Chapter 4

Role of Oxygen in the Electronic Structure of Pentacene

Abstract:

The possible presence of oxygen in pentacene in the form of \( \text{O}_4 \) molecules is investigated. Two stable sites are proposed in pentacene: one in and another in between the layers. This way the influence of oxygen on the conductivity is interpreted. We employed \textit{ab initio} electronic structure calculations based on density functional theory (DFT) to verify our model and reveal the mechanism of hole-doping by oxygen in \textit{light} and \textit{dark} conditions. From our calculations we derive that \( \text{O}_4 \) in between the layers introduces \textit{one hole} in \textit{light}. The \( \text{O}_4 \) in the layer introduces \textit{one hole}, regardless whether in \textit{light} or \textit{dark}, provided injected holes have enough kinetic energy to induce an excitation analogous to the principles of electron energy loss spectroscopy (EELS). We make contact with experimental work and propose new experiments to test the hypothesis and add to the understanding of the influence of the atmosphere on the performance of organic devices. *

*This chapter is based on I. Shokaryev, R. W. A. Havenith, G. A. de Wijs, A. H. Arkenbout, T. T. M. Palstra, R. A. de Groot to be Submitted
4.1. Introduction

Molecular oxygen, O$_2$, is the most stable and common form of oxygen in a wide range of temperature and pressure. Oxygen diffuses into many materials, leading to interesting phenomena. It has already been known for quite some time that oxygen can influence the electrical conductivity. The results of the earlier measurements on photoconductivity of solid anthracene [1,2] are represented in Fig.4.1. It shows clear amplification of the photocurrent originating from the presence of oxygen, diffused in the material. As the possible explanation the photo-oxidation (formation of peroxide) was put forward [2,3]. However, it must be taken into account that diffusion is completely reversible, implying physisorption rather than chemisorption of oxygen.

Oxygen affects the transport properties in organic semiconductors, the key materials for plastic electronics [4]. This fact raised the further interest in the studying of this phenomena particularly in the organic materials used for making small organic devices. Several groups reported that the hole current, both under illumination and also in the dark, depends on the amount of atmospheric oxygen diffused into organic material [3,5–10]. Oxygen acts in a way that it introduces additional mobile holes ($p$-type doping), leading to an increase in the total hole current. This is an important issue since electronic devices are operating in air. Therefore the use of organic devices as gas sensors has been considered [11–13].

The effect of oxygen is likely to be universal for a wide variety of organic materials: pentacene [7,10], rubrene [9], carbon nanotubes [14], phthalocyanine [15]. The origin of this effect is not understood. So far there were only few theoretical papers on this subject [16–18] proposing different models. However, these works, as will be discussed, have some difficulties with explaining these phenomena. The reversibility of oxygen diffusion into organic materials concludes that the mechanism of $p$-type doping is very unusual. It differs from the mechanism of $p$ and $n$-type doping in inorganic semiconductors.

4.2. Experimental Evidence on Pentacene

Our interest in oxygen in pentacene was aroused by the results of Jurchescu et. al. [3,7]. The key experimental findings are shown in Fig.4.2 which was adapted from reference [7]. The influence of ambient air, containing some amount of water, is to decrease the conductivity since the water molecule has a dipole moment which interacts strongly with injected holes and play a role of a scattering center. Dry air enhances the space charged limited (hole) current (SCLC) in dark. In light the effect is stronger (the effect doubles). The value of the hole current at a given value of electric...
4.2 Experimental Evidence on Pentacene

Figure 4.1: (a) Curve-1 (solid) corresponds to exposure of solid antracene to oxygen and curve-2 (dashed) corresponds to vacuum measurements of photocurrent in solid antracene. (Excerpted and translated from ref. [1]). (b) The transfer properties of pentacene FET. (Excerpted from ref. [6])
field strength $E$ is written as:

$$J_p(t) = e\mu_p p(t)E$$  \hspace{1cm} (4.1)$$

where $e$ is the elementary charge, $\mu_p$ is the mobility and $p(t)$ is hole density in the conductive channel. The increase in the current, as it was discussed previously, is solely due to oxygen. The increase in the hole current can be associated with the increase in the concentration of charge carriers $p(t)$ in the active channel between the contacts. Based on these observations it is possible to correlate quantitatively the increase in the total hole current $J_p(t)$ (Fig.4.2) with the amount of absorbed air (see the inset of the Fig.4.2) which contains about 21% of oxygen at normal conditions. The diffusion of air is completely reversible, suggesting that no irreversible chemical reaction between oxygen and pentacene can occur.

The main conclusion of the experimental studies [3, 7] can be summarized as following:

- Oxygen diffuses reversibly in pentacene.
- Four oxygen molecules introduce one hole in dark and two oxygen molecules introduce one hole in light only.

\[
\begin{align*}
4O_2^{\text{dark}} & \rightarrow e^+ + 2O_2^{\text{h}} \\
2O_2^{\text{h}} & \rightarrow e^+ + h\nu
\end{align*}
\]

- The efficiency of introducing holes by oxygen is independent of time.
- The microscopic details of air diffusion (sites of oxygen) are not known.
- The concentration of oxygen in pentacene is very low (approx. 1 oxygen per 50 unit cells) which is a major problem for various kind of experiments.
- The linear regime (below the SCLC) is unaffected by oxygen in the dark.

These remarkable experimental results suggest an unconventional explanation. In order to clarify and obtain a coherent physical picture of $p$-doping triggered by oxygen we involved \textit{ab initio} DFT calculations.

### 4.3. Interpretation of the Experiment

Our interpretation is based on the hypothesis that oxygen in pentacene has the form of weakly coupled dimers $(O_2)_2$, denoted as $O_4$. Based on this hypothesis we reformulate the experimental results as following: one $O_4$ molecule introduces one hole in dark and another $O_4$ molecule introduces one hole in light only. In other words one $O_4$, which occupies a site in the layer, introduces one
Figure 4.2: Taken from Jurchescu et. al. [7]. The bunch of I-E curves corresponds to different exposure times shown in the inset. In the inset is shown the time evolution of the fractional molar loading of air in pentacene. Upon the exposure to ambient air (containing some percentage of H$_2$O) the current was decreasing with respect to the vacuum value. Upon exposure to the dry air the current was increasing with respect to the vacuum value and moreover in daylight the effect was doubled. The schematic device geometry (two-point measurements) is also shown. The crystal plate size is about $3 \times 3$ mm. The linear-regime ($J \propto E$) and SCLC-regime ($J \propto E^2$) are separated by $\sim 30$ V.

hole regardless of illumination and another one, which resides in between the layers of pentacene, introduces one hole under exposure to light.

$$2O_4^{\text{dark}} \rightarrow e^+$$
$$2O_4^{hv} \rightarrow 2e^+$$

Our key idea about oxygen in the form of O$_4$ is based on entropy. In the gas phase it is favorable to have two isolated oxygen molecules rather than O$_3$ since the entropy increases with the number of particles. The situation changes in the solid. This is mainly due to the fact that there is no significant
gain in entropy from the dissociation of O$_4$ into two O$_2$ in pentacene, contrary to in air. This can be understood on the basis of the simplest formula for the entropy $S = k_B \ln \Gamma$, where $\Gamma$ is the number of all possible configurations. The concentration of oxygen in air and in the crystal of pentacene are the same but the number of possible configurations $\Gamma$ is significantly different, because only a limited number of sites for O$_2$ in the pentacene host are allowed ($\Gamma_{\text{gass}} \gg \Gamma_{\text{solid}}$). Therefore the formation of a significant amount of O$_4$ is not contradicting this physical picture. It should be also understood that the diffusion process of O$_2$ in the bulk of pentacene is solely via the (001) surface, which has the lowest energy [19]. Since the microscopic details of air diffusion are not known, we do allow oxygen in the form of O$_4$ in the search for stable sites.

An interesting aspect is the O$_4$ complex itself. In 1906 the existence of O$_4$ was postulated [20] and named by Harries as oxozon [21]. Since that time the existence of isolated O$_4$ was under debate [22]. It was first emphasized by Lewis [23] that two O$_2$ molecules can form an antiferromagnetically coupled molecule O$_4$ - the so called tetraoxygen. The existence of a metastable O$_4$ was confirmed in series of neutralization–reionization mass spectroscopy (NRMS) experiments by Cacace [24, 25]. The solid oxygen [26, 27] formed at high pressures is likely to consist of an O$_4$ molecular lattice. An interesting ab initio electronic structure calculation result showed the possibility of O$_4$ formation on the surface of rutile TiO$_2$(110) [28]. This has recently been confirmed experimentally [29]. The geometry and ground state properties of O$_4$ are not easy to determine experimentally. This gives a significant challenge for ab initio quantum chemical calculations [30–41].

The qualitative model of O$_4$ influence on the electronic structure of pentacene (see Fig. 4.3) needs a quantitative support. We employed ab initio DFT electronic structure calculations as an efficient and accurate approach, successfully applied to similar systems, [16,19] to verify the model.

### 4.4. Why O$_4$?

The first explanation for the effect of oxygen on pentacene single crystals was the formation of an oxygen adduct, bridging the middle ring of pentacene [3], the so called pentacene-endoperoxide [43] (C$_{22}$H$_{14}$O$_2$). From our calculations we found the ground state and geometry of the endoperoxide molecule by placing O$_2$ on top of the central ring (which is the most reactive site) of the pentacene molecule. The optimized structure of endoperoxide is shown in Fig. 4.4. We calculated the binding energy to be 1.58 eV (LDA) and 0.71 eV (GGA) with respect to oxygen-pentacene dissociation. About the same picture is valid for the pentacene crystal. O$_2$ was placed on top of the central ring of pentacene in the super cell (2a×2b×c). The optimized geometry shown in Fig. 4.5 implies dissociation of the O$_2$ and a total energy consideration (LDA) showed binding by 1.65 eV while GGA results 0.15 eV only. A similar conclusion was obtained by Tsetseris et.al. [16] who showed...
4.4 Why $O_2$?

![Figure 4.3: Schematic representation of the key-idea explaining the experimental results. We allow two stable sites for $O_2$ in and in between the layers of pentacene. The one in the layer is excited by incident hole current beyond some critical value of kinetic energy of incident holes, determined by $V_c$ and termed as SCLC-regime (Fig.4.1). Another $O_2$ (between the layers) gets excited only in light since the hole current is mainly in the layer and not in between.](image)

that it is energetically favorable for oxygen to dissociate and form the oxygen bridge in the pentacene layer. However oxygen dissociation contradicts the reversibility of oxygen loading in pentacene [7].

It should also be taken into account that DFT underestimates the barrier of a chemical reaction: molecular oxygen is in a triplet state while defect states such as shown in Fig. 4.5 are singlet states. The kinked shape of the pentacene-endoperoxide molecule suggests that the conjugation of the $\pi$-system is broken as the molecule is no longer planar, leading to a structural defect that in turn would certainly lead to a decrease in conductivity. Preliminary Raman studies of pentacene with oxygen found no evidence of the endoperoxide formation [3] i.e. the O–O vibration mode (800 cm$^{-1}$) was absent. The chemical bond formation between oxygen and pentacene would lead to a shift of Fermi energy which has not been observed in ultraviolet photoelectron spectroscopy (UPS) studies of pentacene exposed by oxygen [44]. All discussed above shows that attempts to explain the effect in terms of $O_2$ suffer from incompatibility with experimental findings. The idea of $O_2$ is based on the entropy argument as discussed in the introduction. The quantitative support for this follows from studying an isolated pentacene molecule constrained to be flat and a single oxygen molecule landed on top of the middle site of pentacene. It follows from the total energy calculations that oxygen cannot come closer than $\sim$3 Å to the pentacene plane, which on the scale of the unit cell of bulk
Figure 4.4: Pentacene-endoperoxide molecule (optimized geometry) with its Lewis structure. The kink angle is about 123.4°. The interatomic distance between the oxygens is 1.5 Å.

Figure 4.5: (a) Optimized geometry of the bulk pentacene with a single O₂ on top of central ring. The interatomic distance between the oxygen atoms in this geometry is about 3 Å indicating that the oxygen molecule tends to dissociate. This is a stable defect. (b)

pentacene, excludes many sites. It was discussed in detail in Chapter 3 of this thesis.

The O₄ is significantly different from O₂ by its magnetic structure. This means that considering O₄ rather than O₂ opens a new avenue for various calculations and conclusions.

4.5. Ground State of O₄-(tetraoxygen)

From the early experimental work of Lewis [23] it was implicitly clear that the ground state of oxygen at zero temperature is not O₂, as it is at ambient conditions, but O₄. Pauling stated that for the particular case of the O₄ molecule the dominant van der Waals interaction might be strong enough to think of it as a bond formation [45]. This initiated extensive studies of O₄ via various \textit{ab initio} quantum chemical approaches [30–41].

There are three types of geometries and corresponding point group symmetries known from previous studies of O₄ molecules: planar rectangular (D₂h) [32–34], cyclic (D₂d) [35–39] and pinwheel
4.5 Ground State of O₄-(tetraoxygen)

Table 4.1: Cohesion (insertion) energies for various oxygen defects. The results of this work have been compared with analogous calculations [16] which semi-empirically includes the van der Waals interactions. The values given in the table are for the singlet state. The triplet state is marginally (∼0.1 eV) lower than the singlet for Fig. 4.5 (a,b).

<table>
<thead>
<tr>
<th></th>
<th>Fig 4.5 (a)</th>
<th>Fig 4.5 (b)</th>
<th>Fig 4.7 (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{LDA}}$ (eV) This work</td>
<td>1.65</td>
<td>0.31</td>
<td>0.16</td>
</tr>
<tr>
<td>$E_{\text{LDA}+\text{vdW}}$ (eV) Ref. [16]</td>
<td>1.78</td>
<td>0.55</td>
<td>0.13</td>
</tr>
</tbody>
</table>

(D₃h) [40, 41] structures. We found the D₂d and D₃h geometries to be metastable and the D₂h, stable with respect to dissociation into two O₂ molecules. The energy of O₄ with respect to two single O₂ molecules varies from one calculation to another depending on the basis set and the method used in the calculations [38, 39]. The main difficulty is coming from the dispersive nature of interactions and the open shell structure of the oxygen molecules [39]. We calculated dissociation energies for the three geometries. They differ from the more accurate results of other publications but the main conclusions and trends remain the same. This result is quite remarkable since in our calculations the van der Waals (vdW) corrections to the total potential were not taken into account as it is the case for some work [16, 47, 48]. However it must be stressed that this is not a rigorous first principles treating of vdW interactions which needs a more elaborate description [49].

The results for optimized geometries and energies of dissociation ($O_4 \rightarrow O_2(3\Sigma^-) + O_2(3\Sigma^-)$) are shown in Fig. 4.6. The energy of dissociation $\Delta E_{\text{diss}}$ was corrected for zero point vibrational energy ($ZPVE$)-correction eq. (4.2). The result for (D₂h) is closer to the result given by Lewis [23] (5.55 meV) than to the recent and more accurate quantum chemical calculation [33] which gives about 17 meV. Neglecting $ZPVE$-correction leads to an overestimation of the dissociation energy by an order of magnitude.

$$\Delta E_{\text{diss}} = (E_{O_4} + E_{ZPVE}^{O_4}) - 2(E_{O_2} + E_{ZPVE}^{O_2})$$ (4.2)

The reason to do these calculations is to show that DFT is capable in this case to describe satisfactorily the antiferromagnetic part of interaction between two O₂ molecules. This conclusion is essential for the description of O₄ molecules in the bulk of pentacene. The DFT approach has shown reasonable results for solid oxygen in form of O₄ [46].

It is very important to know the molecular geometry of O₄. Experiment on gaseous oxygen [53], presumably containing O₄ in D₂d symmetry gave frequencies consistent with calculated ones for the same structure. Moreover, a Raman experiment on solid oxygen [53] gave frequencies that agreed with those calculated for the D₂h structure. We calculated Raman and infrared (IR) frequencies for all three symmetries of O₄ molecules (Tables 4.2, 4.3, 4.4) and found them in very good agreement with experimental values as well as previous theoretical calculations. The vibrational spectrum of
tetraoxygen would be interesting to compare with the Raman spectrum of pentacene loaded with oxygen. The appearance of similar modes would be an argument supporting our idea about $O_4$ in pentacene. We also calculated vibrational frequencies for $O_4$ with point symmetry $D_{3h}$. Some of the calculated frequencies are quite distinct from the frequencies calculated for the separate pentacene molecule [50]. Therefore the appearance of clear intensities at calculated frequencies in the Raman spectrum of pentacene with oxygen could be a signal from $O_4$ species. The calculated Raman fundamental frequency of a single oxygen molecule is 1555 cm$^{-1}$ which is very close to the $A_{1g}$ mode of $O_4$ (Table 1) and the experimental value of 1556 cm$^{-1}$ [51]. Since oxygen does not react chemically with pentacene at ambient conditions, its Raman spectrum in the pentacene host should not differ very much from that of the isolated oxygen molecule. The ground state of $O_4$ is in a singlet state (antiferromagnetically coupled oxygen species), therefore it can be distinguished from $O_2$ which is in a triplet state. This could be verified by electron-spin resonance (ESR) measurements on pentacene loaded with oxygen. ESR measurements have been successfully applied to pentacene in order to reveal the spacial distribution of injected charge carriers [54].

![Figure 4.6: Energies (GGA) of different geometries of tetraoxygen with respect to the two isolated ground state ($^3\Sigma_g^-$) oxygen molecules. The corresponding point group symmetry labels and calculated bond lengths of relaxed structures are given. The energy of rectangular $O_4$ calculated with LDA is 0.29 eV per $O_2$.](image)

or IR spectra of pentacene with oxygen could be a signal from $O_4$ species. The calculated Raman fundamental frequency of a single oxygen molecule is 1555 cm$^{-1}$ which is very close to the $A_{1g}$ mode of $O_4$ (Table 1) and the experimental value of 1556 cm$^{-1}$ [51]. Since oxygen does not react chemically with pentacene at ambient conditions, its Raman spectrum in the pentacene host should not differ very much from that of the isolated oxygen molecule. The ground state of $O_4$ is in a singlet state (antiferromagnetically coupled oxygen species), therefore it can be distinguished from $O_2$ which is in a triplet state. This could be verified by electron-spin resonance (ESR) measurements on pentacene loaded with oxygen. ESR measurements have been successfully applied to pentacene in order to reveal the spacial distribution of injected charge carriers [54].
### Table 4.2: Calculated frequencies for the rectangular structure (D$_{2h}$) of tetraoxygen.

<table>
<thead>
<tr>
<th>Mode</th>
<th>This work (cm$^{-1}$)</th>
<th>Ref. [52] (cm$^{-1}$)</th>
<th>Ref. [52] exp. (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}(R)$</td>
<td>1552 1634 1600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{1g}(R)$</td>
<td>192 – 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{1u}(\sim)$</td>
<td>306 –</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{1g}(R)$</td>
<td>559 – 400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{2u}(IR)$</td>
<td>226 204 –</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{3u}(IR)$</td>
<td>1442 1465 1500</td>
<td></td>
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</tbody>
</table>

### Table 4.3: Calculated frequencies for the quasi square structure (D$_{2d}$) of tetraoxygen.

<table>
<thead>
<tr>
<th>Mode</th>
<th>This work (cm$^{-1}$)</th>
<th>Ref. [53] (cm$^{-1}$)</th>
<th>Ref. [53] exp. (cm$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>$A_{1}(R)$</td>
<td>965 877 –</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{1}(R)$</td>
<td>415 396 411–419</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{1}(R)$</td>
<td>795 783 –</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{2}(R)$</td>
<td>792 793 –</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E(R)$</td>
<td>708 678 –</td>
<td></td>
<td></td>
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</table>

### Table 4.4: Calculated frequencies for the D$_{3h}$ structure (pinwheel) of tetraoxygen.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Freq. (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>$E'(IR,R)$</td>
<td>1018</td>
</tr>
<tr>
<td>$A_{1}(R)$</td>
<td>867</td>
</tr>
<tr>
<td>$A_{2}(\sim)$</td>
<td>627</td>
</tr>
<tr>
<td>$E'(IR,R)$</td>
<td>574</td>
</tr>
</tbody>
</table>
4.6. Results for the Bulk

A series of DFT calculations for bulk pentacene was performed for the search of the stable sites of oxygen and tetraoxygen. We disagree with the oxygen p-doping mechanism proposed by Lu et. al. [17]. Their model allows high concentration of oxygen (one oxygen per polythiophene unit), implying the existence of an oxygen band just above the valence band. Typical concentration of oxygen in pentacene at atmospheric pressure is about 1 molecule per 50 unit cells, which is considerably lower than in the proposed model.

The cohesion energy is the gain in energy by bringing isolated pentacenes to form a crystal. It is expressed in a simple formula, eq. (4.3), for the cohesion energy per one molecule of pentacene

\[ E_{coh} = -\frac{(E_{cryst} - 2E_{mol})}{2}, \]  

(4.3)

where \( E_{cryst} \) is ground state total energy per unit cell of bulk pentacene and \( E_{mol} \) is the total energy of a single isolated pentacene. The calculated \( E_{coh} \) with LDA results in \( E_{coh}^{LDA} = 1.32 \) eV which agrees with previously calculated value 1.3 eV [19]. It was somewhat unexpected to find that GGA results in no bonding at all. The cohesion energy calculated with GGA showed that \( E_{coh}^{GGA} \) is 0.18 eV above the energy of isolated pentacene molecules. This result points that the overbinding in LDA is offset by the absence of van der Waals interactions.

Bulk pentacene with oxygen was simulated in a supercell which was doubled in \( a \) and \( b \) lattice parameters, to ensure that the oxygen species in the neighboring cells do not interact. We consider \( O_2 \) and \( O_4 \) sites both in the layers and in between the layers. Since the rectangular structure of \( O_4 \) (D\(_{2h}\)) has the lowest energy compared to other geometries of \( O_4 \), we focus on this particular form of \( O_4 \) inserted in pentacene. The stable positions of the oxygen species were determined by optimizing the positions of all atoms in the unit cell while the unit cell parameters were kept fixed. For these stable sites we calculated the insertion energies. The insertion energy shows the gain in energy by bringing isolated oxygen from the vacuum to the bulk. It is given by eq. (4.4) for \( O_2 \) and by eq. (4.5) for \( O_4 \).

\[ E_i = -\left[ E_{Pn+O_2} - (E_{Pn} + E_{O_2}) \right] \] \hspace{1cm} (4.4)

\[ E_i = -\left[ E_{Pn+O_4} - (E_{Pn} + 2E_{O_2}) \right]/2 \] \hspace{1cm} (4.5)

where \( E_{Pn} \) is the total energy of the supercell of pentacene, \( E_{Pn+O_2} \) and \( E_{Pn+O_4} \) are the total energies of the supercell with \( O_2 \) and \( O_4 \) sites occupied and \( E_{O_2} \) is the total energy of a single isolated \( O_2 \). The calculated insertion energies for \( O_2 \) and \( O_4 \) in the layer and between the layers of pentacene are shown in Table 4.5. A (meta) stable oxygen site is identified between the layers of pentacene, which is in a triplet state. This is 0.46 eV lower than the singlet state. Energy is gained if two triplet \( O_2 \) between the layers unite into \( O_4 \).
4.6 Results for the Bulk

<table>
<thead>
<tr>
<th></th>
<th>Inter-layer</th>
<th>Intra-layer</th>
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<tbody>
<tr>
<td>$E_{\text{coth}}^{\text{LDA}}$ (eV)</td>
<td>0.16</td>
<td>0.26</td>
</tr>
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Table 4.5: Insertion energies (LDA) per oxygen ($O_2$) for two different sites between the layers (Inter-layer) and in the layer (Intra-layer). The insertion energy of $O_2$ in the layer is negative (omitted from the table).

A single $O_2$ in the layer is not stable while $O_4$ is. It is not easy to say what is the cause for this binding but the LDA binding energy per $O_2$ for the isolated rectangular $O_4$ was calculated to be 0.29 eV (see the caption of Fig.4.6) which can be compared to the results for $O_4$ in Table 4. This means that $O_4$ in the layer has an energy lower than that for isolated $O_4$ implying that $O_4$ has also some binding with pentacene, while for $O_4$ between the layers the binding is solely between the oxygens.

Although the site of $O_4$ in the layer has a lower energy as compared to $O_4$ in between the layers, this does not necessarily imply that the second site is not occupied, since this is kinetically easier to realize.

The equilibrium positions are shown in Fig. 4.7 (a,b,c). For these structures we calculated the density of states (DOS) as shown in Fig. 4.9 (a,b,c). The first immediate observation is that the calculated ground state of pentacene with $O_2$ is magnetic in contrast with both pentacene with $O_4$ at the intra-layer as well as at the inter-layer position. First we will consider in detail the inter-layer position of $O_2$ and $O_4$. The densities of states show that $O_2$ and $O_4$ introduce states in the gap Fig. 4.9 (a,b). Qualitatively the same result was obtained by Tsetseris [16] for another site of oxygen, namely for the oxygen bridge defect in the layer. In order to obtain one hole one needs light to excite the electron from the valence band (pentacene) to the LUMO (oxygen state in the bandgap), as can be concluded from the DOS. Due to the well known limitation of DFT to predict the bandgap energy, it is not possible to determine accurate values of excitation energies.

The much stronger interaction of pentacene with $O_4$ in the layer makes the separation into ‘oxygen’ and ‘pentacene’ states difficult but the excitation towards the localized $O_4$-induced impurity state at 0.37 eV (see Fig. 4.9 (c)) is possible and leaves a mobile hole behind.

Another issue connected to the magnetism, we want to stress, is magnetoresistance in organic materials. The presence of oxygen can greatly influence magnetoresistance. The dissimilarity in spin-up and spin-down DOS in Fig. 4.9 (b) at the edge of valence band which amounts to 17 meV implies an influence on magnetoresistance. Recently magnetoresistance has been found in pentacene [55]. So far there were no experimental studies of this issue with regard to oxygen and we believe it might be very interesting to study it. It is also worth to mention the spin density distribution ($\rho_\uparrow(r) - \rho_\downarrow(r)$) for tetraoxygen sites in pentacene. In Fig. 4.8 it is shown for $O_4$ in the layer.
The spin density is localized at one pair of oxygen in O$_4$ complex and delocalized over the nearest pentacene molecule. The spin density distribution is completely different for O$_4$ between the layers. For O$_4$ between the layers the spin density localizes only at O$_2$-s, like that on O$_4$ in vacuum, and not at pentacene. Hence follows the conclusion that O$_4$ in the layer polarizes pentacene that in turn can influence the magneto-resistance.
4.6 Results for the Bulk

Figure 4.7: Stable sites of $O_2$ and $O_4$ in pentacene. (a) and (b) between the layers, (c) in the layer. The corresponding sets of coordinates for each unit cell can be found in the Supporting Information.

Figure 4.8: Spin density $(\rho_+ (\mathbf{r}) - \rho_- (\mathbf{r}))$ plots for the $O_4$ in the layer (Fig.4.7 (c)). Polarization density satisfies the following constraint $\int (\rho_+ (\mathbf{r}) - \rho_- (\mathbf{r})) d^3 \mathbf{r} = 0$ since the total magnetic moment is zero. (a)-positive (spin-up) and (b)-negative (spin-down). The spin density is delocalized over the pentacene molecule, nearest to $O_4$. 
Figure 4.9: DOS (spin-up and spin-down channels) of pentacene with O$_2$ (a) and O$_4$ (b) between the layers. It is clear that states in the gap are mostly due to oxygen. (c) DOS of pentacene with O$_4$ in the layer. The states in the gap are mostly due to pentacene and not oxygen. At the top of the valence band oxygen hybridizes with pentacene in (c) more than in (a) and (b) which qualitatively agrees with Table 4.5.
4.7 Effect of Illumination

The effect of oxygen on the hole current is dependent on the illumination [7]. Optical excitations are possible from the valence band (HOMO), primarily of pentacene character, to the lowest unoccupied molecular orbital (LUMO), primarily derived from oxygen states as shown in Fig.4.9 (a,b). As already mentioned in the introduction, we assume that particularly O$_4$ between the layers introduces one hole in light. The reason for this assumption is the following. The hole current is mainly in the layer of pentacene and not in between because the interactions between the layers are very weak. Therefore the incident holes cannot excite O$_4$ between the layers in contrast to O$_2$ in the layer (see the next section). Hence the other source and mechanism of excitation, namely by light, should be considered. In order to test this idea we performed calculations of the oscillator strengths of the transitions for the three different stable sites of O$_2$ and O$_4$ in pentacene shown in Fig. 4.7. We approximate the first excited state as a one-electron excitation from the HOMO to the LUMO. The reason for not considering optical excitations from HOMO to LUMO+1 is that the LUMO+1 already is located in the lower edge of the ultraviolet (UV) range (3 eV) [56], whereas the optical excitations were most effective in daylight, corresponding to the HOMO-LUMO transition.

The oscillator strength ($f$) is calculated from

$$f = \frac{2 m_e}{3 \hbar^2} \Delta E | \langle i | e(x,y,z) | f \rangle |^2,$$

where $\Delta E$ is the excitation energy, and $\langle i | e(x,y,z) | f \rangle$ the transition dipole moment between the initial $|i\rangle$ and final $|f\rangle$ states. The initial (ground) state in our approximation is described with a single Slater determinant with different spin-up and spin-down molecular spin-orbitals. Two final (excited) states are constructed from this determinant by consecutive replacement of the HOMO for the LUMO for each spin-channel. The transition dipole moment then becomes $\langle \text{HOMO} | e(x,y,z) | \text{LUMO} \rangle$. We further approximate the transition energy by the HOMO-LUMO energy difference. This approach provides insight in the relative values of the oscillator strengths. We performed the calculation of the transition dipole moments on clusters using the GAMESS-UK package [58]. These molecular clusters of stable tetraoxygen sites with pentacene molecules were constructed from the optimized crystal structure by taking one O$_4$ or O$_2$ and the nearest neighbouring pentacenes as shown in Fig. 4.10. Note that the HOMO-LUMO energy differences were taken from the calculations of DOS (see Fig.4.9). The calculated transition dipole moments and oscillator strengths, obtained using eq.4.6, are summarized in Table 4.6. For technical details, see Appendix B.

From this table we can clearly distinguish the three orders of magnitude difference in the oscillator strengths for O$_4$ in and between the layers. Hence, we can conclude that O$_4$ between the layers has the highest oscillator strength which confirms our initial assumption that O$_4$ between the layers
Table 4.6: Matrix elements (in a.u.) of the electric transition dipole moments in x, y and z orthogonal directions and oscillator strengths, normalized by the highest value for the stable sites of O$_2$ and O$_4$. The x-axis has similar direction to c-crystallographic axis of the unit cell. For each case x, y, z are somewhat different.

<table>
<thead>
<tr>
<th>Matrix elem. (a.u.)</th>
<th>Inter-layer</th>
<th>Intra-layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$_2$</td>
<td>O$_4$</td>
</tr>
<tr>
<td>$\alpha$-channel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_x$</td>
<td>-0.3872</td>
<td>-4.0829</td>
</tr>
<tr>
<td>$d_y$</td>
<td>0.5974</td>
<td>-0.3728</td>
</tr>
<tr>
<td>$d_z$</td>
<td>0.7440</td>
<td>0.5910</td>
</tr>
<tr>
<td>$\beta$-channel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_x$</td>
<td>-0.4662</td>
<td>3.4507</td>
</tr>
<tr>
<td>$d_y$</td>
<td>1.0322</td>
<td>-0.3412</td>
</tr>
<tr>
<td>$d_z$</td>
<td>0.2361</td>
<td>-0.7172</td>
</tr>
<tr>
<td>$f^{\alpha}$</td>
<td>0.0618</td>
<td>1.0000</td>
</tr>
<tr>
<td>$f^{\beta}$</td>
<td>0.1067</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

has the highest probability of optical transition, generating the hole. Another important observation is that the value of the transition dipole moment is the highest for one particular direction only, showing a strong anisotropy. Following Table 4.6 the value of $d_x$ (approx. in c-crystallographic direction) for O$_4$ between the layers is an order of magnitude larger than for the other directions. This means that light, polarized along $d_x$, most efficiently induces the optical transition. This provides a reference for spectroscopic measurements for the direction of incident light and its polarization in order to induce an optical transition.
Figure 4.10: Clusters for transition dipole moment calculations: $O_2$, $O_4$ (a,b) between the layers and (c) in the layer of pentacene viewed perpendicularly to $ab$-plane. View along the $ab$-plane is shown in Fig. 4.7(a,b,c). The corresponding sets of coordinates for each cluster can be found in Supporting Information.

4.8. Dark Conductivity

Although most of the experimental work was focused on the influence of oxygen on photoconductivity of organic materials, Jurchescu et. al. [7] clearly showed that the hole current increases also in dark. It should be stressed that this increase in the current due to oxygen is observed only beyond a threshold voltage. This occurs in the SCLC regime (marked by 30 V threshold) as was outlined in the introduction. This leads to the conclusion that in order to excite the electron, which would generate a hole, there should be a hole current i.e. holes of specific kinetic energy. In this physical picture holes, injected from the contacts, have enough kinetic energy (>30 eV) to create an extra hole. This is very similar to the principles of electron energy loss spectroscopy (EELS) [59], where excitation is realized by incident electrons of a specific kinetic energy, [60] in contrast to an optical excitation that is realized by a photon of specific frequency. In our case the role of incident electrons is played by the injected holes. The selection rules for EELS are more complex compared to those for optical transitions. For electrons with high kinetic energy (~100 keV) the selection rules are similar to those for the optical dipole transitions. At low energy (~10 eV) no clear selection rules exist and only resonances in electron cross section occur [59]. All above might explain why some
of the I-V measurements [5] under exposure to oxygen in dark show very little or no evidence of doping. This is because at low operational voltages (< 30 V) charge carriers do not have enough kinetic energy to generate additional charge carriers in the active channel, leaving the electric current unchanged.

As was shown in the previous section, O₄ in the layer has a low probability of being excited by light, therefore the EELS-like mechanism discussed above might be appropriate. In this perspective the incident hole scatters off and excites the pentacene which relaxes to \([Pn(O₄^-)] + e^+(E')\). The hole \(e^+(E')\) is delocalized over the pentacene while its negative counterpart is localized at the O₄ site forming \(O^-\). It should be realized that the O₄ complex is expected to show singly excited states only. Doubly excited states are very rare and usually require intense radiation. We did not study the stability of \(O^-\), however it is found to be stable in earlier work [61]. This generation/annihilation of an extra hole by O₄ in the layer may be schematically written as:

\[
e^+(E) + [PnO₄] \rightarrow e^+(E - \delta E) + [Pn(O₄^-)] + e^+(E') \quad \text{(creation of extra hole)}
\]

\[
[Pn(O₄^-)] + e^+(E) \rightarrow [PnO₄] \quad \text{(annihilation of extra hole)}
\]

where \(E > 30 \text{ eV}\), \(\delta E\) is the energy loss of incident hole injected in the pentacene channel upon the scattering and \(E'\) is the energy of the generated hole. The second process leads to a steady state. Since a constant electric field is applied along the channel, the incident and generated holes gain kinetic energy.

### 4.9. Computational Methods

The first principles electronic structure calculations were performed using density-functional theory (DFT) [62] implemented in the Vienna \textit{ab initio} Simulation Package (VASP) [57, 63–67] where the projected augmented wave (PAW) method [66–68] is implemented. We used the PW91 [69] generalized gradient approximation (GGA) and the local density approximation (LDA) to the exchange correlation potential. The crystal structure of pentacene supercell \((2a \times 2b \times c)\) was taken from ref. [70] (at \(T = 90 \text{ K}\)) and further optimized. For each of the bulk calculations the positions of the atoms in the supercell were relaxed (while the shape and the volume were kept fixed) using a conjugate gradient algorithm and a tolerance of 10 meV/Å on interatomic forces. For Brillouin zone integration we used a Monkhorst-Pack k-point mesh [71] with \(4 \times 4 \times 2\) points. The energy cutoff on the plane-wave basis set used in all calculations was 500 eV.

For a separate O₄ molecule we used a cubic supercell of \(20 \times 20 \times 20 \text{ Å}^3\) which ensures that the periodic molecular replicas do not interact. Frequencies were calculated using a finite difference method [72]. The total energies for isolated molecules were calculated using the GGA rather than the
LDA approximation to the exchange correlation potential, since LDA results in too strong binding. The total energies were corrected for the zero point vibrational energy \( (ZPVE) \) \( (E_{ZPVE} = \sum_i \frac{\hbar \omega_i}{2}) \), where \( \omega_i \) is the frequency of \( i \)-th vibrational mode.

To calculate the transition dipole moments for the molecular clusters we used the quantum chemical code GAMESS-UK [58]. The UDFT, PW91 method with the 6-31G basis set was used.

4.10. Conclusions

We consider oxygen in pentacene in the state of \( O_4 \) as a qualitative explanation for the results of transport measurements. Our calculations provide a quantitative support. We found stable sites for \( O_4 \) in and in between the layers of pentacene. The simple model of an optical transition from the top of the valence band to the oxygen state in the bandgap indicates that \( O_4 \) between the layers dopes pentacene with one hole under illumination. The \( O_4 \) in the layer is responsible for the increase in the dark current beyond a critical electric field strength, in a way comparable with EELS. The DOS of bulk pentacene suggests that the presence of oxygen might influence the magnetoresistance. Thus, the experimental study of magnetoresistance of organics in oxygen might be very interesting. ESR experiments are of great importance since they are aimed to study the magnetic structure of pentacene with oxygen. Raman and IR active fundamental frequencies are provided for comparison with future measurements. The main difficulty for all kinds of experiments is the low concentration of oxygen in pentacene and the dependence of the oxygen concentration on external pressure. An interesting question is whether the influence of oxygen has the same effect on other organic semiconductor materials such as antracene, tetracene and rubrene. We hope that the model and mechanism of doping proposed in this work will raise both theoretical and experimental interest for further study of this phenomenon.

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