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Characterization of 2,5-Di-*p*-tolyl-1,3,4-oxadiazole Crystals by Atomic Force Microscopy

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Aromatic 1,3,4-oxadiazoles are used as dyes, light screening agents, and scintillators or in photographic materials. In all these applications they are used as dissolved components in amorphous solids. But, for new electrical or electrooptical devices a high degree of molecular order is necessary. To understand more about the structure–properties relationship in organized 1,3,4-oxadiazoles, the structure of crystals of aromatic oxadiazoles as the materials with the highest degree of order were investigated. Here, the characterization of 2,5-di-*p*-tolyl-1,3,4-oxadiazole crystals by atomic force microscopy (AFM) and FTIR spectroscopy is presented. The experimental data are interpreted by molecular modeling. It is shown that there is a difference between molecular structure of the surface, as detected by AFM, and the structure in bulk determined by X-ray diffraction. All results show that the oxadiazole molecules are oriented perpendicular to the crystal surface.

Introduction

In the past 30 years aromatic 1,3,4-oxadiazoles gained great practical significance. This concerns primarily drug synthesis, the preparation of dyes, uses in photography, as light screening agents, and as scintillators.[1] The 1,3,4-oxadiazole system has an electronic spectrum equivalent to that of benzene and the maxima of the oxadiazole derivatives are only slightly shifted hypsochromically compared with benzene. 2,5-Diaryl-1,3,4-oxadiazoles exhibit strong flourescence in solution on stimulation by UV or β-irradiation and some of them show an electroluminescence behavior with radiation of blue light.[2] Besides, most of these materials have an extraordinarily high thermal and oxidative stability.[3]

The combination of these properties makes aromatic 1,3,4-oxadiazoles of interest for the development of new microelectronic and microoptoelectronic devices. For this, thin or ultra-thin layers are nessecary in which the active molecules have a high degree of order and orientation. Although in the recent literature liquid crystalline 1,3,4-oxadiazoles[4] and the first Langmuir–Blodgett films[5] are described, little is known about the molecular and supramolecular order of solid materials containing aromatic 1,3,4-oxadiazoles. Therefore, we have started our investigations on relationships between the structures and properties of organized heterocyclic thin films with the characterization of crystals of aromatic 1,3,4-oxadiazole derivatives.

Here, we present the experimental results of IR spectroscopic and AFM investigations on 2,5-di-*p*-tolyl-1,3,4-oxadiazole (DTO) crystals and their interpretation by molecular modeling.

Experiments

2,5-Di-*p*-tolyl-1,3,4-oxadiazole was synthesized by direct condensation of *p*-toluic acid with hydrazine hydrate in polyphosphoric acid. *p*-Toluic acid (2.72 g, 0.02 mol) and hydrazine hydrate (0.55 g, 0.011 mol) were stirred in 50 g of polyphosphoric acid (84.6% P_2O_5) at 160 °C for 3 h. After cooling, the clear solution was poured into water and filtered, and the product was dried in vacuum. The product was recrystallized three times from ethanol. The DTO crystals are white needles; melting point: 176 °C (lit. 175–176 °C[6,7]). Calc for $C_{16}H_{14}N_2O$: C: 76.80%; H: 5.60%; N: 11.20%; O: 6.40%; exp: C: 76.88%; H: 5.60%; N: 11.05%; solid ^{13}C NMR: O–C=N: 163 ppm; CH_3: 22 ppm.

All investigations discribed here were made with DTO crystal needles wich have typical dimension of 5 × 0.5 × 0.1 mm³. Due to these small dimensions only one surface plane could by characterized, as shown in Figure 1.

The transmission spectra were determined with a NICOLET-MAGNA-550-FTIR spectrometer. The main parameters for data-collection were resolution 4 cm^{-1}, number of scans 1000; an apodization function according to HAPP-GENZEL was used. The crystal was fixed on the sample holder over a 0.3 mm hole and the spectra were registered with perpendicular incidence under different polarizer positions.

The STM/AFM equipment SA1/BD2 from Park Scientific Instr. S.A. (USA) was used under the following conditions: air; 20 °C; 55–70% relative humidity. The AFM has an optical system (beam-deflection) to measure

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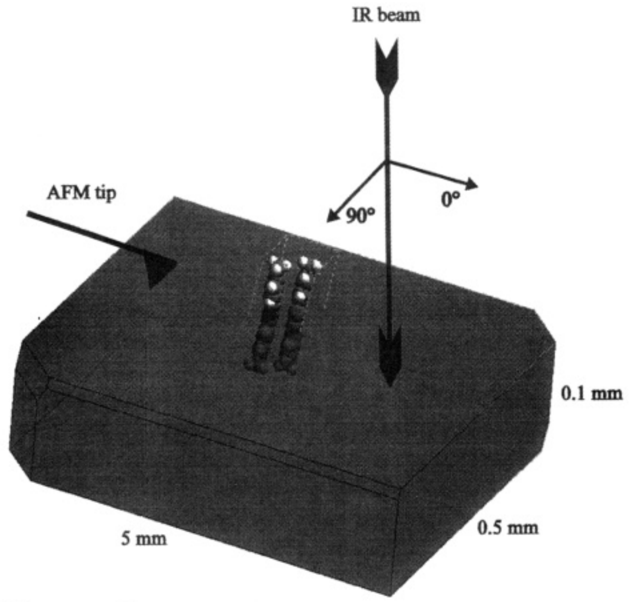

Figure 1. Orientation of the DTO crystal in FTIR and AFM experiments.

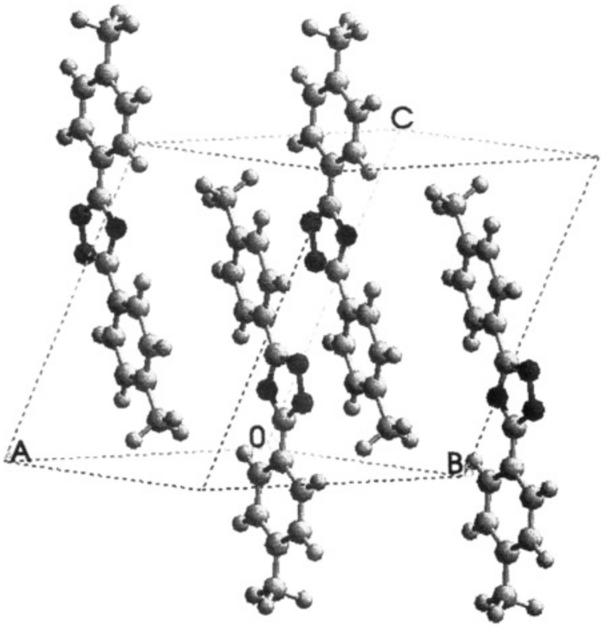

Figure 2. Unit cell determined by X-ray diffraction.[8]

the repulsive forces between cantilever and sample ($F \approx 10^{-8}$ N) in contact mode. A 2.5 μm scanner and a soft cantilever (200 μm; $k = 0.0032$ N/m) were used. Whereas the micrometer-scale picture show a raw data image, pictures with molecular resolution are filtered in order to reduce the noise.

Molecular mechanic calculations were performed using the programs CERIUS and POLYGRAF of MSI.

Results and Discussion

The experimentally determined unit cell of DTO is shown in Figure 2.[8] The symmetry group of the crystal is *C*2/*c*. The unit cell parameters are *a* 11.404 Å, *b* 11.751 Å, *c* 10.870 Å, α 90°, β 116.62°, and γ 90°.

The best-fitting force field was found by comparison of the simulated structures with data from single-crystal X-ray diffraction.[8] The overall features of the experimental structure are simulated correctly with quantitative deviations smaller than 5%. A combination of the DREIDING II force field and Gasteiger charges[9] for the atoms proved to be the best choice to reproduce the experimental structure. Using our optimized DREIDING II force-field parameters for 1,3,4-oxadiazoles, the modeled structure of 2-phenyl-5-[(4-methoxy)benzyl]-1,3,4-oxadiazole agree with the experimental data given by Saalfrank et al.,[10] who have determined the crystal structure of this compound by X-ray diffraction. The symmetry group of these triclinic crystals is $P\bar{1}$-(2) with two molecules per unit cell.

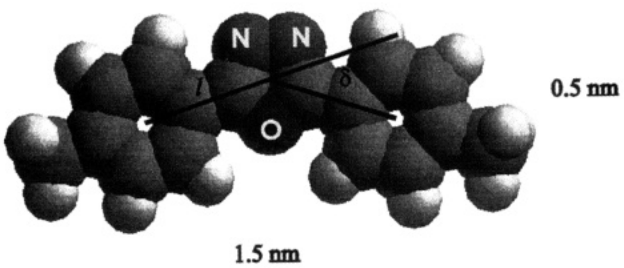

Figure 3. Structure of the DTO molecule; the bonding length l is 1.41 Å (determined by X-ray and calculated); the value of δ is 38.2° (X-ray) and 35.6° (calculated).

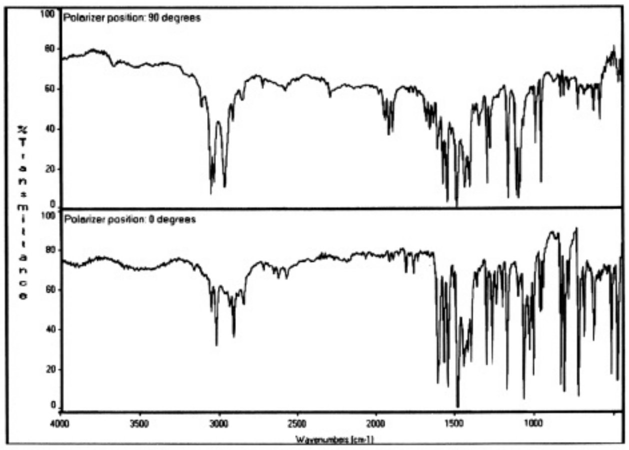

Figure 4. Transmission IR spectra of the DTO crystal for 0° and 90° polarizer position.

The X-ray diffraction data as well as our results of molecular modeling show that DTO is a flat molecule where the phenylene rings and the oxadiazole heterocyclus nearly lie in one plane. The main molecular parameters are given in Figure 3.

The transmission spectra observed by IR spectroscopy with polarized IR radiation show an evident dichroism as shown in Figure 4. The intensities of several characteristic groups are summarized in Table 1.

The data show that both the phenyl ring vibrations which are localized in the ring plane (3062 and 1120 cm^{-1}) and the characteristic oxadizole vibrations (1555 and 966 cm^{-1}) have the same dichroic behavior. Phenyl ring vibrations which are localized perpendicular to the ring plane (823 and 700 cm^{-1}) show an opposite dichroism. These results are confirm to the high-ordered parallel molecular arrangement of phenyl and oxadiazole rings in the same plane, as determined by the X-ray

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Table 1. Intensities of Characteristic Absorption Bands in Dependence on the Polarizer Positions

deg	ring ν(C−H) 3062 cm^{-1}	oxadiazole 1555 cm^{-1}	ring δ(C−H) 1120 cm^{-1}	oxadiazole 966 cm^{-1}	ring δ(C−H) 823 cm^{-1}	ring δ(C−C) 700 cm^{-1}
0	0.165	0.857	0.043	0.229	1.032	0.377
30	0.214	0.713	0.100	0.250	0.516	0.279
45	0.292	0.826	0.201	0.326	0.431	0.232
60	0.420	0.864	0.360	0.436	0.263	0.182
90	1.012	1.397	1.045	0.727	0.068	0.071
120	0.247	0.392	0.274	0.287	0.141	0.066
135	0.347	0.748	0.274	0.362	0.281	0.167
150	0.133	0.395	0.071	0.158	0.347	0.181

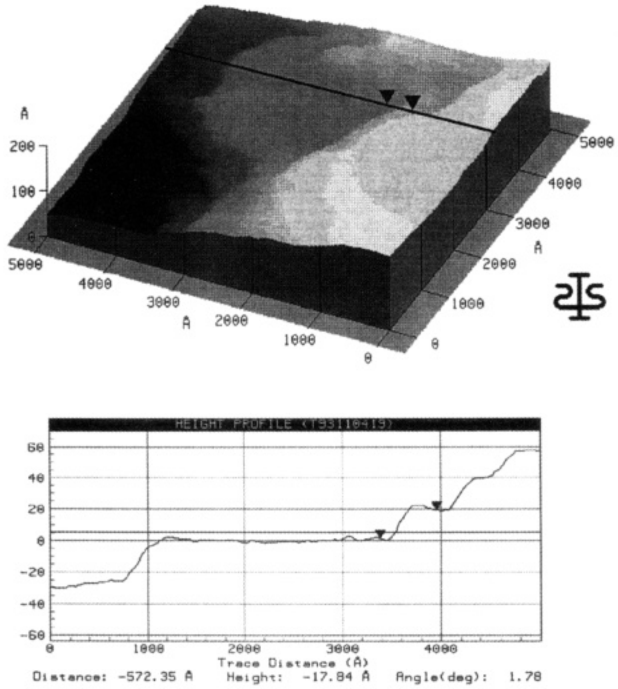

Figure 5. AFM image (0.55 × 0.55 μm^2) of the crystal surface. The height of the terraces is 18 Å.

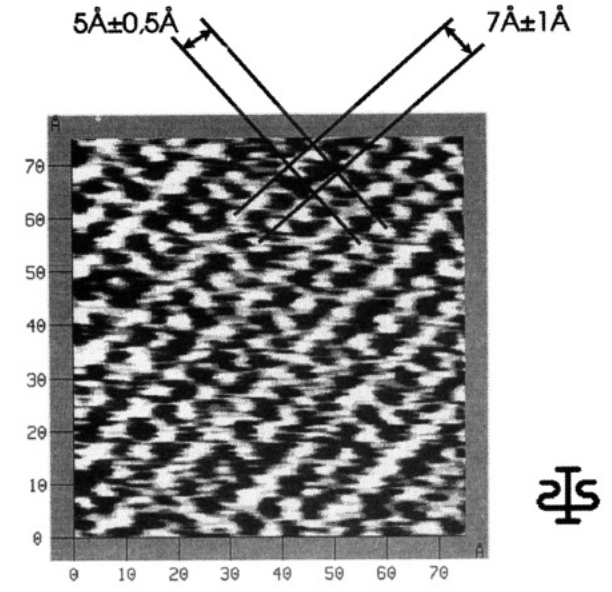

Figure 6. 100 × 100 Å^2 image of the DTO crystal surface with molecular resolution.

investigation. This plane is arranged parallel to the IR-radiation direction, e.g., perpendicular to the crystal surface. An arrangement of this plane parallel to the surface does not agree with the presence of vibrations perpendicular to the phenyl ring plane in the spectra.

In the past few years the AFM was developed as a powerful method for investigation of materials in molecular scale.[11] Among them organic crystals are of special interest. It was shown that the arrangement of the molecules on the surface of tetracene crystals allows the assignment of lattice parameters. For other fused aromatic crystals less correspondence between surface and bulk structures was found.[12] Therefore more extensive studies are required on different kinds of crystals. In this connection also AFM investigations of crystal growth and decomposition processes are of interest.[13] AFM investigations on crystals of aromatic 1,3,4-oxadiazoles are not described in the literature up to now.

Large scale (1 × 1 μm) AFM images of the DTO crystal surface show large flat terraces which are separated by steps with a height of 18 Å (Figure 5). This value is identical with the calculated length of a DTO molecule and sustains the conclusion from IR spectroscopic data that the length axis of the DTO molecules are oriented perpendicular to the crystal surface.

Using a measuring force of 10 nN between the sample and the cantilever tip some material is removed, especially at the edges of terraces. Nevertheless, the stability of the layers inside the terraces is good enough to get reproducible images with molecular resolution. In molecular scale the resulting pattern can be described by almost perpendicular periodicities of 5 and 7 Å (Figure 6).

Molecular modeling was used to compare both the three-dimensional structure as found by X-ray analysis and the two-dimensional patterns given by AFM. As the result of molecular modeling it was found that the AFM images could not been reproduced by any of the planes in the crystal. That means the surface layer structure of the DTO crystal does not reflect the bulk structure. To interpret the AFM images a model crystal was generated using some features of the volume structure. Thus the pairwise arrangement of DTO molecules was retained with the oxygen atoms pointing in oppposite directions (Figure 7). This intramolecular packing is typical for 2,5-diphenyl-1,3,4-oxadiazoles, the dipole moments of the neighboring oxadiazole rings are compensated. Using a $P\overline{1}$ symmetry the calculated cell parameter of the modeled crystal with minimal packing energy are *a* 6.64 Å, *b* 7.11 Å, *c* 16.54 Å, α 89.8°, *β* 66.3°, *γ* 102.0° (Figure 7). As compared to the (001) plane of the real crystal the (001) plane of the modeled crystal

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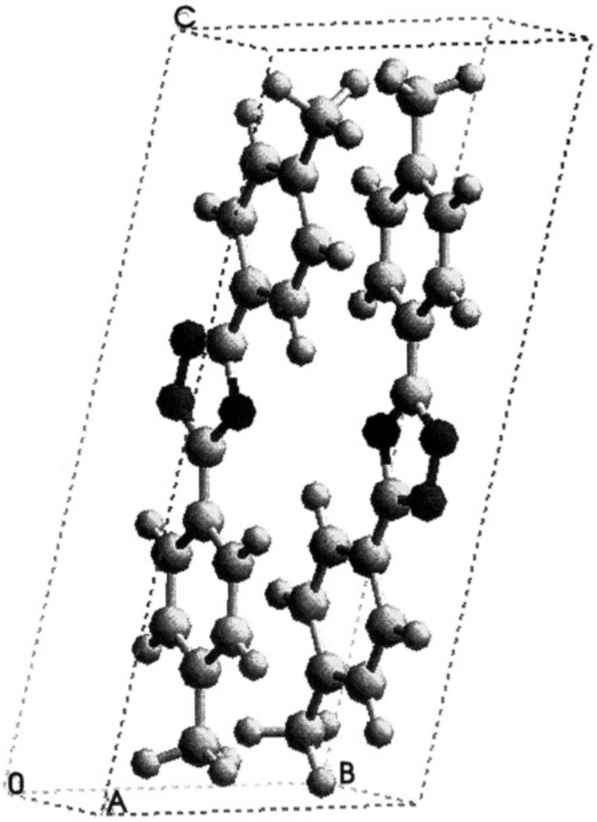

Figure 7. Position of two DTO molecules calculated for a minimum of the potential energy. In this pairwise arrangement of the molecules the oxadiazole rings are opposite directed and the dipoles are compensated.

is smooth at atomic level. A simulated surface layer using the (001) plane of the modeled crystal gives a pattern with line distances of 5 and 7 Å (Figure 8).

The energy per unit cell of the modeled crystal is higher then that of the experimentally determined crystal. Both structures (Figure 2 and Figure 8) can be transformed into each other by translation of one pair of molecules of the unit cell along the *c* axis. Whereas in the bulk the crystal structure exists which was observed by X-ray analysis in layers near the surface the molecules are shifted parallel to each other and form the smooth layer which is observed by AFM. For this process an activation energy of ≈5 kcal/mol is calculated. It is assumed that the driving force for this translation process is the minimation of the crystal surface energy.

Thus, from AFM investigations and molecular modeling it can be concluded that all DTO molecules are ordered perpendicular to the crystal surface in such a way that the surface is formed only by the methyl groups of the molecules (Figure 8). These methyl groups are the reason for the observed "softness" of the crystal surface in the AFM experiment.

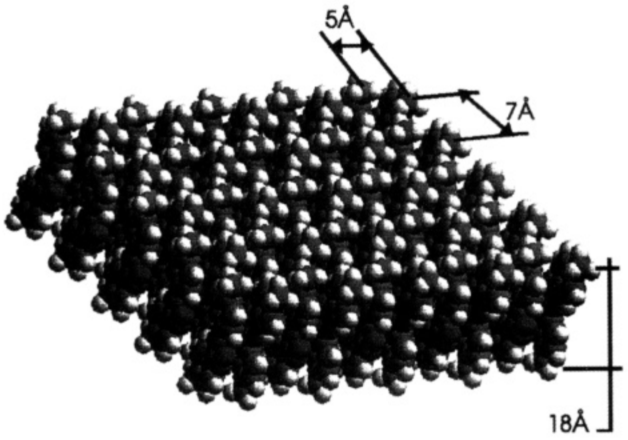

Figure 8. (001) layer of modeled DTO molecule. The intermolecular distances correlate with data from AFM images of the crystal surface (see Figure 6). The surface is only formed by methyl groups.

Conclusions

It was shown by AFM investigations that the molecular structure of the surface layer of DTO crystals differ from the bulk structure determined by X-ray diffraction analysis. The difference can be explained by the assumption that two of the four molecules of the unit cell are shifted parallelly to one another. This translation forms a planar surface in molecular scale. The DTO molecules are oriented perpendicular to the crystal surface in such a way that only the methyl end groups form the upper layer.

The crystal structure for DTO differs from that reported for the analogous 2,5-bis(4-(methoxycarbonyl)-phenyl)-1,3,4-oxadiazole (DMPO).[14] In DMPO all molecules are parallel oriented to the surface in such a way that the surface is formed as well as by the nitrogen atoms of the heterocyclic rings and the methyl groups of the ester substituents.

Whereas in DMPO the interactions of carbonyl groups are more important for the crystallization process, in DTO the crystal growth step is determined by the interactions between the aromatic rings. This different behavior in the crystallization process will be important for preparation of ordered ultrathin films from different derivatives of 1,3,4-oxadiazoles by vapor deposition processes, self-assembling methods, and Langmuir–Blodgett techniques, respectively.

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