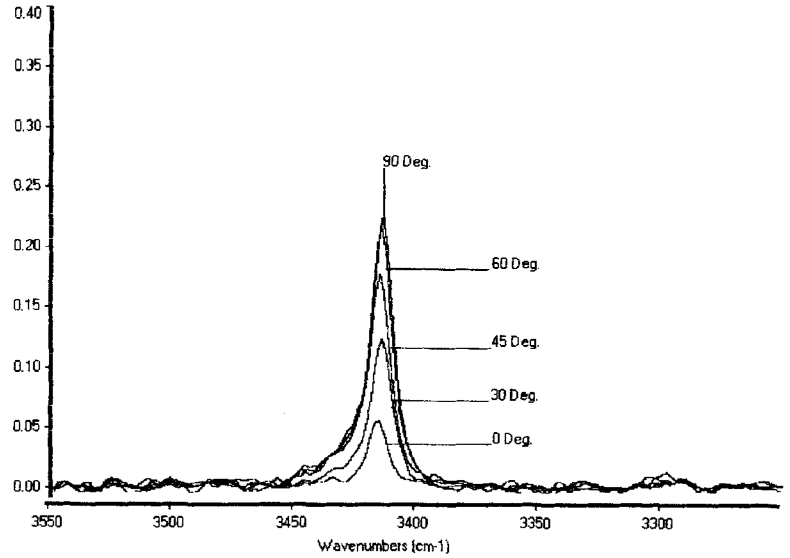

FIGURE V: Investidation of the C=O overtone vibration depending on different polarizer position

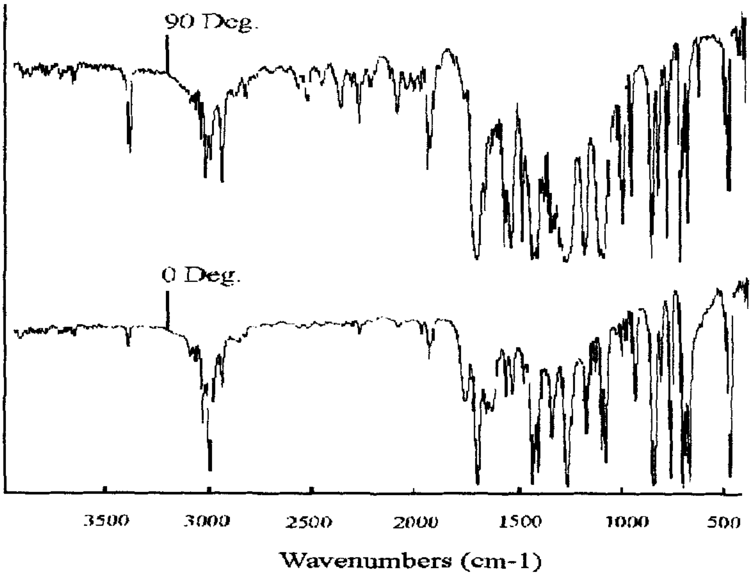

FIGURE VI: Transmission - IR - spectra of the investigated crystal for 0°- and 90°-polarisation position

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The intensities of all these bands show a maximum between the 60° and 90° polarizer position.

Because of their contrary dichroic behaviour some other absorption bands of the phenyl ring at 3057 cm^{-1} and 3018 cm^{-1} belong to a second group of vibrations. The spatial arrangement of the molecules in the unit cell of the crystal was determined by X-ray investigations and AFM-micoscopy. The experimental data were supported by the molecular modelling of the crystal.

According to these results the phenyl- and oxadiazole ring nearly lie in the same plane within a single molecule. The periodic structure of the crystal is formed by a parallel arrangement of such planes.

Consequently all dipole moments which are parallel directed to this plane show the same dichroism whereas such dipole moments which are perpendicular directed to this plane follow a contrary dichroic behaviour.

The obtained IR-data are in good agreement with the mentioned conclusions from the other experimental investigation methods and the molecular modelling too. An exact assignment of the absorption bands of the registered spectra to possible vibrational modes of the molecule is required for further investigations to enlarge the knowledge about the discussed system.

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REFERENCES

1. P. Leibnitz, unpublished results
2. The authors thank E. Leibnitz for synthetic work
3. P. Hopza, H.L. Selze and E.W. Schlag; J. Phys. Chem., 97, 3937 (1993)
4. C.J. Craven, P.D. Hatton, C.J. Howard and G.S.Pawley;J. Chem. Phys. 98, 8236 (1993)