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Citation: J. Chem. Phys. **126**, 164704 (2007); doi: 10.1063/1.2727480
View online: http://dx.doi.org/10.1063/1.2727480
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First-principles theoretical investigation of the electronic couplings in single crystals of phenanthroline-based organic semiconductors

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(Received 23 February 2007; accepted 19 March 2007; published online 24 April 2007)

The electronic couplings between adjacent molecules in the phenanthroline-based bathocuproine (BCP) and bathophenanthroline (Bphen) crystals have been studied using density functional theory on model dimers. Within the frame of the "two-state model" of charge-transfer theory, a generalized definition of the "effective transfer integral" is proposed. This definition addresses the issue arising when the lowest unoccupied molecular orbital (LUMO) [highest occupied molecular orbital (HOMO)] and LUMO+1 (HOMO−1) of the single molecules both have significant contributions to the dimer LUMO (HOMO) level. Charge-transfer integrals based on the new definition are compared with those from previous models; significant differences are found. The authors' results indicate that, within a simple Marcus theory approach, the charge-transport parameters of the BCP and Bphen crystals are expected to be similar. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2727480]

I. INTRODUCTION

In devices based on organic π-conjugated materials,[1] such as organic light-emitting diodes, field-effect transistors, or solar cells, the charge-transport characteristics of the organic layer(s) play a critical role in determining device performance.[2] The electron/hole transport mechanism in organic molecular or polymer devices is usually different from that in bulk metals or inorganic semiconductors. In the latter, electron-phonon coupling is generally weak, electronic coupling dominates, and the effective-mass approximation based on band theory can be applied to evaluate the charge carrier mobilities in the system. However, in organic materials, both the electronic couplings between molecules and the electron-vibration interactions due to *intramolecular* and *intermolecular* relaxations do impact the carrier mobilities;[3] in addition, few organic materials used in devices are crystalline, which implies that disorder effects also need to be considered.[4]

It is generally accepted that transport in (disordered) organic materials takes place via charge carrier hopping between adjacent molecules. Since such an electron hop corresponds to an electron-transfer reaction, Marcus theory has been used extensively in recent studies to understand the impact of the chemical structure and packing mode on the charge-transport parameters. In the high-temperature limit, the intermolecular hopping rate, that is, the Marcus electron-transfer rate,[5–7] is expressed as

$$k_{if} = \frac{2\pi}{h}|V_{if}|^2\sqrt{\frac{1}{4\pi k_B T\lambda}}\exp[-(\Delta G^0+\lambda)^2/4\lambda k_B T],$$

where $V_{if}=\langle\psi_i|V|\psi_f\rangle$ is the electronic coupling (tunneling) matrix element (or transfer integral) between the initial and final states $|\psi_i\rangle$ and $|\psi_f\rangle$, λ is the reorganization energy, which takes account all vibrational relaxation/polarization processes, and ΔG^0 is the change in Gibbs free energy from initial to final state. In theoretical investigations, the transfer integral V_{if} has often been evaluated by considering the energy splittings obtained in a system composed of two molecules (two "monomers"), a method referred to as the "energy splitting in a dimer" model.[8–13] Various computational techniques based on *ab initio* or semiempirical quantum-chemical methods have been developed to calculate the transfer integral.

(i) The first is based on Koopmans' theorem and estimates the transfer integral (electronic coupling matrix element) for electron transport (hole transport) as half the lowest unoccupied molecular orbital (LUMO) [highest occupied molecular orbital (HOMO)] energy splitting present in the dimer system.[8–13] However, for strongly coupled systems, this approach should be applied with much caution since the LUMO or HOMO splittings can be significantly different from the actual value of the electronic coupling matrix element due to large spatial overlap.[14] Rather, the rigorous definition of the charge-transfer integral $V_{if}=\langle\psi_i|V|\psi_f\rangle$ has to be used, which is done below.

(ii) In the second method,[14] the molecular orbitals obtained from a calculation on the isolated monomer are used as the basis set for the calculation on the dimer system. The electronic coupling matrix element is calculated from the eigenvalue equation $HC=SCE$ (where H is the Hamiltonian operator within tight-binding approximation, C the eigenvector matrix, S the overlap matrix, and E the diagonal eigenvalue ma-

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trix), under the assumption that the initial and final states of the dimer system can be simply described as a (plus or minus) linear combination of the "pure" LUMO (or HOMO) levels of the two monomers.[14] However, in more complicated cases such as those we discuss below, this assumption no longer holds and a more general definition of the transfer integral should be considered.

(iii) The third method is strictly derived from the definition of the charged initial and final states in the framework of perturbation theory. In this approach, an extra charge (hole or electron) is first added to one molecule in the dimer as the initial state and then transferred to the other as the final state, simulating the process of charge hopping from one molecule to the other. This type of calculation, however, is more complex than the former two, in particular, because of the difficulty in attaining well-converged unrestricted Hartree-Fock wave functions.[15]

In this work, we study the charge-transfer parameters in the bathocuproine (BCP) and bathophenanthroline (Bphen) crystals with density functional theory (DFT). BCP and Bphen are phenanthroline derivatives, with the rigid quasi-planar phenanthroline moiety as the central segment; there is a significant interest in these materials as they have often been incorporated in organic electronic devices due to their ability to act as hole- or exciton-blocking materials and/or electron-transporting materials.[16–19] From time-of-flight experiments,[20] Bphen amorphous films have been shown to display electron mobilities on the order of 10^{-4} $cm^2/V\,s$ (for an electric field of 5.5×10^5 V/cm);[16] to the best of our knowledge, no measurement has been reported on the electron mobility of BCP.

II. METHODOLOGY

To evaluate the charge-transfer parameters from a dimer system, we use the second approach introduced above; we consider that the charge is initially localized on the first monomer, hereafter referred to as monomer 1, and then transfers and localizes on the other monomer (monomer 2) as the final state. The description of the initial and final states of the dimer system with the charge localized on one monomer is based on the LUMO (for electron transfer) or HOMO (for hole transfer) of the isolated neutral monomer. This assumption is justified in many widely investigated systems, such as pentacene, where the LUMO (or HOMO) energy level of a single molecule is well separated (usually by a few tenths of an eV) from the LUMO+1 (or HOMO−1) level. Thus, in a dimer composed of such monomers, the dimer LUMO (or HOMO) level has significant contributions only from the LUMOs (or HOMOs) of the two monomers. Then, the transfer integral can be defined as

$$t_{1A,2A} = \langle \varphi_{1A}|H|\varphi_{2A}\rangle, \tag{1}$$

where $|\varphi_{1A}\rangle$ and $|\varphi_{2A}\rangle$ are the LUMO (or HOMO) levels of monomers 1 and 2. This approach has been employed in calculations of both intramolecular and intermolecular transfer integrals and is referred to as a "two-state model."[8–13,21]

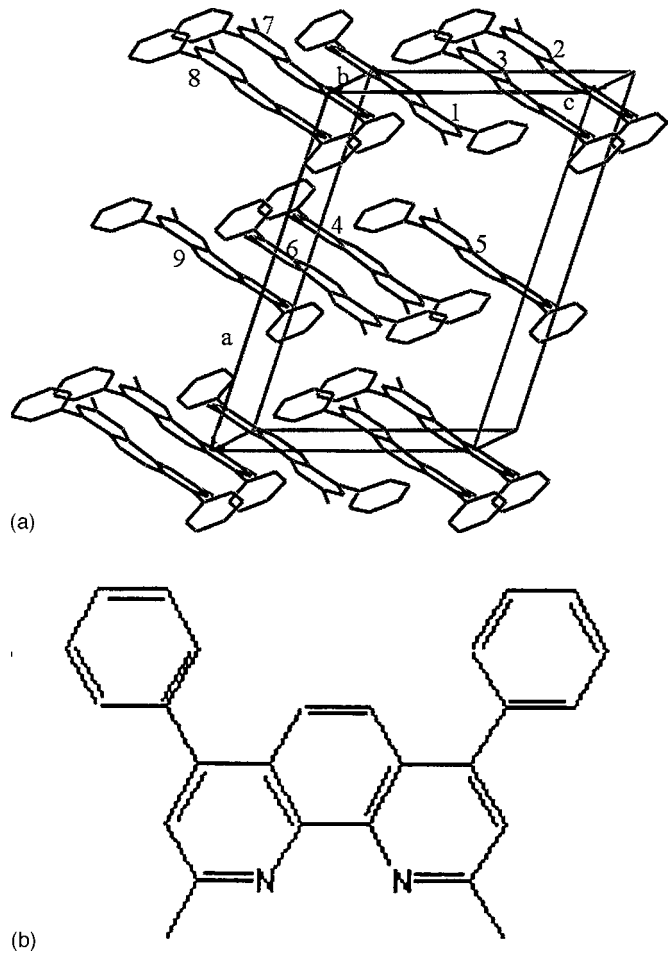

FIG. 1. BCP crystal structure (a) and chemical structure (b).

In a recent work,[22] it was emphasized that a proper orthogonalization of the initial and final states is crucial in obtaining correct values of transfer integrals.

However, when the monomer LUMO and LUMO+1 (or HOMO and HOMO−1) levels are energetically very close to one another (this is the case, for instance, in the BCP molecule where the LUMO/LUMO+1 energy difference is a mere 0.02 eV), the LUMO (or HOMO) of the dimer becomes a combination of the LUMO and LUMO+1 (or HOMO and HOMO−1) levels of both monomers. As a result, Eq. (1) is no longer appropriate to describe the transfer integral between the two monomers. To obtain a more realistic description of the initial or final state in such a system, a generalized definition should be considered, which includes the LUMO and LUMO+1 (or HOMO and HOMO−1) levels of the monomers in both initial and final states of the coupled dimer system. Generally, the dimer LUMO (or HOMO) level can be described as

$$|\Psi\rangle = c_{1A}|\varphi_{1A}\rangle + c_{1B}|\varphi_{1B}\rangle + c_{2A}|\varphi_{2A}\rangle + c_{2B}|\varphi_{2B}\rangle = |\psi_1\rangle + |\psi_2\rangle. \tag{2}$$

Here, subscripts A and B represent the LUMO and LUMO+1 (or HOMO and HOMO−1) levels of the isolated monomer; coefficients c_{1A}, c_{1B} and c_{2A}, c_{2B} provide the description of the dimer LUMO (or HOMO) levels with the molecular orbitals of the isolated molecule ($|\varphi_A\rangle, |\varphi_B\rangle$) taken as basis

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TABLE I. Transfer integrals calculated for electron transport in the BCP crystal from Eq. (1) (with and without orthogonalization) and from Eq. (9). The C–C values refer to the distance between the centers of mass of the two monomers. P is the perpendicular distance between the two phenanthroline molecular planes, L is the displacement along the molecular long axis, and X is the displacement along the short axis.

BCP		C–C (Å)	P (Å)	L (Å)	X (Å)	$t_{1A,2A}$ (eV)	$t^{o}_{1A,2A}$ (eV)	t_{eff} (eV)
5→4 (1→3,8)	Pair 1	7.053	1.620	5.500	4.107	0.095	0.058	−0.035
5→7,8	Pair 2	12.842	1.129	11.622	5.345	−0.022	−0.014	−0.022
5→1	Pair 3	8.363	4.468	6.961	1.233	−0.023	−0.015	−0.015
5→6 (1→2,7)	Pair 4	8.730	3.338	4.661	6.584	−0.009	−0.005	−0.004
5→2,3	Pair 5	9.736	7.806	2.299	5.345	0.000	0.000	0.000

set (this basis set can of course be expanded as needed). The eigenfunction $|\Psi\rangle$ can be re-written as a combination of two components,

$$|\psi_1\rangle = c_{1A}|\varphi_{1A}\rangle + c_{1B}|\varphi_{1B}\rangle, \tag{3}$$

$$|\psi_2\rangle = c_{2A}|\varphi_{2A}\rangle + c_{2B}|\varphi_{2B}\rangle, \tag{4}$$

which are mixed states of $|\varphi_A\rangle$ and $|\varphi_B\rangle$, with $|\psi_1\rangle$ localized on monomer 1 and $|\psi_2\rangle$ on monomer 2. In this context, $|\psi_1\rangle$ is the most adequate description for the initial state (that is, the state of monomer 1 in the coupled dimer system prior to charge transfer) and $|\psi_2\rangle$ for the final state (state of monomer 2 after charge transfer), provided that a proper orthogonalization of the two states is carried out. Thus, in relation to the definition of the transfer integral in Eq. (1), a generalized definition can be proposed as follows:

$$t_{12} = \langle\psi_1|H|\psi_2\rangle. \tag{5}$$

In comparison with Eq. (1), Eq. (5) represents a linear combination of the monomer LUMO and LUMO+1 (or HOMO and HOMO−1) levels as the initial and final states, which are determined by the electronic Hamiltonian of the dimer system. The new basis set $|\psi_1\rangle$ and $|\psi_2\rangle$ can also be considered as an auxiliary basis set of $|\varphi_{1A}\rangle$ and $|\varphi_{2A}\rangle$. When c_{1B} and c_{2B} are both zero, this definition reduces to Eq. (1).

We have carried out our calculations at the DFT level, using the generalized gradient approximation and the PW91 functional in the ADF package.[23] To identify the contributions of each monomer to the dimer molecular orbitals, electronic-structure calculations on isolated molecules were first carried out; the resulting monomer molecular orbitals were then used as basis set in calculations on the dimer systems.[14] The coefficients c_{1A}, c_{1B} and c_{2A}, c_{2B} in Eqs. (3) and (4) are obtained from the dimer calculations, and the new states $|\psi_1\rangle$ and $|\psi_2\rangle$ are considered as the initial and final states in the evaluations of the transfer integrals. We note that, in all the cases examined in the present work, contributions to $|\psi_1\rangle$ and $|\psi_2\rangle$ from levels other than the monomer LUMO and LUMO+1 (or HOMO and HOMO−1) levels were negligible.

A symmetric orthogonalization process has to be applied to states $|\psi_1\rangle$ and $|\psi_2\rangle$. Although a total of four levels (for instance, LUMO and LUMO+1 of both monomers 1 and 2) is included, the eigenvalue equation $HC=SCE$ remains a two-state problem since the basis set is made of the two states $|\psi_1\rangle$ and $|\psi_2\rangle$. In matrix form, the eigenvalue equation can be written as

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}, \tag{6}$$

where $H_{11}=\langle\psi_1|H|\psi_1\rangle$, $H_{22}=\langle\psi_2|H|\psi_2\rangle$, $H_{12}=H_{21}=\langle\psi_1|H|\psi_2\rangle$, $S_{11}=\langle\psi_1|\psi_1\rangle$, $S_{22}=\langle\psi_2|\psi_2\rangle$, and $S_{12}=S_{21}=\langle\psi_1|\psi_2\rangle$. It should be noticed that the overlap matrix diagonal elements S_{11} and S_{22} are not equal to 1, since $|\psi_1\rangle$ and $|\psi_2\rangle$ are not normalized. As pointed out in Refs. 8 and 22, to obtain correct values of transfer integrals, a standard symmetric orthogonalization process[24] should be applied to basis set $(|\psi_1\rangle, |\psi_2\rangle)$ and Hamiltonian matrix H, so that

$$H' = X^{+}HX, \tag{7}$$

and the new basis set is expressed as

$$|\psi_1'\rangle = X_{11}|\psi_1\rangle + X_{21}|\psi_2\rangle,$$

$$|\psi_2'\rangle = X_{12}|\psi_1\rangle + X_{22}|\psi_2\rangle, \tag{8}$$

where X is the transformation matrix. The new basis set $\{\langle\psi_1'\rangle$ and $\langle\psi_2'\rangle\}$ is orthogonal and the off-diagonal matrix elements of H' are defined as the "effective transfer integrals,"

$$t_{\mathrm{eff}} = \langle\psi_1'|H'|\psi_2'\rangle. \tag{9}$$

III. RESULTS

Applying the generalized definition given above, we have calculated the effective transfer integrals for several nearest-neighbor molecular pairs in both BCP and Bphen crystals.

A. BCP crystal

The BCP crystal has a monoclinic structure with space group $C2/c$, as illustrated in Fig. 1. There are four equivalent molecules in each unit cell, represented by labels 1, 2, 4, and 5 in Fig. 1; the unit-cell parameters are $a=16.275$ Å, $b=10.692$ Å, $c=11.467$ Å, $\alpha=90.0°$, $\beta=109.198°$, and $\gamma=90.0°$. Molecules 1 and 2 are in an "antiparallel" configuration and so are molecules 4 and 5, with the nitrogen sides pointing to opposite directions. Molecules 3 and 6 correspond to the periodic translations of molecules 2 and 4 along the **−b** direction; molecules 7, 8, and 9 are the translations of

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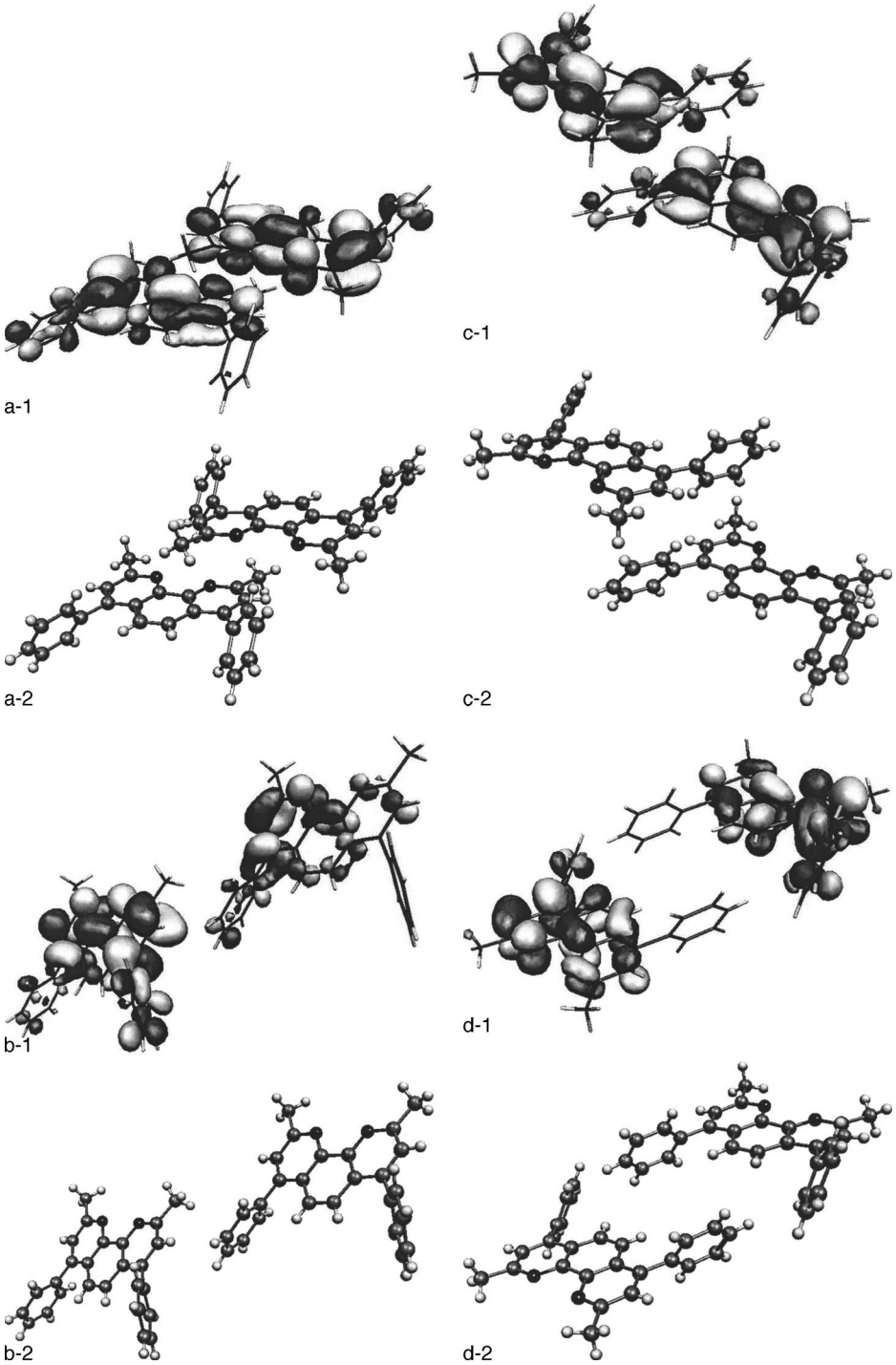

FIG. 2. LUMOs and geometry configurations of the BCP dimer pairs 1–4 [(a)–(d)]. The black spheres represent the nitrogen atoms, dark gray is for carbon, and light gray for hydrogen.

molecules 2, 3, and 5 along the **−c** direction. All the molecules at the bottom of the unit cell are the translations along the **+a** direction of the molecules on the top. Therefore, all the molecular backbones in the lattice are either in parallel or antiparallel configurations.

Taking molecule 5 as the central molecule, all the nearest-neighbor pairs were chosen as individual dimers; the effective transfer integrals defined in Eq. (9), as well as the "pure-state" transfer integrals $t_{1A,2A}$ (without orthogonalization) and $t^{o}_{1A,2A}$ (with orthogonalization), were calculated using the ADF package as described in the previous section. The numerical orthogonalization process of $|\psi_1\rangle$ and $|\psi_2\rangle$ was performed using the OCTAVE package.[25] The transfer integrals relevant for electron transport, obtained from the pure-state assumption and from the generalized definition, are given in Table I.

For planar molecules, extensive investigations have been carried out to study the relation between the transfer integrals and the dimer configurations.[26–28] When the two molecules are in cofacial or near-cofacial configurations, it is considered that the perpendicular distance and the lateral displacement between the two molecules are crucial factors in determining the transfer integrals. A dimer with a short perpendicular distance and negligible lateral displacements is expected to lead to a large transfer integral. In Table I, we

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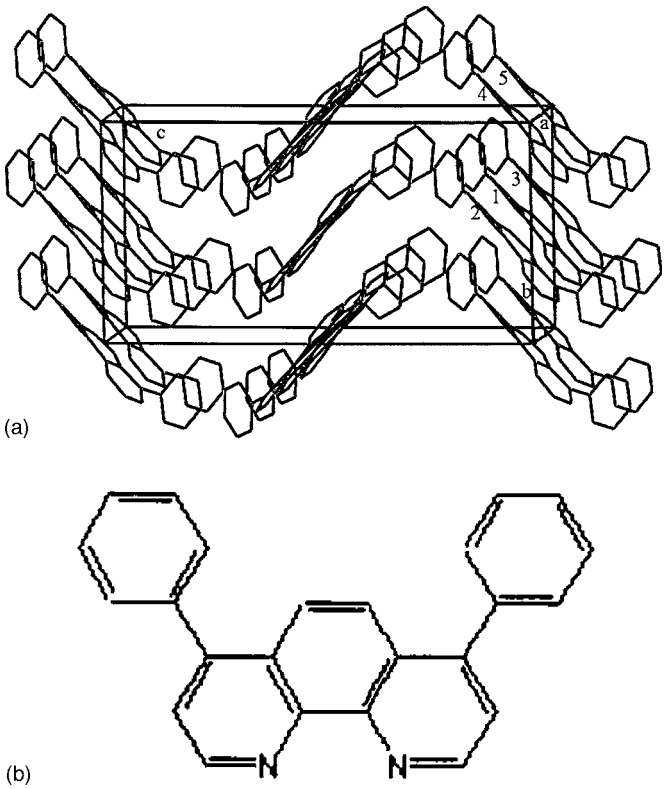

FIG. 3. Bphen crystal structure (a) and chemical structure (b).

give for each dimer the perpendicular distance and lateral displacements as well as the distance between the centers of mass (c.m.'s) of the monomers.

We note that, when comparing the $t_{1A,2A}$ and $t^{o}_{1A,2A}$ values for pair 1, the value including the orthogonalization procedure is about 40% smaller than the one in the absence of orthogonalization, which is due to the removal of the nonzero overlap between the initial and final states. This result is consistent with the trends observed in Ref. 22. The same trends are observed in all the other pairs reported in Table I.

The results obtained from Eq. (9), using the generalized definition of the transfer integral, indicate for pair 1 an absolute value for t_{eff} about 40% smaller than for $t^{o}_{1A,2A}$ and a different sign. (In Marcus theory, since the electron-transfer rate depends on the square of the transfer integral, such a sign change does not affect the rate.) The largest transfer integral, on the order of 0.04 eV, is found between molecules 5 and 4 (or molecules 1 and 3 or 8), which have a perpendicular distance of 1.620 Å. The second largest value is between molecules 5 and 7 (or 8), which have a perpendicular distance of 1.129 Å. Although pair 2 has a shorter perpendicular distance than pair 1, the lateral displacement along the molecular long axis in pair 2 is twice as large as in pair 1, which significantly reduces the transfer integral of pair 2.

Applying a tight-binding approximation for an infinite stack of molecules 5 and 4 along the c direction would lead to an electron bandwidth on the order of 0.15 eV. For the sake of comparison, we note that such a value is more than twice smaller than the hole bandwidth in rubrene,[29] for which hole mobilities on the order of 20 $\mathrm{cm}^2/\mathrm{V\,s}$ at room temperature have been reported.

Another interesting aspect comes from the comparison between pairs 2 and 3. The $t_{1A,2A}$ and $t^{o}_{1A,2A}$ transfer integrals are very close to one another (within 1 meV); however, the transfer integral t_{eff} of pair 2 is about one-half (7 meV) larger than that of pair 3. This result comes from the balance between two opposite structural features: on the one hand, there occurs a much larger perpendicular distance (by a factor of 4) in pair 3; on the other hand, pair 3 has much smaller lateral displacements. It is important to realize that this difference can also be highlighted via a comparison of the $(c_{1A}, c_{1B}, c_{2A}, c_{2B})$ coefficients between the LUMO levels of pairs 2 and 3 (which are directly provided in the ADF output). The coefficients for the LUMO of pair 2 have values of −0.3883, −0.2624, −0.858, and 0.1882; for the LUMO of pair 3, they are −0.7526, −0.0115, −0.6544, and 0.0195. Thus, for pair 2, the contributions from the LUMO+1 levels of each monomer to the LUMO level of the dimer are significant, which is consistent with t_{eff} being significantly different from $t^{o}_{1A,2A}$. In contrast, for pair 3, the contributions from the LUMO+1 levels of the two monomers are negligible; as a consequence, the t_{eff} value is not modified with respect to the $t^{o}_{1A,2A}$ value.

The effective transfer integral of pair 4 is very small, although the perpendicular distance in the dimer is about 1.1 Å shorter than in pair 3 while the c.m. distances are similar. A simple explanation of this large difference can be found by examining the geometry configurations and LUMO orbitals of the two pairs, see Figs. 2(d) and 2(c). Figure 2 shows that the LUMOs in all pairs are more localized on the nitrogen side of the phenanthroline moiety. In pair 4, the two monomers are arranged in a configuration where the nitrogen sides point in opposite directions, so that the segments where the LUMOs are mainly localized have the largest spatial separation. In pair 3, the two monomers are in a configuration, with the nitrogen sides quite close to one another, that results in a much larger transfer integral. From this observation, it is useful to point out that not only the distance between the monomers has to be considered to understand the rate of charge transfer but also the degree of localization of the charge carrier wave function on a given molecule. As for

TABLE II. Transfer integrals calculated for electron transport in the Bphen crystal from Eq. (1) (with and without orthogonalization) and from Eq. (9). The C–C values refer to the distance between the centers of mass of the two monomers. P is the perpendicular distance between the two phenanthroline molecular planes, L is the displacement along the molecular long axis, and X is the displacement along the short axis.

Bphen		C–C (Å)	P (Å)	L (Å)	X (Å)	$t_{1A,2A}$ (eV)	$t^{o}_{1A,2A}$ (eV)	t_{eff} (eV)
1→4	Pair 1	6.509	3.415	4.190	3.6265	−0.073	−0.047	−0.037
1→2	Pair 2	7.253	0.000	0.000	7.253	0.023	0.015	0.015

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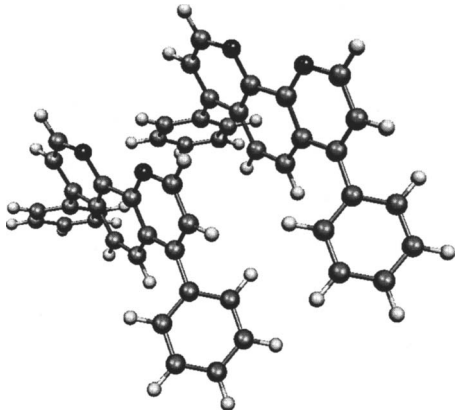

FIG. 4. Dimer configuration of pair 1 in the Bphen crystal. The black spheres represent the nitrogen atoms, dark gray is for carbon, and light gray for hydrogen.

pair 5, the transfer integral is vanishing due to the much larger perpendicular distance than in all other pairs.

B. Bphen crystal

The same procedure was carried out for the Bphen crystal, which has an orthorhombic structure with *C*2*cb* space group and lattice parameters $a=7.253$ Å, $b=10.810$ Å, and $c=21.14$ Å, as shown in Fig. 3. The molecules are arranged in columns perpendicular to the *c* direction; as a result, the transfer integrals between molecules in adjacent columns are all vanishing, so that they will not be discussed below. In Fig. 3, molecules 3 and 2 are periodic translations of molecule 1 along the $\pm\mathbf{a}$ direction, and molecules 4 and 5 are the translations of molecules 1 and 3 with a displacement of $(+\mathbf{a}/2-\mathbf{b}/2)$. In contrast to the BCP crystal, where the molecules are arranged in either parallel or antiparallel configurations, the Bphen molecules are all arranged in a parallel configuration within a column, with the nitrogen sides pointing to the same direction.

Taking molecule 1 as the central molecule, the calculated transfer integrals from 1 to 4 (or 3–5), pair 1, and from 1 to 2 (or 3), pair 2, are given in Table II. The largest transfer integral is calculated for pair 1, that is, along the diagonal direction within the *ab* plane; the second largest value, obtained for pair 3, corresponds to charge transfer along the *a* axis. The values of the transfer integrals calculated for pairs 1 and 2 in the Bphen crystal thus turn out to be very similar to those for pairs 1 and 3 in BCP, although the dimer configurations are completely different (see Fig. 4 for pair 1 of Bphen and compare to Fig. 2).

We have also calculated the intramolecular reorganization energies for an electron transfer in Bphen and BCP, following the procedure detailed in the literature.[28] Values of 0.41 and 0.46 eV are obtained, respectively, at the B3LYP/6-31G(d,p) level. These are large values although somewhat smaller than in silole-based electron-transport materials [where they reach 0.5 eV (Ref. 30)]. The presence of the extra methyl groups in BCP explains the increase in intramolecular reorganization energy versus Bphen.

We tried to obtain a very crude comparison of the respective hopping rates in Bphen and BCP at room temperature by applying the simple Marcus equation given in the Introduction. We considered in each compound: (i) the direction with the highest transfer integral, (ii) the intramolecular reorganization energies given above, and (iii) values for the medium reorganization energy (λ_s) varying between 0.0 and 0.5 eV (taken to be identical for the two compounds). Whatever the choice of λ_s, the hopping rates are found to be of the same order of magnitude for the two compounds and about twice larger for Bphen; for instance, for $\lambda_s=0.5$ eV, the room-temperature rates are calculated to be 5.8×10^8 s^{-1} for Bphen and 3.1×10^8 s^{-1} for BCP (interestingly, applying Einstein's diffusion equation to this room-temperature Bphen rate results in a mobility estimate of 10^{-4} cm^2/V s).

IV. CONCLUSION

Although the molecular configurations for adjacent molecules of BCP or Bphen systems in the amorphous state are not well characterized, our calculations on the dimer configurations in the crystalline state provide an initial understanding of the charge-transport properties in these sytems. We find that the largest transfer integrals in both systems as well as the intramolecular reorganization energies present similar values; thus, comparable electron-transport properties can be expected in BCP and Bphen. An electron mobility measurement on BCP would test the validity of this expectation.

We have also shown that it is important to use the generalized definition of effective transfer integral proposed in this work in order to obtain reliable electron couplings in systems where the LUMO (HOMO) level of a dimer is contributed to by more than just the LUMO (HOMO) levels of the monomers. Preliminary results of band-structure calculations on the BCP and Bphen crystals[31] confirm the adequacy of this generalized approach by providing bandwidths along specific crystal directions that agree well with the t_{eff} values reported here.

ACKNOWLEDGMENTS

The work at Georgia Tech has been partly supported by BASF, the Office of Naval Research, and the National Science Foundation CRIF Program under Award No. CHE-0443564 and STC Program under Award No. DMR-0120967. The authors acknowledge many stimulating discussions with Veaceslav Coropceanu and Demetrio da Silva Filho.

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