Analyzing the Electronic Coupling in Molecular Crystals—The Instructive Case of $\alpha$-Quinacridone

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In the present article, an evaluation of different approaches for estimating the electronic coupling and charge-transport parameters in organic semiconductors is provided. As a testbed for that comparison, the $\alpha$-polymorph of quinacridone is chosen. This system is particularly well suited for the purpose, as $\alpha$-quinacridone intermolecular interactions in distinct crystallographic directions are dominated by the three mechanisms most relevant in organic semiconductors: $\pi$-stacking, H-bonding, and van der Waals stacking. Density-functional theory-based simulations yield a comparably complex band structure, which provides the means for demonstrating shortcomings of commonly applied approaches. These include the estimation of transport properties based on bandwidths and the calculation of electronic transfer integrals considering molecular dimers. As a particularly promising alternative, the fitting of suitably complex tight-binding models to the DFT-calculated bands in the entire Brillouin zone is proposed. These fits bear the advantage of directly producing intermolecular coupling constants for all relevant neighboring molecules as input parameters for hopping and dynamic disorder models. They also yield an analytic expression for the electronic bands. These allow the extraction of parameters relevant for band-transport models (like group velocities and effective masses) in the entire Brillouin zone.

1. Introduction

Organic semiconductors have attracted increasing attention over the past years because of numerous advantageous properties, including the tunability of electrical and optical properties,[1] mechanical flexibility,[2] and the possibility to build biocompatible electronics out of small hydrogen-bonded pigments.[3–5] For all these applications, the charge transport properties of the employed materials are highly relevant. Their description is, however, far from straightforward, as one is dealing with systems in which the electronic coupling between neighboring molecules is typically on the same order as the electron–phonon coupling.[6]

Therefore, various models have been developed (or adapted from related fields) to describe the carrier mobilities of organic semiconductors, $\mu$. The approaches comprise band-transport models explicitly considering electron–phonon coupling (and the associated band narrowing) via the Holstein–Peierls Hamiltonian,[10–12] dynamic disorder–based models,[13–18] and purely hopping-based approaches building on Marcus theory.[6–8,19] The popularity of these models has varied over time and their suitability for a given system typically depends on the types of considered molecules, their arrangements, the temperature range of interest, and the degree of disorder present.[6–9] Still, an essential ingredient for all these transport models is the electronic coupling between neighboring molecules. Especially for hopping and dynamic disorder models, it can be expressed through transfer integrals, $t$, while for band-transport parameters like the effective masses, $m^*$, are more relevant.[6–9,18]

A seemingly straightforward and often applied approach for determining that coupling, at least for crystalline materials, is to calculate the electronic band structure of the system. This is usually done applying state-of-the-art density functional theory (DFT) methods. In principle, this band structure then contains all information on transfer integrals and effective masses, including the full crystal environment for each molecule. Nevertheless, it turns out that extracting the parameters quantifying the intermolecular electronic coupling from band structures can be difficult, misleading, and dependent on the methods and approximations used.

Thus, as a first step, we recapitulate commonly used methods for extracting transport relevant quantities from electronic band structures of crystalline materials. One of the simplest ways is to consider the widths of the electronic bands in high-symmetry directions. When employing a one dimensional nearest-neighbor tight-binding model, one obtains the following relation between the energy of the electronic states, $E$, and the wavevector, $k$:[20]

$$E(k) = \varepsilon - 2t \cdot \cos(k \cdot a)$$

(1)

Here $\varepsilon$ is the on-site energy, $t$ the transfer integral between neighboring units, and $a$ is the real space distance between the lattice
sites. Notably, Equation (1) also holds for orthogonal 3D unit cells in the unit cell directions, as long as only nearest neighbors are considered. For such a band shape, the transfer integral, $t$, is obtained as a quarter of the bandwidth, BW. Comparing transfer integrals or, equivalently, BWs obtained for different directions, one can then try to rationalize the anisotropy of charge transport within the material.\cite{21–23}

A more elaborate approach to obtain transfer integrals is to fit DFT-evaluated bands along high-symmetry directions by a 3D nearest-neighbor tight-binding expression considering the actual symmetry of the crystal. In this way, one gets direct access to the transfer integrals as fit parameters.\cite{26–31} A limitation of this strategy is that only information on the calculated directions is considered in the fit, which becomes problematic for low-symmetry systems, where a more homogeneous sampling of the Brillouin zone is necessary. Even when the latter is done, the question remains, how many and which of the neighboring molecules need to be taken into account for setting up the “ideal” tight-binding Hamiltonian. In particular, it needs to be determined under which circumstances one needs to go beyond nearest neighbors and what consequences this will have.

Finally, when band-transport mechanisms dominate, another option for determining preferential transport directions is to identify the band extrema and then to calculate the effective mass tensors at these $k$-points by numerical differentiation of the ab initio data. This then allows an analysis of the effective mass $m^*$ as a function of direction.\cite{21–23,25,26}

All above-described approaches build on band structure calculations. As an alternative approach that is particularly widespread in the field of organic semiconductors, transfer integrals are routinely extracted from calculations of molecular dimers\cite{26–31} employing the “energy splitting in dimer” (ESD) method or related, more advanced approaches.\cite{6,7,32} These approaches are often computationally less demanding than band structure calculations and are particularly useful when dealing with non-crystalline materials. Moreover, simulations on dimers are also insightful when trying to understand the impact of shifting or rotating neighboring molecules relative to each other.\cite{30,33–35} The obtained transfer integrals can then be employed for calculating hopping rates and also charge-carrier mobilities.\cite{36–40} For obtaining these mobilities, the transfer integrals are often combined with Monte Carlo–based approaches.\cite{37–41} Dimer-derived transfer integrals have also been used to construct tight-binding model functions, which can then be employed for calculating band structures and effective masses.\cite{42,43} The molecules surrounding the dimers in the actual crystalline environment are typically not considered in such approaches. Therefore, they bear the risk of missing relevant physical effects resulting from more complex intermolecular coupling effects beyond mere pair interactions.\cite{44}

In the following, we will critically assess the above-mentioned methods for extracting the electronic coupling in organic semiconductors, including implications for charge-carrier transport properties. This will be done for the instructive case of the $\alpha$-polymorph of quinacridone. To overcome the encountered limitations of the above approaches, we will present a strategy based on comparably complex tight-binding fits, which we find well suited for obtaining the electronic coupling parameters needed in hopping as well as band-transport models.

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**Figure 1.** Crystal structure of the quinacridone $\alpha$-polymorph. a) View of the unit cell with the molecule in the original cell marked by a blue rectangle and the closest H-bonding partner in $a_1 + a_2$ direction marked by a purple rectangle. b) Side view of the crystal structure along $a_1 + a_2$. c) View to indicate the H-bonding and stacking directions. The most important directions for assessing the anisotropic charge-transport parameters are indicated by colored arrows: gray for $\pi$-stacking, purple for H-bonding, and green for vdW stacking.

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### 2. Studied Model System

The choice of $\alpha$-quinacridone as test system is motivated by the observation that in this material the intermolecular interactions are fundamentally different in all three spatial directions. Notably, they comprise the most relevant interaction motifs typically found in organic semiconductors: (seemingly ideal) $\pi$-stacking, H-bonding, and van der Waals stacking. Moreover, applying the approaches mentioned in the introduction section is comparably straightforward for $\alpha$-quinacridone, as it contains only one molecule per unit cell. This results in comparatively simple expressions for the tight-binding models and avoids band-crossings involving the frontier bands.

Different views of the crystal structure of the quinacridone $\alpha$-polymorph\cite{45} are shown in Figure 1, where $a_1$, $a_2$, and $a_3$ denote the unit cell vectors in real space. The directions of the different interactions are indicated by colored arrows: the green arrow indicates the direction of van der Waals stacking ($a_1 + a_2 + a_3$), the purple arrow the direction of hydrogen bonding ($a_1 + a_3$), and the gray arrow the direction of $\pi$-stacking ($a_1$). There are several additional aspects that make $\alpha$-quinacridone ideally suited for the present study (as will become apparent from the discussion below): i) Along certain spatial directions, one observes noncosine-shaped bands implying that in those directions a nearest-neighbor tight-binding description cannot be sufficient. ii) In other directions, diagonal couplings become relevant. These massively modify the calculated band structures. (iii)
Moreover, for certain directions, the interactions with the surrounding molecules in the crystalline environment turn out to be particularly relevant resulting in improper results obtained from dimer models.

3. Analyzing the Electronic Band Structure

The valence-(VB) and conduction bands (CB) of \( \alpha \)-quinacridone calculated using dispersion-corrected density-functional theory at the Perdew–Burke–Enzerhof (PBE)\[46,47\] level are shown in Figure 2.

The widths of these bands (defined as the energetic difference between the highest and lowest energy states for a specific \( k \)-path within the first Brillouin zone, BZ) are compiled in Figure 3b. The high-symmetry directions in reciprocal space are neither parallel to the real-space lattice vectors \( a_1, a_2, a_3 \) (representing the periodic arrangement of the molecules) nor to the directions of H-bonding, \( \pi \)-stacking, and vdW stacking. They are also not parallel to the short (S) or long (L) molecular axes, or perpendicular to the molecular plane (P). Therefore, we also calculated the bandwidths along paths between the \( \Gamma \)-point and the Brillouin-zone boundary parallel to \( a_1, a_2, a_3, S, L, \) and \( P \), as indicated in Figure 3a. Note that the aforementioned vectors in the following discussions will also be used as labels for the corresponding \( k \)-paths.

Observing a large bandwidth, \( BW \), along a certain path suggests that the electronic coupling in that direction is large. Thus, the comparison of the bandwidths in Figure 3 allows first conclusions concerning the anisotropy of the electronic coupling. Within the simple 1D tight-binding model mentioned in the introduction, this also yields a first estimate of the anisotropy of the associated transfer integrals, \( t = BW/4 \). For the valence band, the \( BW \) is largest along a path parallel to the \( \Gamma Y \) direction, similarly large parallel to \( a_2 \), and only somewhat smaller along the short molecular axis (S). It is intermediate along paths in the \( \pi \)-stacking direction (\( a_1 \)) and along the long molecular axis (L), and smallest for paths perpendicular to the molecular plane (P).

For the conduction band, the main differences are that the bandwidths in all directions close to the long molecular axis (\( a_1, L \), and \( \Gamma Z \)) become particularly small, while they increase somewhat for paths pointing in the \( \pi \)-stacking and in the \( P \) directions. For the latter two, they, however, still remain well below 100 meV.

![Figure 2](image-url)  
**Figure 2.** DFT-calculated electronic band structure of \( \alpha \)-quinacridone along a set of high-symmetry paths (solid thick lines). The first BZ including the chosen \( k \)-path is shown as an inset in the topmost panel. The energies are given relative to the maximum of the valence band, \( E_{VBM} \). The results of the TB fit discussed in Section 4 are shown as dash–dotted black lines (essentially coinciding with the DFT calculated bands). A zoom into the regions of conduction and valence band is shown in the two lower panels.

![Figure 3](image-url)  
**Figure 3.** a) Unit vectors starting at the \( \Gamma \) point and pointing in the directions of the unit cell axes in real space \( (a_1, a_2, a_3) \), the unit cell axes in reciprocal space \( (\Gamma X, \Gamma Y, \Gamma Z) \), the \( \pi \)-stacking direction \( (P) \) and the directions of short (S) and long (L) molecular axes. b) Bandwidth and \( \Delta E_{BZ} \) along the chosen paths in reciprocal space for valence and conduction band. Data sets which describe similar paths are grouped, for example, \( a_2, S, Y \), and \( Y \).

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At first glance, this appears somewhat surprising considering the seemingly ideal π-stacking in α-quinacridone, which one might assume to maximize the corresponding electronic couplings. The reason for the strongly reduced coupling in the π-stacking direction lies in the details of the arrangement of the molecules: The \( P \) and \( a_2 \) directions are not parallel, resulting in a slip of neighboring molecules along their long and short molecular axes. As a consequence of the symmetry of the involved orbitals, this results in a sharply reduced electronic coupling, as discussed in detail, for the examples of tetracene, anthradithio, and sexithiophene in refs. 6, 30, 33.

A closer inspection of the band structure displayed in Figure 2 reveals that along several paths, the bands clearly deviate from the (according to Equation (1)) expected half-wave cosine shape with extrema at \( \Gamma \) and the BZ boundary. To more systematically identify such cases, we define a second parameter related to the widths of the band, namely the (absolute value of the) energetic difference between the state at the \( \Gamma \) point and the state at the BZ boundary along a specific direction, \( \Delta E_{BZ} \).

The values of \( \Delta E_{BZ} \) are also contained in Figure 3. Major deviations between \( \Delta E_{BZ} \) and BW indicate paths along which the simple relation of \( t \) equaling a quarter of the bandwidth no longer holds. Small deviations can also originate from the fact that apart from \( \Gamma X, \Gamma Y, \) and \( \Gamma Z \), the \( k \)-paths for which the bandwidths are displayed in Figure 3 are not parallel to reciprocal lattice vectors. The largest difference between \( \Delta E_{BZ} \) and the BW is found for the conduction band along the \( a_1 \) path. Other paths which are potentially not described correctly by the simple tight-binding expression from Equation (1) are \( P \) and \( L \) for the valence- and \( a_2 \), \( P \), and \( \Gamma X \) for the conduction band. Notably, analyzing bandwidths allows us to identify these problematic directions, but does not provide us with tools for improving the analysis.

4. Tight-Binding Fits versus Dimer Models

Therefore, we have gone beyond the simple model from Equation (1), applying a more general tight-binding ansatz of the following form:

\[
E(k) = \epsilon + \sum_j t_j \cdot e^{i k \cdot R_j} \tag{2}
\]

Here \( \epsilon \) denotes the on-site energy, \( t_j \) is the transfer integral for neighboring molecules along direction \( j \) and \( R_j \) is the vector connecting the central molecule with the respective neighbor. Due to the inversion symmetry of α-quinacridone, the two neighbors at \( R \) and \(-R\) are equivalent. Therefore, the associated transfer integrals are also the same and one obtains two terms \( t_j \cdot e^{i k \cdot R_j} \) and \( t_j \cdot e^{-i k \cdot R_j} \) for each index \( j \), resulting in \( 2t_j \cos(k \cdot R_j) \). When fitting the tight-binding model to the DFT band structure, the fit parameters are \( \epsilon \) and \( t_j \), while \( k \) is determined by the crystal structure. As there is only one molecule per unit cell, the possible values of \( R \) in α-quinacridone are sums of integer multiples of the unit cell vectors \( a_1, a_2, \) and \( a_3 \). In the following, these will also be used for naming the different transfer integrals and when referring to bands for the corresponding \( k \)-paths.

For developing the tight-binding model, we start by considering a subset of nearest neighbor molecules and gradually include more neighbors until the root mean square error between the tight-binding model and the DFT bands falls below 5 meV. In this context, it needs to be stressed that the fitting must not be done along the high-symmetry directions alone, as then one only obtains good agreement in these directions, while there are large errors in other parts of the Brillouin zone. Therefore, we homogeneously sampled the entire BZ employing a tight \( k \)-grid (for details see Section 8). This yields a highly accurate description of the bands not only on that grid, but also along the high-symmetry directions. This is shown in Figure 2 (black line). In passing, we mention that increasing the number of neighbor molecules included in the fit does not change the transfer integrals for the previously considered neighbors. This can be seen in Table 1, when comparing the \( t_j \) for the “simplified” and the “full” model. It is a consequence of the model function representing a Fourier decomposition of the energy dispersion relation, with the transfer integrals serving as Fourier coefficients. Notably, these coefficients are independent of each other (for details see Supporting Information).

An appealing aspect of the tight-binding fit is that it yields an analytical expression for the band structure. From that expression, group velocities and effective masses can also be calculated analytically at any point in reciprocal space from derivatives of the band structure with respect to \( k \) (see below). Additionally, the fit immediately yields the electronic couplings (transfer integrals) between all relevant neighbors considering the full 3D crystal environment.

For organic semiconductors, the transfer integrals are more commonly determined employing the ESD\(^{30}\) method, where they are calculated as half of the energetic splitting between dimer orbitals viewed as bonding and antibonding linear combinations of the frontier orbitals of isolated molecules. In passing we note that more sophisticated approaches like the fragment orbital (FO) methods need to be employed whenever the molecules are symmetry inequivalent, as the ESD approach would not properly account for differences in site energies arising from the molecules polarizing each other differently.\(^n{32}\) This is, however, no major concern here, as the dimers derived from the α-polymorph of quinacridone show inversion symmetry.\(^n{32}\)

A disadvantage of the ESD approach is that it treats the molecular dimer as an isolated entity neglecting the role of most of the neighboring molecules in the crystalline environment. To assess the impact of this approximation, we first compare the transfer integrals from the tight-binding fit with the ones obtained via the ESD method (see Table 1). Overall, there is a rather good agreement between the two approaches for both bands (VB and CB) and most of the considered directions (also considering certain methodological differences in the DFT calculations on dimers and periodic structures – see Section 8). Excellent agreement is found, especially for the \( a_2+a_1 \) direction, for both bands and for \( a_1 \) and \( a_3+a_2 \) for the valence band. Conversely, for the CB, we find a large deviation of 12 meV for the latter direction. To rationalize this discrepancy, one has to remember that the \( a_3+a_1 \) direction is the one of the intermolecular H-bonds (see Figure 1). Notably, one of the properties of quinacridone is that the four H-bonds each molecule undergoes in a crystalline environment (two involving the amine and two involving the ketone groups)
is dominated by the diagonal electronic coupling via a·a band dispersion in the a·a direction. The outcome is shown in Figure 4, where, quite unexpectedly, the main contribution to the band dispersion in the a·a direction does not stem from t_{1+2} but rather from t_{2}. To understand that, one has to realize that the a·a vector has a sizable component in the a·a direction. Consequently, the scalar product k·R_j from Equation (2) is significant also, when R_j = a·a and k is parallel to a·a direction. Therefore, for the conduction band, where t_{2} is much larger than t_{1+2} (which is also true when considering the LUMO/LUMO+1 splitting of the respective dimers) the band structure in the H-bonding direction is dominated by the diagonal electronic coupling via t_{2}. Another interesting aspect is that for the conduction band, t_{2} and t_{1+2} have different signs. Consequently, their superposition reduces the band dispersion in the a·a direction (see Figure 4). Therefore, while the combination of the two couplings provides additional transport pathways for incoherent hopping, for band transport it increases the effective mass and, therefore, is detrimental for charge transport.

Table 1. Parameters for the tight-binding fit of the frontier bands of the quinacridone α-polymorph considering only the molecules with the smallest distance from the central molecule (“simplified”) and for an increased number of transfer integrals included in the fit (“full”). The reason why t_{1+2} is considered in the “simplified” model is that this direction corresponds to the H-bonding direction with particularly short intermolecular distances. Likewise, the distance between (symmetry inequivalent) atoms is shorter in the a·a direction than in the a·a direction, which is the reason why we have included t_{2+4} and not t_{2} (see Figure 6). The root mean square error (RMSE) in the last line is calculated as RMSE = \sqrt{\frac{\sum_{i=1}^{N}(E_{i,TB} - E_{i,DFT})^2}{N}} with E_{i,TB} and E_{i,DFT} referring to the energies of the individual states calculated by the tight-binding, respectively, by the DFT approach. Note that differences smaller than 1 meV are within the convergence errors of our calculations.

| Parameter | VB simplified [meV] | CB simplified [meV] | Dimer [meV] |
|-----------|--------------------|-------------------|-------------|
| t_{1}     | 852.7              | 2462.1            | -17.0       |
| t_{2}     | 4.8                | -18.4             | -14.0       |
| t_{3}     | -9.7               | 38.3              | 44.0        |
| t_{4}     | 0.4                | -0.5              | -0.3        |
| t_{5}     | -9.9               | -5.1              | -17.0       |
| t_{6}     | 0.0                | 0.0               |             |
| t_{7}     | -12.2              | -14.2             | -1.6        |
| t_{8}     | -5.2               | -1.0              | -1.5        |
| t_{9}     | -0.1               | -0.4              |             |
| t_{10}    | 0.0                | 0.1               |             |
| t_{11}    | 2.0                | -13.2             |             |
| t_{12}    | 3.3                | -0.9              |             |
| t_{13}    | -0.6               | 1.3               |             |
| t_{14}    | 0.5                | 0.0               |             |
| t_{15}    | 1.5                | -0.4              |             |
| RMSE      | 3.2                | 1.9               | 26.7        |
Figure 4. Conduction band and main tight-binding components along a path parallel to the H-bonding direction (a₁ + a₂). A₁₂ denotes the Brillouin-zone boundary in that direction. The DFT data are shown as a thick blue solid line. All other lines show contributions evaluated from the TB model. The individual contributions are shown in purple for t₁₁ + a₂, slate blue for t₂₂, and gray for t₂₁. The sum of these contributions is shown by the orange solid line, which is already almost perfectly on top of the DFT data. The top panel shows the crystal structure with the relevant molecules highlighted using the same color code as for the band components. The area around the central molecule is highlighted in dark gray.

The last direction we examine in detail is a₃. Here band dimer transfer integrals agree and also ΔE ßz and BW are the same. Thus, one might expect that for this direction the simple model considering only t₃₃ should provide reliable results. An inspection of Table 1, however, shows that t₃₃ is negligibly small, implying a vanishing bandwidth along a path parallel to a₃ (see dotted line in Figure 6). This is, however, not the case when calculating the full band structure (solid red line in Figure 6).

The explanation for this seeming contradiction is again the appearance of diagonal couplings. The situation is particularly complex here, as several neighboring molecules are at distances only slightly larger than a₁ (namely the molecules at a₁ + a₁, a₂ + a₁ - a₁, and a₂ + a₁ + a₁; see top panel in Figure 6). In fact, when considering the distances between nearby atoms rather than the distances between molecular centers, for some of these neighbors one might even expect electronic couplings larger than t₃₃. This is indeed the case (see Table 1), and consequently, the diagonal coupling contributions t₂₂ + a₁, t₂₂ + a₁ - a₁, and t₂₂ + a₁ + a₁ dominate the band dispersion in the a₁ direction (see Figure 6). At this stage, one might argue that transport in a₁ direction is only of minor relevance, considering the small associated bandwidth (6 meV).

This assessment, however, misses the fact that large intermolecular distances increase hopping mobilities, as will be discussed in the next section.

5. Implications for Hopping Transport

Even for “benign” bands, one must keep in mind that for transport the distance between neighboring molecular sites in a specific direction plays an equally important role as the transfer integrals. For the case of hopping transport, this follows from the diffusion coefficient (for a 1D system) being proportional to \((\langle R_j \cdot |R_j| \rangle)^2\). The latter quantity in the following will be referred to as diffusion parameter, \(d_{R_j}\). Like in the tight-binding ansatz in Equation (2), for a material with only one molecule in the unit cell, the intermolecular center to center distances, \(R_j\), can be expressed as linear combinations of the lattice vectors. In this way, they directly reflect the periodicity of the crystal as they are the distances between all lattice sites. The expression for the diffusion parameter implies that to maximize hopping rates, one needs to maximize transfer integrals especially in directions of large inter-site distances.

Our test system, α-quinacridone, is triclinic[45] with unit cell vectors of significantly different lengths (a combination often observed for semiconductor crystals). Therefore, considering intermolecular distances is crucial for assessing transport anisotropies. Consequently, in Table 2, we summarize the
corresponding diffusion parameters for the directions of dominant transfer integrals. This finally allows us to judge the anisotropy of charge transport in α-quinacridone when a hopping mechanism dominates.

Analyzing the diffusion parameters for holes, one observes an anisotropy that is much more pronounced than for the transfer integrals. This is in part related to the fact that the diffusion parameters are proportional to $t_{k1}^2$. The main reason is, however, that the square of the intermolecular distance also enters into the expression of $d_{Rj}$. This, for a given transfer integral, improves charge transport in directions in which nearest neighbor distances are particularly large. As a consequence, the diffusion rates to neighboring molecules in the $a_2+a_3$ direction are nearly an order of magnitude larger than in any other direction. Conversely, for the $\pi$-stacking direction ($a_1$), characterized by the smallest intermolecular distance, the diffusion parameter becomes particularly small.

For the same reason, electron transport in the $\pi$-stacking direction becomes inefficient, in this case despite the comparably large transfer integral $t_{a1}$. In contrast to the situation for hole transport, the dominant diffusion parameter for electrons is found close to the H-bonding direction along $a_1$.

### 6. Effective Mass and Band Transport

When considering band instead of hopping transport (e.g., at low temperatures), a further complication arises from the observation that the band extrema do not occur at the $\Gamma$-point but rather at $Y$ (for the valence band) and at $E_\text{F}$ (for the conduction band; see Figure 2). Thus, an analysis of the bands in the high-symmetry directions as in Section 3 provides only limited insight into the actual transport properties of α-quinacridone. Considering that the tight-binding fit provides an analytical expression for the entire band structure, it is however straightforward to directly calculate effective mass tensors, $m^\text{eff}$, at any point in reciprocal space. In the following, we will focus on the "diagonal terms" of $m^\text{eff}$. These are obtained from the inverse of the second derivative of the energy with respect to $k$ in a specific direction $d$ according to Equation (3).

$$
\left( m^\text{eff}_{ij} \right)^{-1} = \tilde{d}^T \cdot \left[ \frac{\partial^2 E(k)}{\partial k_i \partial k_j} \right]_{a_i,j=v,y,z} \cdot \tilde{d}
$$

The diagonal terms of $m^\text{eff}$ link carrier flow in a specific direction with the electric field acting in the same direction. They are the most relevant components of $m^\text{eff}$, considering common device architectures. The values obtained at the extrema of the frontier bands projected onto a sphere are shown in Figure 7a,b.

At the valence band maximum ($\Gamma$), we find the smallest effective mass in $a_2+a_3$ direction, which is perfectly in line with the observations made for the transfer integrals and the diffusion parameters (see Table 2). Interestingly, around the $a_2+a_3$ direction, there is quite a large region showing comparable values of $m^\text{eff}$. This suggests that hole transport in α-quinacridone is reasonably efficient, provided that it occurs in directions close to parallel to the long molecular axes. The highest effective masses are found close to the $a_1$ direction implying particularly poor hole transport in the $\pi$-stacking direction consistent with the relatively small value of $t_{a1}$ (Table 1) and the comparatively even smaller one for $(t_{a1} \cdot |a_1|)^2$ (Table 2). For the sake of comparison, we also calculated $m^\text{eff}$ at the $\Gamma$ point. Interestingly, the $a_2+a_3$ direction is still the one associated with the lowest absolute value of the effective mass (see Figure 7c,d). As the $\Gamma$ point is not a band extremum, the sign of $m^\text{eff}$ in that direction is, however, positive rather than negative (see Figure 7e,f). Moreover, $m^\text{eff}$ diverges where the sign of $m^\text{eff}$ changes (i.e., for directions in which the deep blue and deep red regions in Figure 7e,f meet). Both aspects suggest that the effective mass at the $\Gamma$ point and, therefore, also all other quantities

**Figure 6.** Valence band in $a_1$ direction. The DFT data are displayed in red. The green dotted line shows the contribution from $t_{a3}$, the sienna colored line from $t_{a1+a3}$, and the violet and cyan lines those from $t_{a2+a3+a1}$ and $t_{a1+a3+a3}$. The sum of the latter three contributions is shown by an orange line. The top panel shows the crystal structure with the relevant molecules highlighted using an equivalent color code.

**Table 2.** Comparison of diffusion parameters $d_{Rj} = (t_{Rj} \cdot |R_j|)^2$ and transfer integrals for electrons and holes, obtained by fitting a TB model to the electronic band structure.

| Directions | Holes | Electrons |
|------------|-------|-----------|
| $R_j$      | $|R_j| [\text{\AA}]$ | $d_{Rj} 10^{-3} [\text{eV} \cdot \text{\AA}^2]$ | $t_{Rj} [\text{meV}]$ | $d_{Rj} 10^{-3} [\text{eV} \cdot \text{\AA}^2]$ | $t_{Rj} [\text{meV}]$ |
| $a_1$      | 3.80  | 0.3       | 4.8    | 4.9    | -18.4  |
| $a_2$      | 6.61  | 4.1       | -9.7   | 64.1   | 38.3   |
| $a_3$      | 14.49 | 0.0       | 0.4    | 0.1    | -0.5   |
| $a_1+a_2$  | 6.90  | 4.7       | -9.9   | 1.2    | -5.1   |
| $a_2+a_3$  | 14.77 | 32.5      | -12.2  | 0.4    | -1.3   |
Figure 7. Effective mass $m^*$ of VB and CB evaluated at the respective band extrema (top panels). Additionally, for the VB, $m^*$ is also evaluated at the $\Gamma$ point (central and bottom left panels) and for the CB at a k-point that is within $kT$ from the minimum (i.e., at $Y$, central and bottom right panels). The two central panels contain absolute values of $m^*$, while in the other panels the sign of the effective electron mass is considered (note that a negative effective electron mass means a positive effective hole mass).

derived from paths originating at the $\Gamma$ point contain quite misleading information regarding band transport in $\alpha$-quinacridone.

For the conduction band with its minimum at $E_2$, we find particularly large effective masses for directions close to $a_1$ and $a_1 + a_3$, in sharp contrast to the situation for the valence band. The smallest effective mass for the CB is found in direction $a_2$, consistent with the particularly large transfer integral in that direction. This suggests that electron transport is most efficient in directions close to the short molecular axis and the H-bonding direction ($a_1 + a_2$). Thus, also for band transport, the preferred transport directions for $\alpha$-quinacridone are fundamentally different for electrons and holes.

As the bands in organic semiconductors are comparably flat, the question arises whether the effective mass tensor changes significantly for other thermally accessible states. For the conduction band, we tested that for the $Y$ point, which is only 5 meV above the $E_2$ point. There, the absolute value of $m^*$ becomes intermediate around directions $a_1$ and $a_1 + a_3$. At the same time, the sign of $m^*$ changes in that region (not surprisingly, as the $Y$ point is not a minimum of the conduction band). This suggests that merely considering a single effective mass for electrons and holes for each direction is not necessarily sufficient for modeling band transport in organic semiconductors. In such cases, for obtaining a semi-classical description of charge transport properties within the band picture, it becomes inevitable to consider the full band structure. From the tight-binding fits, this quantity is readily available as an analytical function through Equation (2).

7. Conclusions

The current paper provides a comparison of commonly applied approaches for analyzing the electronic coupling in organic semiconductor crystals. This is done for the instructive example of $\alpha$-quinacridone. Our study reveals shortcomings of merely considering bandwidths or transfer integrals, when the latter are based on dimer simulations. While both approaches provide certain basic insights regarding the anisotropy of the electronic coupling in molecular crystals, an analysis of bandwidths fails when dealing with comparably complex band structures. A
complication of dimer simulations (beyond the well-known issues for non-centrosymmetric structures)\cite{1} is that they neglect the actual 3D crystalline environment. This becomes particularly problematic for the class of H-bonded chromophores. They also neglect next-nearest neighbor coupling effects mediated by a bridge molecule. Moreover, transport in specific directions can be dominated by diagonal coupling elements, and in certain directions, coupling to a sizable number of close-lying neighbors can become relevant. Finally, in situations dominated by band transport, further complications can arise from band extrema being located neither at the $\Gamma$ point nor at the Brillouin zone boundary. To overcome these problems, we recommend a fitting of the full band structure by tight-binding models considering a number of neighboring molecules, which is sufficient for mimicking the actual band structure of the crystal. This allows a straightforward extraction of transfer integrals that can be employed in hopping and dynamic disorder models. It also provides an accurate analytical expression for the band structure. The latter, for example, allows the straightforward calculation of parameters relevant for band transport (like effective masses and group velocities) at any point in reciprocal space without any numerical effort.

8. Experimental Section

For all calculations relying on periodic boundary conditions, dispersion-corrected density-functional theory (DFT) was used as implemented in VASP 5.3.3\cite{2,3,4}. The exchange-correlation part was treated employing the PBE\cite{5,6,7,8} functional in combination with the Tkatchenko–Scheffler (TS) dispersion correction method\cite{9} to account for long-range van der Waals interactions. Furthermore, the electronic band structure of the α-polymorph was also calculated using the HSE06 functional and compared to the PBE results. This comparison was triggered by the study of Lüftner et al.,\cite{10} who showed that for obtaining a correct ordering of the molecular orbitals of quinacridone, a proper treatment of exchange interactions is important. As far as the frontier bands are concerned, no fundamental differences between PBE and HSE06 (see Supporting Information) together with a plane-wave cut-off energy of 700 eV were used for all calculations. In the self-consistent-field (SCF) procedure, the Brillouin zone was sampled in two independent steps: i) using a $32 \times 20 \times 8$ Γ-centered k-point grid (the charge density resulting from this calculation was also used to non-self consistently calculate the band structures in the high-symmetry directions) and ii) using a $32 \times 20 \times 8$ k-grid, which was shifted by a vector of (0.5, 0.5, 0.5) times the reciprocal lattice vectors. The eigenvalues obtained by these two calculations were then combined in order to densely sample the Brillouin zone. An option for larger systems would be to perform the SCF calculation for a smaller grid and then to calculate the eigenvalues to sample the Brillouin zone with a more dense grid in a non-self-consistent manner using the previously obtained charge density. This strategy was tested using a smaller $16 \times 10 \times 4$ k-grid in the SCF procedure, obtaining essentially the same eigenstates (for all considered k-points) and electronic couplings as for the full calculations. To describe the occupation of the electronic states, the Methfessel–Paxton\cite{11} occupation scheme with a width of 0.1 eV was used. The relaxed geometry of the test system was obtained by taking the crystal structure of α-quinacridone from literature\cite{12} and relaxing the atomic positions until the largest force component on the atoms was smaller than 0.01 eV Å$^{-1}$, while keeping the unit cell vectors fixed.

For the quinacridone dimers, which have been extracted from the full calculations, orbital energies were obtained by performing single-point calculations using the Gaussian 09 program package\cite{13} in combination with the PBE functional and a 6-311++G(d,p) basis set. The transfer integrals $t$ were obtained from the orbital energies applying the ESD method.\cite{14} The sign of the transfer integrals was determined depending on whether the bonding (positive) or antibonding (negative) linear combination of the molecular orbitals was higher in energy.

To ensure the stability of the tight-binding fits, various algorithms were tested, like conjugate-gradient, least-squares (Levenberg–Marquardt), Powell, and Nelder–Mead, all as implemented in the LMFIT package for Python. Furthermore, the fitting procedure was started with randomly initialized starting guesses for the transfer integrals ranging between 0 and 5 meV. In all cases the same minimum was found regardless of the algorithm and the initial guesses.

Additionally, the stability of the fit was tested as a function of the number of k-points for a fixed number of transfer integrals (fit parameters). To do that, a subset of k-points from the high-density grid was randomly chosen and the fit was performed on these points. The fit turned out to be stable (changes of the RMSE well below 1 meV) for a k-grid containing only 100 points, provided that the k-points were homogeneously distributed in k-space. Here, it is, however, important to keep in mind that such results depend on the investigated material, as the minimum grid density depends on the highest-frequency component contained in the Fourier decomposition of the bands; that is, one needs to make sure that the sampling rate is such that none of the actually occurring frequency components of the band structure is above the Nyquist frequency.\cite{14}

The crystal structures were visualized using Ovito and the electronic band structures were plotted using the Python libraries NumPy and Matplotlib.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electronic coupling, organic semiconductors, tight-binding, transfer integrals

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