

1 Introduction

The intense research conducted over the last decades concerning the physical properties of films of organic semiconductors has already led to the development of several potential applications, the most promising being organic light emitting diodes (OLEDs), organic solar cells, and organic field effect transistors. A special aspect of the organic molecules of these films is their functionality, making them interesting candidates for future molecular electronic devices. By means of organic chemistry they can be designed to exhibit desired properties like wavelength-selective absorption and fluorescence, especially suitable for optoelectronic applications.

Thin organic films on arbitrary substrates can easily be prepared by different techniques. However, it is a well-known fact that the optical properties of such films strongly depend on their morphology. Not only is there a difference between highly ordered and polycrystalline or amorphous films, but also a slight variation of the lattice parameters of crystalline films may lead to significantly altered optical properties. Additionally, exciton theories predict a strong dependence of the optical properties of organic films on the film thickness, especially for ultrathin films on the order of a few monolayers. This theoretical situation is in practise most closely matched by highly ordered organic films due to the well-defined locations of the single molecules within the films. Thus, film structure and film thickness are one of the most important parameters by which the optical properties of films of organic molecules can be controlled.

In this work, we investigate the optical properties of ultrathin films of organic semiconductors, grown by Organic Molecular Beam Deposition (OMBD), on a variety of different substrates. The main focus of the study is to relate the measured optical properties to exciton confinement (thickness dependent) effects and structural aspects of the films. For that, organic films of different thicknesses are prepared on different substrates and are optically characterized *in situ*. Another issue to be clarified is how the optical properties of the organic films are affected by conducting substrates. This should be of major interest for future molecular electronic devices, since electrical contacts between the nanoscopic and macroscopic world have to be established. Finally, the influence of slightly different crystal modifications of the organic films on their optical properties are to be addressed.

We will show that the optical properties of organic films do indeed strongly depend on the film thickness, as predicted by exciton theories. Based on the choice of the substrate, different film morphologies are induced, leading to strongly different optical spectra in the course of film growth. Furthermore, the optical properties of the first layer are most significantly affected by interactions of the molecules with conducting substrates. In some cases, these interactions are not restricted to the first layer but extend into the next layers as well. We also observe partially charged molecular films, exhibiting a largely different optical spectrum as compared to neutral films.

Chapter 2 gives an overview of existing literature, addressing theoretical aspects of exciton theories as well as experimental findings, concerning the influence of several parameters on the optical properties of organic films. The measurement technique used in this work is

introduced in Chapter 3. Since we deal with optical properties of thin films, a detailed discussion of the basic principles of thin film optics is given in Chapter 4 with special focus on ultrathin films and island films. We will present several examples which demonstrate the influence of a polarizable substrate and island growth on the optical properties of thin films. In Chapter 5, a method is proposed which enables one to determine the optical constants of a thin film, i.e. index of refraction and absorption index, from just one spectral measurement. The development of such a method is necessary since the measurement technique used only provides one spectral measurement for each film thickness. We apply this method to experimentally measured optical spectra of organic thin films in Chapter 6. A detailed discussion concerning the influence of parameters like film thickness, morphology and nature of the substrate on the absorption behavior of the organic thin films is given. This work is concluded in Chapter 7 by a summary of the results.

2 Review of Literature

2.1 The organic semiconductors PTCDA and HBC

Nowadays, there exists an almost unlimited number of organic compounds which can be used as building blocks in molecular crystals and thin films. Especially interesting are perylene derivatives, since they exhibit high spectral selective absorption and semiconducting properties along with sufficient thermal stabilities, which makes them excellent candidates for designing molecular electronic devices.

For this work, two organic semiconductors have been chosen: the archetype molecular semiconductor PTCDA (3,4:9,10-perylene-tetracarboxylic dianhydride) and HBC (perihexabenzocoronene). Both molecules belong to the class of planar molecules and are known to readily form highly ordered films on a variety of substrates [1]. Their chemical structures are shown in Fig. 2.1.

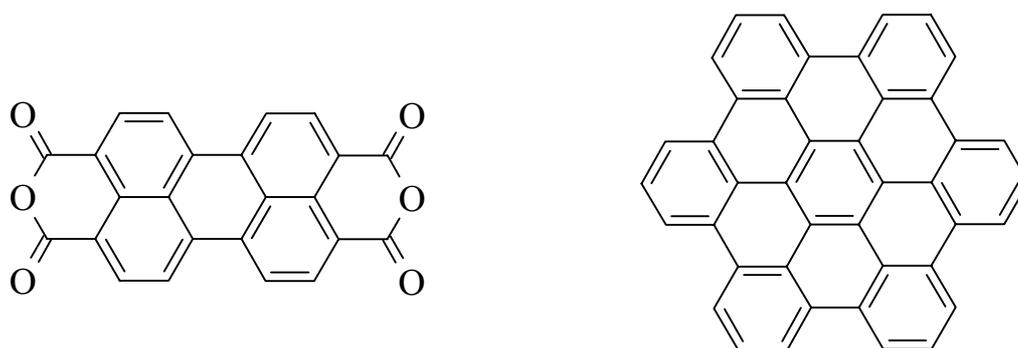


Fig. 2.1: Chemical structure of the investigated molecules PTCDA (left) and HBC (right).

2.2 Properties of an isolated single molecule

The lowest optically excited state of an isolated molecule is basically governed by the extended conjugated π -electron system and its vibronic coupling to the carbon backbone. The absorption spectra of PTCDA, dissolved in DMSO (dimethyl-sulfoxide) [2], and HBC, dissolved in trichlorobenzene [3] are shown in Fig. 2.2.

The two spectra look rather different. For PTCDA, the absorption spectrum is dominated by the S_0 - S_1 transition and its vibronic replicas. This rather simple structure stems from the fact that the lowest lying excited state couples only to one effective vibrational mode.

A theoretical model for the coupling of the lowest excited state to one effective vibrational mode was proposed by Hennessy et al. [4,5]. They found a vibrational spacing of $\hbar\omega = 0.18$ eV and a coupling constant $g = 0.82$. Their calculations are based on the Franck-Condon principle [6], which basically attributes the observed vibronic progression to different geometries of the molecule in the ground state and excited state. After excitation, the nuclei

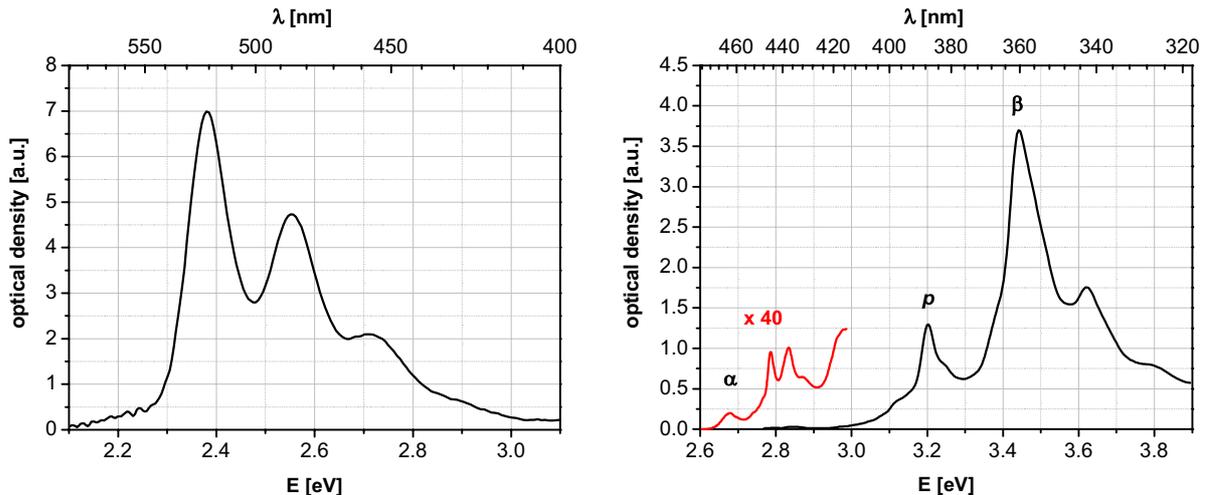


Fig. 2.2: Absorption spectra of PTCDA dissolved in DMSO [2] (left panel) and HBC dissolved in trichlorobenzene [3] (right panel). The weak α -transition (enhanced by a factor of 40) is dipole forbidden by symmetry considerations, but weakly allowed in trichlorobenzene.

will relax into a geometrical arrangement which will not necessarily be the same as it was in the ground state. One now assumes that the vibronic part of the wavefunction only depends on one effective coordinate q , which describes the displacement of the nuclei from their ground state equilibrium position. If these displacements are small, the approximation of a one-dimensional harmonic oscillator with potential $V(q)$ becomes appropriate. The excitation from the ground state into the eigenvalue states of the excited molecule is described by the Franck-Condon factors F_v , where v labels the vibronic levels of the harmonic oscillator. These factors are a measure for the oscillator strength of the corresponding excitations and are responsible for the observed vibronic structure in the absorption spectrum of an isolated molecule. However, if there is more than one vibrational mode with significant phonon-exciton coupling, the picture becomes more complicated. A more detailed description of the Franck-Condon principle can be found in e.g. [6].

The absorption spectrum of single HBC molecules does not have such a simple structure like it is the case for PTCDA. Three distinct absorption bands are observed [7], labeled as α -, p - and β -band. The α -band is a very weak spectral feature and corresponds to the dipole forbidden 0-0 transition of the lowest state due to the six-fold symmetry of the HBC molecule. The specific labeling is motivated by empirical findings [8] as well as quantum mechanical calculations [9] and is characteristic for any polycyclic aromatic hydrocarbon (PAH) [7]. The observation of the three bands can be explained by looking at the two highest occupied and lowest unoccupied molecular orbitals of a PAH, schematically drawn in Fig. 2.3. It can be shown [7] that the differences between orbitals $E_m^{MO} - E_{m+2}^{MO}$ and $E_{m-1}^{MO} - E_{m+1}^{MO}$ are identical. This leads to the energy diagram of Fig. 2.3 (b) in which the two energetically highest states are degenerate. Configuration interaction now causes the degeneracy to be lifted and produces two well separated transitions, labeled α and β . Depending on the strength of the interaction, the α -transition can lie below or above the so called para- or simply p -state. The β -transition always lies at higher energies as compared to the α - and p -transition and carries the highest oscillator strength, followed by the p - and α -transition, respectively. It has also been found empirically [10] that a simple relationship between the energetic positions of

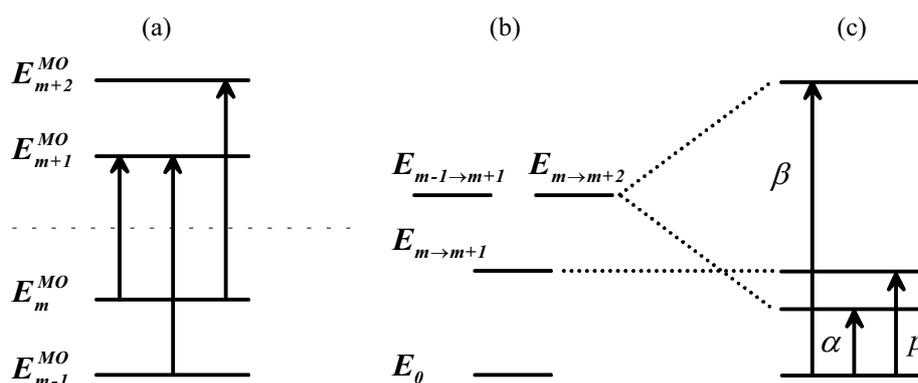


Fig. 2.3: Molecular orbitals (a), configuration energies (b) and transition energies (c) for a typical polycyclic aromatic hydrocarbon. For detailed explanation, see text.

α - and β -band exists: $E_\beta / E_\alpha \approx 1.35$. In practice, this value varies from 1.25 to 1.45; for HBC it corresponds to 1.27.

Although this simple model can qualitatively account for the observed electronic transitions, it does not take care of the vibronic modes of the molecule. These have to be added into the description of the absorption spectrum and lead to additional finestructure, as can be seen in Fig. 2.2. Especially the vibronic replicas of the symmetry forbidden 0-0 transition of the lowest lying state are weakly dipole allowed [11,12].

To obtain the electronic structure of a single molecule *theoretically* one has to apply quantum chemical calculations, which search for electronic molecular wavefunctions for a certain fixed geometry of the nuclear skeleton. The general outline of this method is to find a ground state wavefunction by variational principles, where the set of basis functions is a linear combination of atomic orbitals of the single atoms of the molecule. Simply spoken, one takes the wavefunctions of the single atomic orbitals, includes Coulomb interaction and overlap integrals for charge-transfer between any orbitals in the total Hamiltonian and minimizes the energy of the system. The details are much more complicated (see e.g. [13] and references therein) and can be solved only numerically by computer programs using methods like PPP (Pariser-Parr-Pople) or ZINDO (Zerner's version of Intermediate Neglect of Differential Overlap). The result of such calculations is a set of spatial molecular orbitals. The highest occupied orbital is called HOMO (highest occupied molecular orbital) and the lowest unoccupied orbital LUMO (lowest unoccupied molecular orbital).

These calculations have been carried out for PTCDA in [2,13]. The situation is remarkably simple: HOMO and LUMO are not degenerate and well separated from other orbitals. Therefore, the excitation of an electron from the HOMO to the LUMO can clearly be assigned to the $S_0 - S_1$ transition of the solution spectrum (see Fig. 2.2)¹.

Similar calculations have been performed for coronene [14,15,16], a molecule closely related to HBC, and show a good agreement between theoretically modeled and experimentally observed absorption spectra, especially concerning the observation of the α -, p - and β -bands as well as the symmetry forbidden 0-0 transition of the α -band (also present in coronene).

¹ This does, however, not mean that the energy of the $S_0 - S_1$ transition is equal to the HOMO - LUMO gap in the ground state. The calculation of the optical transition involves further steps (see [13]).

2.3 Properties of two interacting molecules

2.3.1 Frenkel- and Charge Transfer Excitons

After discussing the orbital energies of HOMO and LUMO of a single molecule, one can now turn to the possible interactions between two molecules in close proximity, also called a (physical) dimer. In general, four electronic excitations are possible, which are schematically drawn in Fig. 2.4. The energetic positions of HOMO and LUMO of the molecules A and B are labeled $H_{A/B}$ and $L_{A/B}$, respectively.

Two excitations are molecular excitations, that means, an electron is promoted from the HOMO of molecule A/B to the LUMO of the same molecule. Such an excitation is called a Frenkel Exciton (FE). It is a small radius exciton, because its generation is localized on one molecule.

There is another possible mechanism of excitation, where one electron is excited from the HOMO of molecule A/B to the LUMO of molecule B/A. In this case, the electron is not localized on a single molecule, but rather delocalized over the complete dimer. This is called a Charge Transfer Exciton (CTE) and has a larger radius than the Frenkel Exciton.

Thus, in addition to the Frenkel excitation in the single molecule, there may now be a second kind of excitation involved, the CTE. How does this influence the electronic structure of the dimer? First of all, several interactions have to be taken into account [17,18]:

- i) Frenkel exciton transfer M , i.e., a transfer of the Frenkel exciton from molecule A/B to molecule B/A,
- ii) charge-transfer ϵ , i.e., the transfer of one electron (ϵ_-) or hole (ϵ_+) from the site of the molecular excitation to the other molecule, and
- iii) coupling to vibronic modes of the molecules.

The physical meaning of the interaction and consequences for the energy levels of the excited singlets are shown in Fig. 2.5.

We start without any interactions ($M = \epsilon_- = \epsilon_+ = 0$), which corresponds to the left part of the figure. It shows the uncoupled Frenkel and Charge-Transfer states of the dimer. By turning on the molecular excitation transfer ($M \neq 0$) but still omitting the charge-transfer ($\epsilon_- = \epsilon_+ = 0$), the degenerate FE-levels split into a dipole allowed $|FE_+\rangle$ and a dipole forbidden $|FE_-\rangle$ state. The magnitude of the splitting is $2M$. As a result, the upper $|FE_+\rangle$ state becomes

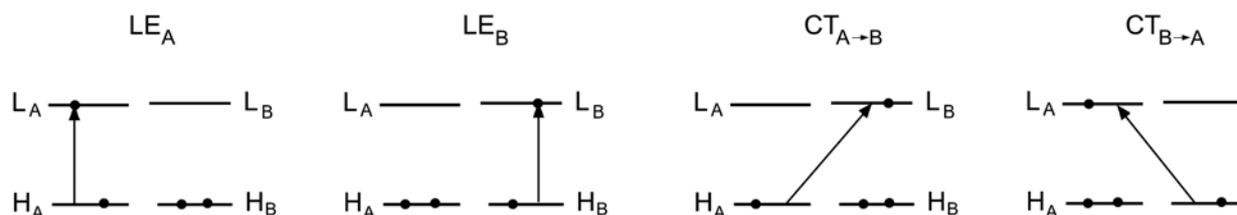


Fig. 2.4: Schematic view of the possible different electronic excitations in a dimer, adapted from [2].

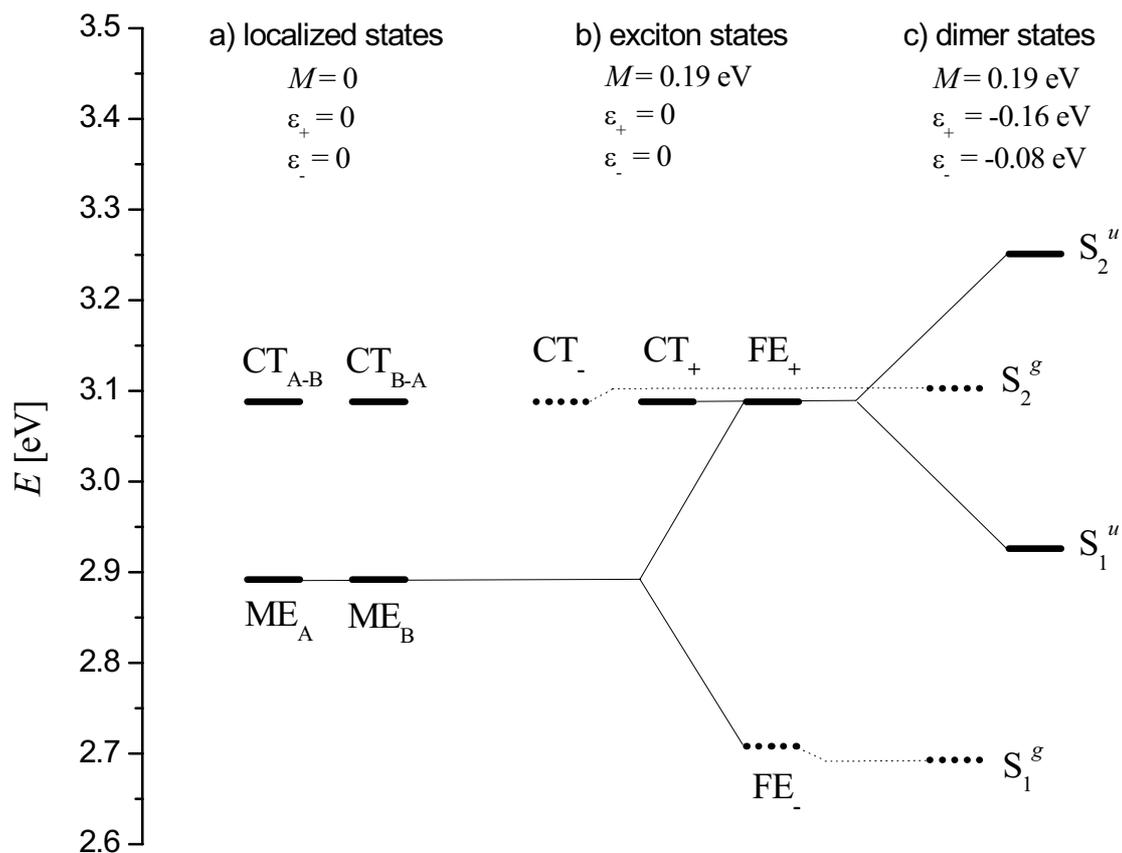


Fig. 2.5: Quantum chemical dimer model with interaction parameters for PTCDA, adapted from [13]. In b) and c), dipole allowed states are denoted by solid lines and dipole forbidden states by dotted lines.

resonant with the CT-levels. If we now also turn on the charge-transfer ($\epsilon \neq \epsilon_+ \neq 0$), the $|CTE_+\rangle$ state and the $|FE_+\rangle$ state can mix and split into two dipole allowed states S_1^u and S_2^u .

Therefore, including the CT-excitation influences the electronic structure in a way that a new dipole allowed state S_2^u is created, which is due to the strong mixing of Charge Transfer and Frenkel Excitons. It has to be noted, however, that mixing of FE- and CT-states can only occur if their corresponding energies are rather close to each other so that strong coupling can take place. If FE- and CT-excitation are energetically well separated, no such mixing should be observed. The resulting dimer spectrum is than a simple splitting into a dipole-allowed and dipole-forbidden state, depending on the relative orientation of the two molecular dipoles [6].

2.3.2 The model dimers AA and AB

From the considerations of the previous section the question arises, whether it is *always* possible to have CTEs in dimers, i.e., an electronic excitation from one molecule to the other, or if there is actually a limiting factor for the appearance of charge-transfer states. It has been shown [2] that there indeed *is* such a limitation, namely the dependence of the CT states on the overlap of the wavefunctions, i.e., the geometrical arrangement of the single molecules in the dimer.

Schmidt [2] investigated the electronic structure of the model dimers AA and AB, which correspond to the geometrical arrangements in the stacking direction of thin films of PTCDA and in the (102) plane, respectively, which will be explained in more detail in Section 2.4. For now, the only important fact is that the intermolecular distance of dimer AA is much smaller than in dimer AB.

The calculations show that the molecular orbitals of the dimer AA are delocalized over the two molecules, whereas for the dimer AB they are localized on one single molecule. This is due to the fact that for larger intermolecular distances like in the dimer AB, the monomer orbitals of the single molecules do not overlap as strong as in the dimer AA.

The consequences for the electronic transitions are rather drastic: for the dimer AA, where the overlap of the monomer orbitals is sufficiently strong, two energetically well separated, dipole allowed states show up, which corresponds to the physical situation described in the previous section. The picture is completely different for the almost vanishing overlap of the monomer orbitals in the dimer AB. Since the molecular orbital of the AB dimer is localized on one molecule, the HOMO and LUMO level of this molecule will slightly shift, so that the FE states of both molecules are not exactly degenerate anymore, and the CT states lie energetically well separated from each other and from the FE states. The result is a small splitting of the FE states but no coupling to the CT states as in the case of the dimer AA. This effectively yields one pure FE transition for the dimer AB, compared to two mixed FE-CT transitions for the dimer AA.

It is now clear that the geometrical arrangement of the molecules in a thin film is of crucial importance for the optical absorption spectrum. Therefore, great care has to be taken to identify the geometrical structure of the film prior to comparing the experimental data to theoretical models like the ones described above.

2.4 Properties of the molecular crystal

Highly ordered growth of thin films of PTCDA and HBC molecules can be achieved by means of organic molecular beam epitaxy (OMBE). For ultrathin layers, the molecular structure strongly depends on the choice of the substrate [1], but for increasing coverage both molecular films should relax into their crystal structure. Crystals of PTCDA molecules are known to form two polymorphs, called α - and β -phase. Since these two phases show strong similarities, only the structure and unit cell of α -PTCDA is shown in Fig. 2.6 along with the lattice parameters in Tab. 2.1. The most remarkable fact is that PTCDA builds parallel (102)-planes with an interplane distance of $d(102) = 0.322$ nm, which is much shorter than the intermolecular distance in the (102)-plane. This indicates that the molecular orbital overlap in stacking direction will be much stronger than in the (102)-plane, resulting into a situation which correspond to the picture of AA- and AB-dimers of the previous section.

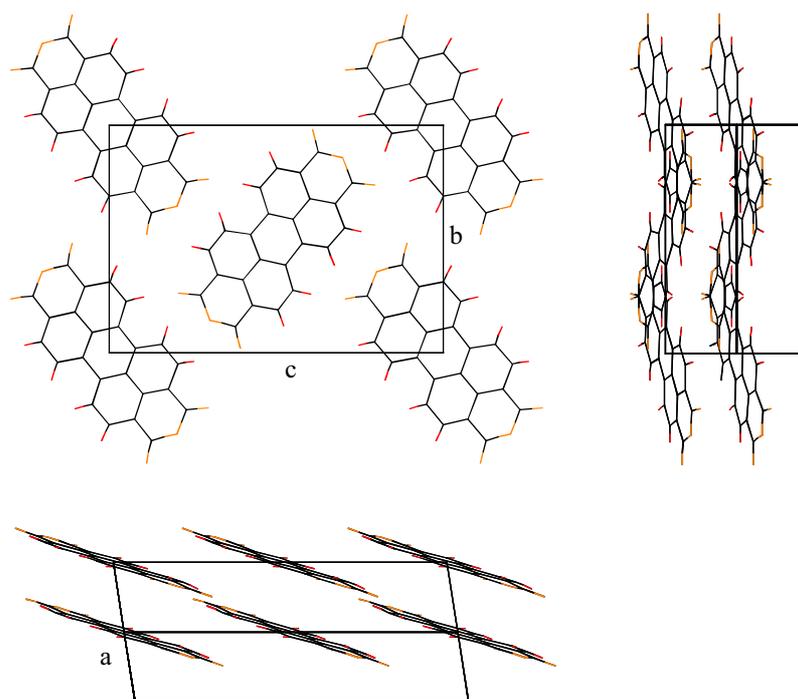


Fig. 2.6: Arrangement of the molecules in α -PTCDA: *bc*-plane (top), *ab*-plane (right), and *ac*-plane (below), adapted from [1].

For HBC only one polymorph is known [1] whose crystal structure does not possess a bulk crystal plane where the molecules are arranged flat like in the case of PTCDA. The crystal structure and unit cell of HBC is shown in Fig. 2.7 along with the crystal data in Tab. 2.2. It is described in literature [19] as a flattened-out herringbone structure in which the main interaction takes place between parallel translated molecules.

However, the crystal structures of both molecules have one aspect in common: the intermolecular distance between adjacent molecules in stacking direction is much smaller than between neighboring molecules in the *bc*-plane (PTCDA) and *ac*-plane (HBC), respectively. It is therefore appropriate to speak of quasi-one-dimensional crystals. For such crystals, several theoretical models exist which will be briefly reviewed now.

The aim of all these theories is to model the optical properties (i.e. the absorption behavior) of molecular crystals or films by means of only a few intrinsic parameters. To the best of our knowledge, basically two models can be found in literature which are able to describe the optical properties of PTCDA-crystals (as a textbook example for quasi-one-dimensional crystals) in two rather different ways.

Hoffmann et al. [13,18,20] consider a one-dimensional, infinite chain of molecules (motivated by the strong molecular overlap in the stacking direction of the crystal) and calculate the electronic structure of that chain. They explicitly use FE *and* CT excitons in a similar way as described in Section 2.3 and also account for vibronic replicas of FE and CT-states as well as the dielectric background of the crystal itself. This is probably the most accurate theory to model the physical situation of molecular crystals within the picture of FE- and CT-excitations. Applied to the absorption spectra of the molecular crystals of PTCDA and MePTCDI (N-N'-dimethylperylene-3,4,9,10-dicarboximide), their theory can quite