Charge Hopping in Molecular Wires as a Sequence of Electron-Transfer Reactions

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Received: January 28, 2003; In Final Form: March 5, 2003

Charge transport in molecular wires is investigated theoretically within the framework of a simple hopping model. The model suggests that each elementary hopping step can be treated as an electron-transfer reaction between ionic and neutral states of π-conjugated structural units coupled through σ-bonded spacers. Within this mechanistic picture, the ability of wire to transport a charge depends crucially on the internal reorganization energy, λ. Using unrestricted Hartree−Fock and density functional theory methods, we evaluate λ for benzene, 3-methylbiphenyl, 2,6-dimethyl-1-phenyl-pyridinium (DMPP), and 4-(*p*-suflhydrylphenylpyridinium-1′-yl)-2,6-dimethylpyridinium, selected as representative examples of structures used for chemical attachment to σ-bonded structural spacers in real molecular wires. The results are exploited to estimate the upper and lower limits of hole and electron mobility in wires that consist of aromatic ring units linked to the antipodal bridgeheads of σ-bonded molecular "cages", bicyclo[1.1.1]pentane (BCP), cubane (CUB), and bicyclo[2.2.2]-octane (BCO). Our calculations show that the highest mobility of holes is expected for coplanar alignment of aromatic rings at the end of molecular cages as, in this configuration, the electron coupling is most efficient. We also analyze the situation in which thermally induced twisting motion destroys coplanarity of aromatic rings. The obtained results suggest that, for wires with the BCO spacer, hopping transitions are slower than twisting motion and, therefore, the mean hole mobility is determined by the equilibrium average twist angles. In the opposite case, relevant to the benzene/BCP and benzene/CUB systems, large deviations of the twist angles from the equilibrium value represent a bottleneck for the transport process.

1. Introduction

According to the simplest definition, a molecular wire consists of a molecule connected between two reservoirs of charge carriers, usually metallic leads. The molecular orbitals coupled to the leads provide favorable pathways for electrons or holes. As was suggested in the early 1970s,[1] such systems should have the ability to rectify current. Since then, conductance in molecular wires has become an exciting, challenging, and rapidly expanding field of molecular electronics,[2] crossing the borders between many areas of physics, chemistry, and engineering. Experimental studies have increased over the past few years as a result of recent developments in nanofabrication, self-assembly, and scanning tunneling microscopy techniques.[3−7] The application of these techniques to molecular wires has led to discoveries of negative differential resistance[4] and reversible conductance transitions,[5] which can form the basis for a completely new class of electronic devices with properties quite different from CMOS (complementary metal oxide semiconductor) semiconductor devices and with applications ranging from memory cells to high-frequency oscillators and logic components. A key point in providing guidelines for the design of such nanoscale electronic devices is a deeper understanding of the relation between structure and electrical conductivity of molecular wires, and significant research efforts are currently being made to achieve progress in this direction.[3c,8]

Theoretically, conducting properties of wires are expected to depend on their molecular structure for two reasons. The first lies in the fact that structure defines the width and the position of the HOMO/LUMO gap with respect to the Fermi level of the contacts. Therefore, the barrier for charge injection at the metal/molecular junction will depend on the structural building blocks of a wire. The second reason is the influence of molecular structure on transport of injected charge carriers. For the coherent mechanism of motion, this influence can be associated both with the structure-dependent energy level alignment at the surface of the metal/molecular interface and with the electronic mixing along the molecular chain. For instance, if the molecular structure of the wire and the work function of the contact cause the Fermi level to be in the middle of the broad HOMO/LUMO gap, transport properties are controlled by the unistep superexchange-mediated charge transfer.[2e,9] This mechanism, with the characteristic exponential length dependence of conductance, is expected to be dominant for short alkanes and for short conjugated wires. If, however, a structure is favorable for the resonant or nearly resonant alignment of the wire site energy levels and the Fermi level, charge carriers are transported via coherent or incoherent electron tunneling. Contrary to superexchange-like transport, injection at resonance will result in only weak length dependence of the coherent conductance, which should scale linearly with the transmission coefficient and therefore with the number of transverse eigenmodes in the wire. As follows from measurements of the low-temperature electric

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10.1021/jp034225i CCC: $25.00

conductance,[10] single-wall carbon nanotubes furnish a representative example of such behavior.

In both cases considered above, charge carriers are suggested to move along the wire coherently. This implies that the primary phase of the wave function characterizing a moving particle remains unchanged. The disruption of conjugation, caused for instance by steric repulsion, defects in structural unit packing, or incorporation of saturated bonds within π-conjugated molecules, can strongly disturb the phase of coherent motion. Furthermore, recent experimental and theoretical studies of charge transport in columnar stacks of a triphenylene dimer[11] and in stacks of Watson−Crick base pairs[12−14] suggest that the initial phase randomizes in time because of strong electron−vibration interaction. This leads to a temporal localization of electrons and/or holes on the sites with proper energetics and, hence, to another mechanism of charge motion: now, transport along the wire occurs via a series of hops between neighboring sites serving as centers of temporary charge localization. The same result can be obtained from a density matrix treatment that considers the vibrational interaction as a dissipative term.[15] If the overlap between wave functions of a charge residing on two adjacent centers is strong, each elementary step of such hopping motion can theoretically be treated within the framework of the tight-binding approximation.[16] For weak overlap, however, the mechanism of the elementary hopping step becomes analogous to an electron-transfer reaction, in which an electron is exchanged between two neighboring molecules C_i and C_{i+1}, one being in the neutral state and the other being in the ionic state. For electron- and hole-transfer processes, this mechanism of the elementary hopping step can be symbolized as follows

$$C_i^- + C_{i+1} \rightarrow C_i + C_{i+1}^- \tag{1a}$$

$$C_i^+ + C_{i+1} \rightarrow C_i + C_{i+1}^+ \tag{1b}$$

where the subscript i defines only the position of the molecule C rather than its chemical nature. The rate constant of these elementary hopping steps can be expressed in terms of the free energy difference between reactants and products, ΔG^0, and the reorganization energy.[17,18] Because the right- and left-hand sides of eq 1 are chemically identical, $\Delta G^0 = 0$.

Recently, Sakanoue et al.[19] undertook a molecular orbital study of several arylamines to ascertain whether the hole mobility is related to the internal reorganization energy, λ. As follows from their results, λ decreases in the order dimethylaniline > methyldiphenylamine > triphenylamine, whereas the hole mobility for dimers of these amines changes in the reverse sequence. This suggests that the reorganization energy can be an important factor that governs the mobility of charge carriers in molecular wires consisting of π-conjugated units connected by σ-bonded organic spacers. Recent proposals to exploit "cage" molecules such as bicyclo[1.1.1]pentane (BCP), cubane (CUB), and bicyclo[2.2.2]octane (BCO) as spacers revives interest in such wires, which are expected to be potentially important elements in molecular electronic circuits and logic devices.[20]

Mechanisms of charge transport in molecular wires composed of alternating π-conjugated and σ-bonded structural units have two main aspects. The first includes electron coupling that provides the pathway for charge transfer through spacers with saturated bonds. Different issues related to this aspect of the problem have been addressed in a number of experimental[21] and theoretical works.[22−24] In particular, Pati and Karna[24] recently investigated the relation between electron coupling and molecular structure of σ-bonded cages using BCP, CUB, and BCO as representative examples of spacers important for molecular electronics. The second aspect is energetics of charge-transfer states arising as a result of temporal localization of carriers within π-conjugated units of the wire.

In the present paper, we focus on this energetic aspect with special emphasis on the relationships among geometric configurations, electronic structure, and transport properties of molecular wires with π-conjugated and σ-bonded units. Our main concern is the effects governing motion of charge carriers once their generation has already occurred. Therefore, various mechanisms of charge injection, the distribution of the applied electric field along the wire, the field dependence of the injection barrier height, and other factors controlling charge generation remain beyond the scope of our consideration. Instead, we concentrate on the analysis of charge-migration phenomenon in terms of the hopping model, which treats the motion of electrons or holes as a series of hops between π-conjugated units of the wire. In addition, the overlap between wave functions of a charge temporarily localized on two neighboring π-conjugated units is assumed to be sufficiently small to consider each elementary hopping step as the nonadiabatic electron-transfer reactions in eqs 1. In this case, the internal reorganization energy λ becomes an important parameter that establishes a link between transport coefficients and structural features of π-conjugated units of molecular wires. Using unrestricted Hartree−Fock (UHF) and unrestricted density functional theory (UDFT) methods, we evaluate λ for several "molecular wire" candidate molecules suitable for their chemical attachment to the termini of BCP, CUB, and BCO cages.

The results suggest that the computational methodology exploited in our studies can be used to select molecules that provide higher drift mobilities of hopping charges than other candidates for π-conjugated units because of the lower reorganization energy. Our estimates of λ together with information about electronic coupling[21−24] allow us to determine conditions under which transport coefficients have maximum values. We show that the upper limit of hole mobility is attained if aromatic rings attached to cage termini are coplanar along the entire system; then hole transport is governed exclusively by the reorganization energy, and the value of the electron-transfer matrix element at zero twist angles. However, thermally induced twisting can strongly reduce hole mobility to much smaller values if electron-transfer reaction 1b is much faster than conformational changes in the wire. On the basis of our estimates of the lower and upper limits of transport coefficients, we infer that information about static electronic coupling is often insufficient to make reliable predictions concerning transport properties of molecular wires composed of π-conjugated fragments connected by σ-bonded cages.

2. Theoretical

2.1. Transport Properties. To describe charge transport in a wire with alternating π-conjugated and σ-bonded structural units, we consider this molecular system as a one-dimensional chain (Figure 1). The chain contains regularly located sites C_i labeled by the index i ($i = 0, 1, ..., N$) that correspond to N identical π-conjugated molecular units. They are linked by spacers (throttles) $S_{i,i+1}$ with saturated bonds only. Because π-conjugated molecules usually have lower ionization potentials and higher electron affinities as compared with saturated molecules,[25] generated charges will localize exclusively on C. Accordingly, charge carriers can be transported along the wire via multistep hopping that involves C^+ cations and C^- anions as "resting states" for holes and electrons, respectively. If we

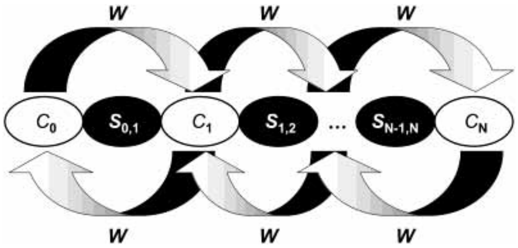

Figure 1. One-dimensional chain formed by chemically connected π-conjugated (sites C) and σ-bonded (sites S) molecular units. A charge carrier initially localized on site C_0 undergoes diffusive motion along the chain as a result of a series of transitions between adjacent sites C_i and C_{i+1} through spacer $S_{i,i+1}$ with saturated bonds only. These transitions, shown by arrows, proceed at the rate W given by eq 2, as explained in the text.

assume now that each step of hopping motion can be viewed as nonadiabatic electron-transfer reactions (eqs 1), familiar theoretical results[17,18] enable one to express the rate of charge motion between neighboring π-conjugated units, W, in terms of the reorganization energy λ and the electronic coupling matrix element V. In the simplest case, where temperature is sufficiently high that vibrational modes can be treated classically, this yields[17a]

$$W = \frac{V^2}{\hbar}\left(\frac{\pi}{\lambda k_B T}\right)^{1/2} \exp\left(-\frac{\lambda}{4 k_B T}\right) \tag{2}$$

where k_B is the Boltzmann constant and T is the temperature.

Once the hopping rate W through the σ-bonded spacer of effective length L is defined, the diffusion coefficient D of charge carriers can be estimated from the expression

$$D = L^2 W \tag{3}$$

This, in turn, allows the evaluation of the drift mobility of hopping charges, μ, from the Einstein relation

$$\mu = \frac{e}{k_B T} D = \frac{e L^2 W}{k_B T} \tag{4}$$

where e is the electronic charge.

Equations 2−4 suggest that, as in other electron-transfer processes,[18d,i,j,n] hopping transport of charge carriers in the molecular wires under consideration is determined both by electronic coupling between C_i^+ (or C_i^-) and C_{i+1} sites through a spacer $S_{i,i+1}$ and by reorganization of π-conjugated units resulting from charge localization and release. Note that, according to eqs 1−3, both the diffusion coefficient D and the drift mobility μ turn out to be independent of the strength of the applied electric field. This can be expected because the external electric field can significantly influence the rate of electron transfer only if this process leads to the formation of the ion pair state through the charge separation.[18o] Obviously, reactions 1a and 1b do not produce ion pairs and cause charge displacement rather than charge separation. Therefore, it is not surprising that the hopping rate W in eqs 3 and 4 remains field-independent.

The values of matrix element V in eqs 1−3, which characterize electron coupling through σ-bonded cage spacers, are available from the results of ab initio Hartree−Fock and semiempirical calculations[18f,21e,21d,21j,22,23,26] performed within the framework of the Marcus−Hush two-state model.[17] Especially efficient is an approximate theoretical approach, which allows an estimate of V based on properties of the CH_2-S-CH_2 diradical (S = spacer) and its oxidized (hole-transfer) and reduced (electron-transfer) forms, where only the energies of certain orbitals or electronic states need to be known.[21j,k] Estimates of V values are also possible on the basis of the measured rate constant for intramolecular charge transfer between a π-conjugated donor and acceptor pair connected by a σ-bonded spacer.[21] Miller and co-workers[21g,j] have studied this process in solution by a pulse radiolysis technique and have used their experimental data to estimate electronic coupling matrix elements for a number of spacers, including such σ-bonded cages as CUB and BCO.[27] Thus, the only unknown parameter in eqs 2−4 for transport coefficients D and μ is the reorganization energy λ. In the next section, we briefly describe a methodology that allows for the calculation of this quantity for relatively simple molecules serving as π-conjugated units of the molecular wires discussed in this work.

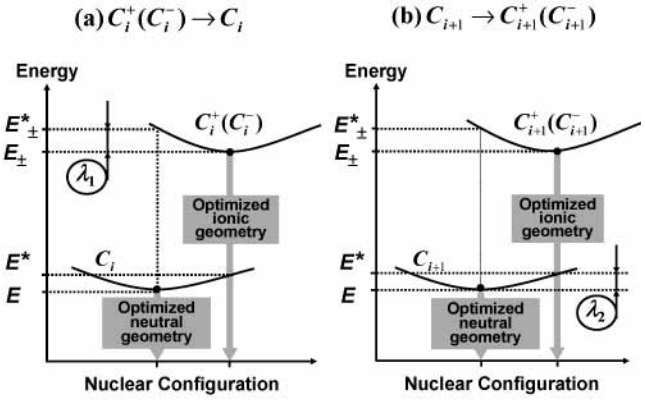

Figure 2. Energetic and geometrical changes involved in the elementary step of charge hopping in molecular wires with π-conjugated structural units and σ-bonded spacers. (a) Removal of a charge from the π-conjugated unit C_i and (b) addition of this charge to the neighboring unit C_{i+1} are shown separately. These two processes are characterized by reorganization energies λ_1 and λ_2, respectively. Other notations are given in the text.

2.2. Reorganization Energy. The reorganization energy λ is usually defined as the change in free energy if the reactant state were to distort to the equilibrium configuration of the product state without transfer of the charge.[17d,18i,j,m,23b] Generally, the λ value is determined by fast changes in molecular geometry (the inner contribution) and by slow variations in solvent polarization of the surrounding medium (the outer contribution). In the case of isolated (solvent-free) wires, however, the latter contribution can be neglected, so that the structure differences between the equilibrium configurations of π-conjugated units in neutral and ionic states become the dominant factor.[28]

Our calculations of the reorganization energy associated with different geometries of these two states are based on the method schematically illustrated in Figure 2. For each of the molecules selected to be a π-conjugated unit in the wire, the geometry is optimized for both neutral and ionic states. This leads to two distinct nuclear configurations of the oxidized C_i^+ (or reduced C_i^-) unit before and after hole (or electron) transfer, as shown in the left-hand side of Figure 2. A similar picture sketched in the right-hand side of this figure pertains to the adjacent unit C_{i+1}, which is assumed to be initially neutral. Accordingly, the elementary hopping step in molecular wires is characterized by a set of four energy values. Two of them, denoted by E and E^*, refer to the neutral unit in optimized neutral and ionic geometries, respectively; another two, $E^*_\pm$ and $E_\pm$, stand for the energies corresponding to the neutral and ionic geometries of the oxidized (or reduced) unit.[29] By definition, the difference $E^*_\pm - E_\pm$ represents the reorganization energy λ_1 associated with the removal of a hole (or electron) from the C_i site of the molecular wire. Analogously, the reorganization energy λ_2 for the addition of a hole (or electron) to the neighboring site C_{i+1} is given by $E^* - E$. As a result, the λ value for the elementary step of charge hopping can be obtained from the expression[8b,d,30]

$$\lambda = \lambda_1 + \lambda_2 = (E^*_\pm - E_\pm) + (E^* - E) \tag{5}$$

In addition to the reorganization energy, the approach considered above allows for an estimation of the vertical ionization potential I (or the electron affinity, EA) of neutral π-conjugated molecules, as exemplified in several publications.[8b,d,30] This possibility becomes evident from the dependencies of energy on nuclear configuration qualitatively shown in Figure 2. For instance, in the case of hole hopping (see eq 1b), inspection of this figure reveals that the vertical ionization potential of the isolated neutral molecule can be written as

$$I = E^*_+ - E \tag{6}$$

while EA of the isolated cation is given by

$$\mathrm{EA} = E_+ - E^* \tag{7}$$

3. Results and Discussion

To calculate energetics of charge-transfer states and transport coefficients of charge carriers within the framework of the theoretical approach considered in section 2, each element C_i and S_i of the model system (see Figure 1) should be replaced by a specific molecular structure. The results presented below are obtained for C_i = benzene, 3-methylbiphenyl, 2,6-dimethyl-1-phenyl-pyridinium (DMPP), or 4-(p-sulfhydrylphenylpyridinium-1′-yl)-2,6-dimethylpyridinium (SPPDMP) and S_i = BCP, CUB, or BCO. These molecules were chosen as representative structures used as localization sites and as σ-bond "throttles" along the chain of the molecular wires that have already been obtained chemically; see, e.g., ref 20. The actual bridging groups in these wires have the protons removed to permit bonding to the next unit in the chain, but for simplicity, we will use the nomenclature appropriate to the closed-shell parent, e.g., benzene for p-phenylene. The choice of benzene and 3-methylbiphenyl as the C_i units of the investigated systems was also convenient for testing the accuracy of our calculations by comparison of the obtained results with experimental and theoretical findings reported in the literature.

Calculations were performed with the Jaguar program[31a] both at the UHF and at the UDFT level with the B3LYP functional. In both cases, we used the 6-31G* basis set and ultrafine numerical accuracy. Gaussian 98[31b] was used for part of the UDFT calculations. Default cutoff values for geometry optimizations and default integration grids were used. Because geometries exhibit distortion when charge is added or removed, symmetry was not used for any calculations, except for estimates of V for electron transfer across spacers.

3.1. Molecular Configurations.

The main results of the UDFT geometry optimization for the neutral, oxidized, and reduced structures of benzene, 3-methylbiphenyl, DMPP, and SPPDMP are presented in Figure 3. As follows from the calculations performed, the only consequence of charge localization for the configuration of benzene is the Jahn–Teller deformation of the aromatic ring due to the alteration of bond lengths and bond angles. For 3-methylbiphenyl, some additional changes occur. In particular, our numerical data show that the geometry of this molecule is less planar than the geometry of ions. Indeed, according to our findings, a torsion angle, φ, between the two aromatic rings reduces from 38.7° for neutral state to 20.7° for the 3-methylbiphenyl cation. Note that the anion structure exhibits a much smaller torsion angle. In this case, $\varphi = 0.4°$, and the reduced geometry of this compound turns out to be almost planar. The ionic structures of 3-methylbiphenyl also have a shorter bond between the two aromatic rings in comparison with the neutral configuration. The changes in the lengths of inter- and intra-ring bonds with respect to the neutral molecule indicate that the bond-length alternation in 3-methylbiphenyl ions acquires a quinoid-like character.

Variations of the 3-methylbiphenyl configuration caused by charge localization are very similar to those reported by Malagoli and Brédas for biphenyl.[8d] In both cases, the geometry of the radical cation shifts toward planarity and the intra-ring bond becomes shorter in comparison with that in the neutral structure. Moreover, the values of geometrical parameters calculated for the neutral molecule and the cation are nearly the same. In particular, a torsion angle and the bond length between the two aromatic rings in the neutral geometry of biphenyl are shown to be 38.4° and 1.49 Å,[8d] respectively, in good agreement with our findings for 3-methylbiphenyl (cf. Figure 3b). For the cation configuration, the values of these parameters are reduced to 19.3° and 1.44 Å, respectively, and the results obtained for 3-methylbiphenyl and biphenyl cations differ by only 1.4° and 0.01 Å. This allows the conclusion that, as expected, the geometries of the investigated neutral and ionic structures are not sensitive to the presence of the CH_3 group in the meta position.

Configuration changes in DMPP induced by charge localization deserve special consideration. The most obvious distinction of DMPP from the molecular systems discussed above is a positive charge on the nitrogen atom. This feature, utilized in fabrication of the potential rectifying molecular diode,[20] can lead to much weaker influence of hole localization on the DMPP geometry as compared to 3-methylbiphenyl and biphenyl. The UDFT studies of DMPP geometry strongly support this expectation. In particular, our calculations show that oxidation has essentially no effect on the torsion angle and the bond length between the two rings (Figure 3c). By contrast, addition of an electron (to form the neutral species) leads to the more planar configuration and to a shorter intra-ring bond as compared to the primary DMPP structure. For the reduced (neutral) geometry, however, the angle between the planes of two rings calculated for DMPP turns out to be almost twice as large as the torsion angle in the neutral 3-methylbiphenyl structure. This can be attributed to the combination of two factors. One of these factors is steric hindrance, which is less pronounced in 3-methylbiphenyl. Another is preferable localization of the electron added to DMPP on the ring containing nitrogen. The lack of such strongly localized orbitals in the case of 3-methylbiphenyl favors a more planar geometry for this compound.[32]

For SPPDMP, the protonated form was considered, as attachment to the spacer requires formation of a positively charged nitrogen. Geometry changes in SPPDMP upon reduction to some extent parallel the changes observed in DMPP; however, two positively charged pyridinium rings are present here. The oxidation of SPPDMP was not considered, as it is energetically unfeasible for a molecule already bearing a double positive charge. Patterns of changes of bond lengths upon reduction in the 2,6-dimethylpyridinium moieties in both DMPP and SPPDMP are the same, but the magnitude of change is smaller in SPPDMP. For example, the C_{ring}–N bond length in DMPP

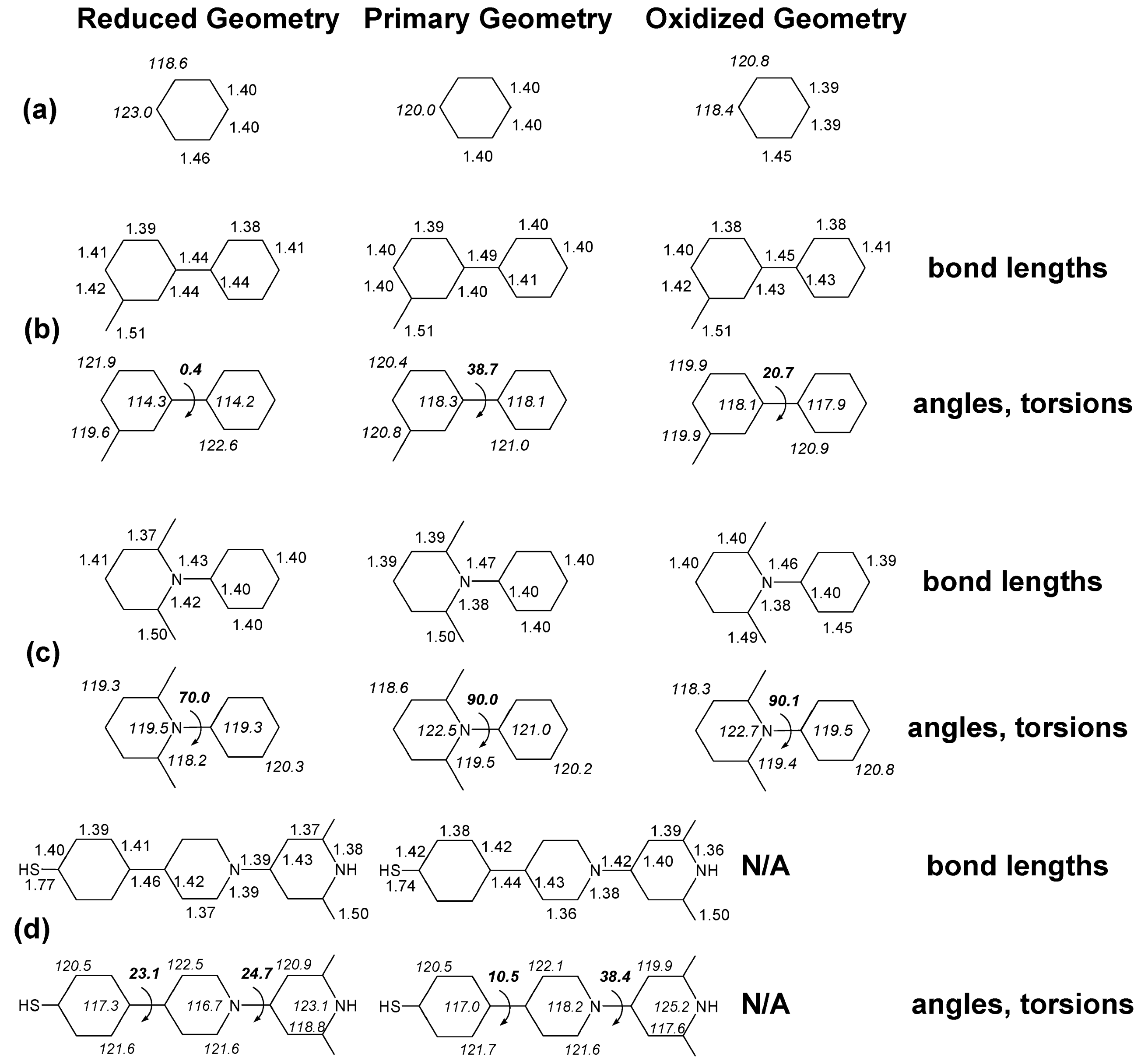

Figure 3. UDFT-optimized geometric parameters for the primary, oxidized, and reduced configurations of (a) benzene, (b) 3-methylbiphenyl, (c) DMPP, and (d) SPPDMP (no oxidized geometry). Calculated bond lengths (Å) and bond angles (degrees) are shown using roman and italic fonts, respectively. A torsion angle between two aromatic rings (degrees) is indicated in bold.

increases by 0.04 Å, whereas in SPPDMP this bond in the 2,6-dimethylpyridine unit increases by only 0.02 Å. An increase in the $C_{ring}-N$ bond length by 0.01 Å upon reduction is also observed in the second pyridinium unit in SPPDMP (middle ring). Significantly, the dihedral angle between the two pyridinium rings of SPPDMP decreases considerably after reduction. Together with the shortening of the bond connecting two heterocycles, this strongly suggests that charge is delocalized between two pyridinium rings in the reduced structure.

3.2. Energetics. To evaluate energy parameters of states involved in the process of electron and/or hole transfer, the primary electronic configuration and two configurations with an extra positive and negative charge were considered for each molecule under investigation, and the energies of these configurations were calculated for three UDFT-optimized geometries. The numerical data obtained (see Figure 4) show the difference in energy between the same electronic configurations at distinct geometries. The results related to hole transfer (panel A) show that the energy difference for the neutral configuration, $\lambda_1 = E^* - E$, is almost equal to the difference $\lambda_2 = E_+^* - E_+$ evaluated for the electronic configuration with an extra positive charge. The approximate equality $\lambda_1 \approx \lambda_2$ also remains valid for electron transfer (see panel B), although, in the latter case, both λ_1 and λ_2 are larger than the values found numerically for the hole-transfer process. These findings suggest that potential energy surfaces involved in the elementary step of charge hopping can be treated as parabolic.

The calculated values of energy parameters characterizing primary (neutral for benzene and 3-methylbiphenyl, cationic for DMPP), oxidized, and reduced structures of benzene, 3-methylbiphenyl, and DMPP at different geometries allow an estimation of the ionization potential I and the reorganization energy λ from eqs 5 and 6. The results of UDFT calculations together with available experimental data[33,34] are summarized in Table 1. The ionization potentials of benzene and 3-methylbiphenyl evaluated with the UDFT method are in reasonable agreement with the measured values. According to our UDFT estimates, 3-methylbiphenyl has the largest internal reorganization energy

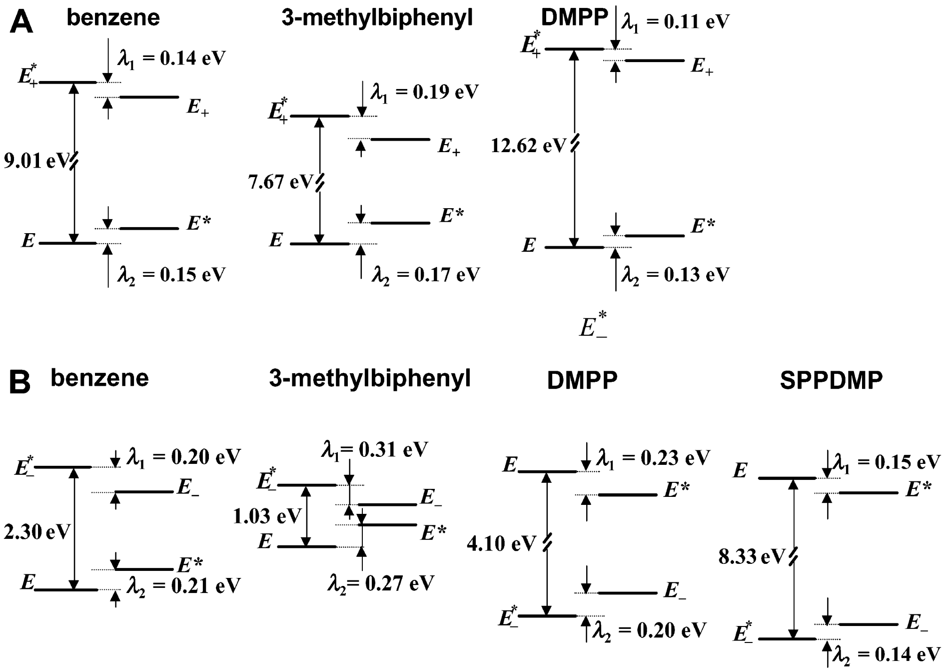

Figure 4. Energy parameters characterizing primary, oxidized, and reduced structures of benzene, 3-methylbiphenyl, DMPP, and SPPDMP (primary and reduced structures only) at different geometries. Parameters *E* and E_+^* pertaining to the primary and oxidized structures at the UDFT-optimized primary geometry are given in panel A, together with energies E_+ and E^* calculated for oxidized and primary structures at oxidized geometry. Analogous data for the UDFT-optimized primary and reduced geometries are presented in panel B. In all cases, the energy of the primary structure at the primary geometry is chosen as the reference point.

TABLE 1: Ionization Potentials and Reorganization Energies for the Molecules Studied[a]

	ionization potential (eV)		reorganization energy (eV)[b]	
molecule	this work[c]	experiment	hole transfer	electron transfer
benzene	9.01	9.24[d]	0.29 (0.37)	0.41 (0.53)
3-methylbiphenyl	7.67	7.95[e]	0.36 (0.84)	0.58 (1.13)
DMPP	12.62	–	0.24 (0.46)	0.43 (0.86)
SPPDMP	–	–	–	0.29 (1.16)

[a] Theoretical values were obtained at the UDFT level with the B3LYP functional and the 6-31G* basis set. Numbers in parentheses are results of UHF/6-31G* calculations. [b] Calculated from eq 5 with values of λ_1 and λ_2 given in Figure 4. [c] Calculated from eq 6. [d] Value taken from ref 33, vapor phase. [e] Value reported in ref 34, vapor phase.

among the compounds investigated. In the case of hole transfer, λ computed for 3-methylbiphenyl coincides with the UDFT estimates for biphenyl made by Malagoli and Brédas.[8d] This coincidence is not accidental and can be explained by the very similar geometries of these molecules in the neutral and cationic states, as has already been discussed in section 3.1.

It is of interest to estimate ionization potentials using Koopmans' theorem and UHF calculations. For benzene, this yields $I = 9.04$ eV, in accord with the UDFT numerical data. This result compares nicely with the experimental value of 9.24 eV.[33] For 3-methylbiphenyl, however, the Koopmans ionization potential is found to be 9.00 eV in obvious contradiction with experimental and UDFT values in Table 1. The difference between the results provided by the two methods becomes even more significant in the case of DPPM: Whereas UDFT calculations yield $I = 12.62$ eV, the evaluation based on Koopmans' theorem gives $I = 8.11$ eV.

Calculations at the UHF level were also employed to obtain information about the internal reorganization energy. For benzene, our UHF results yield $\lambda = 0.53$ eV in the case of electron transfer. This value is consistent with $\lambda = 0.55$ eV found by Klimkans and Larsson[30a] for the same process using the UHF method with the 6-31G* basis. As has been shown by these authors,[30a] correlations included at the MP2 level reduce the internal reorganization of benzene to 0.44 eV. The latter result is compatible with the UDFT value $\lambda = 0.41$ eV obtained in the present work. Note that both UDFT and MP2 calculations include correlation effects absent in UHF. Therefore, it is not surprising that, for all of the molecules studied, UHF overestimates the internal reorganization energies in comparison with the UDFT method (see Table 1). Nevertheless, the UHF calculations demonstrate the same tendency as UDFT estimates: Both methods predict that λ for 3-methylbiphenyl is larger than λ for benzene and DMPP. In addition, our calculations at the UHF/6-31G* level show that, for electron transfer between 3-methylbiphenyl anion radical and neutral 3-methylbiphenyl, $\lambda = 1.13$ eV (0.58 eV at the B3LYP level). This result coincides with the λ value obtained by the UHF/DZP method for biphenyl involved in an analogous process.[35]

Reorganization energies calculated at the UHF level are always higher than those obtained at the B3LYP/6-31G* level (Table 1). Contributions to the reorganization energy are calculated as differences in energy for systems with the same number of electrons at two different geometries (eq 5). For this reason, effects due to the treatment of open- vs closed-shell systems at the UHF/RHF level, which might lead to overstabilization of the doublet species, will not contribute directly to systematic errors in the calculated reorganization energies. Most likely, spin contamination of the unrestricted wave functions results in poor optimized geometries for reduced and oxidized froms. For SPPDMP, the expectation value of S^2 is 1.86 at the UHF/6-31G* optimized geometry of the reduced form, instead of 0.75. The UHF geometry compared to the UB3LYP geometry of the reduced form of SPPDMP is more planar. At the same time, the primary HF geometry (unreduced SPPDMP) is characterized by larger dihedral angles between aromatic rings compared to the B3LYP-optimized structure. This results in

TABLE 2: Upper Bound for the Diffusion Coefficient *D* and the Drift Mobility *μ* of Holes in Molecular Wires at 290 K with Various Alternating *π*-Conjugated and *σ*-Bonded Structural Units[a]

molecular wire			
π-conjugated fragment	*σ*-bonded spacers	diffusion coefficient ($cm^2\ s^{-1}$)	drift mobility ($cm^2\ s^{-1}\ V^{-1}$)
benzene ring	BCP	0.54 (1.15)	21.6 (46.0)
	CUB	0.37 (0.37)	14.8 (14.8)
	BCO	5×10^{-3} (0.03)	0.2 (1.4)
3-methylbiphenyl unit	BCP	0.24 (0.52)	9.6 (20.8)
	CUB	0.16 (0.16)	6.4 (6.4)
	BCO	2×10^{-3} (0.02)	0.1 (0.6)

[a] Estimated from eqs 2−4 for room temperature. Parameters *L* and *V* taken from ref 24. Numbers without parentheses were obtained with *V* calculated at the UHF/STO-3G level. For BCP, CUB, and BCO, these calculations yield $V = 0.37$, 0.26, and 0.03 eV, respectively. Numbers in parentheses correspond to the case where *V* is evaluated at the UHF/DZP level. In this case, $V = 0.54$, 0.26, and 0.07 eV for BCP, CUB, and BCO, respectively. According to ref 24, the effective lengths of BCP, CUB, and BCO spacers are 4.77, 5.58, and 6.20 Å, respectively.

larger geometry differences between the primary and reduced forms at the UHF level as compared to DFT calculations. As a consequence, the UHF level of theory yields much higher values of the calculated reorganization energy. The reliability of the UHF calculations is questionable because of severe spin contamination ($\langle S^2 \rangle = 1.86$ for reduced SPPDMP). Therefore, DFT values of the reorganization energies are used to estimate charge-mobility parameters (Tables 2 and 3).

3.3. Transport Coefficients. The diffusion coefficient and the drift mobility of charge carriers in molecular wires with alternating *C* and *S* units were estimated from eqs 2−4 using the UDFT values of the internal reorganization energy (see Table 1) and information about the electron-transfer matrix element *V* available for BCP, CUB, and BCO spacers from the literature.[21g,j,22,24] Although the exact values of *V* for electron transfer through these *σ*-bonded cages are still unknown, reasonable estimates were made and used to evaluate electron-transfer parameters.

The diffusion coefficient *D* and the mobility *μ* of holes undergoing hopping motion along various molecular wires of general structure $-(CS)_n-$ are given in Table 2. The wires with *C* corresponding to DMPP are not included in the table as they are irrelevant to hole transport. In such wires, hole hopping between neighboring DMPP units is energetically unfavorable, since the ionization potential of DMPP moieties (ca. 12 eV as shown in Figure 4) exceeds the value $I \approx 10$ eV typical for *σ*-bonded spacers; it is more likely that, in this particular case, a charge can be transported along the wire via a series of electron hops. For other wires, the values of hole-transport coefficients presented in Table 2 should be considered as upper limits that correspond to the most efficient electron coupling between two states participating in the charge-transfer process.[36] The results of Paulson et al.[21j] and of Pati and Karna[24] suggest that the strongest coupling can be achieved if aromatic rings attached to the cage termini are coplanar along the entire system. Because twisting motion is able to destroy this ideal geometry, the value of the electron-transfer matrix element will decrease as the arrangement of the end aromatic rings becomes less planar. Hence, both *D* and *μ* should drop below the limits indicated in Table 2 and reduce to the values dependent on the conformation of the wire.

The influence of the relative orientations of aromatic rings on charge transport becomes evident if the mobility of holes is plotted as a function of the twist angle *θ* between two benzene units connected by the *σ*-bonded spacer. A typical example of the dependence of *μ* on *θ* for the wire containing the BCP spacer is shown in Figure 5. At relatively small angles (between 0° and 50°), *μ* slowly decreases with *θ* from the limiting value of 21.6 $cm^2\ s^{-1}\ V^{-1}$ to approximately 10 $cm^2\ s^{-1}\ V^{-1}$. Further deviations from the planar arrangement of aromatic rings at the BCP termini lead to a much stronger decline of the hole mobility, which eventually vanishes at $\theta = 90°$. A qualitatively similar angular dependence of hole mobility was obtained for systems in which CUB or BCO spacers replace BCP.

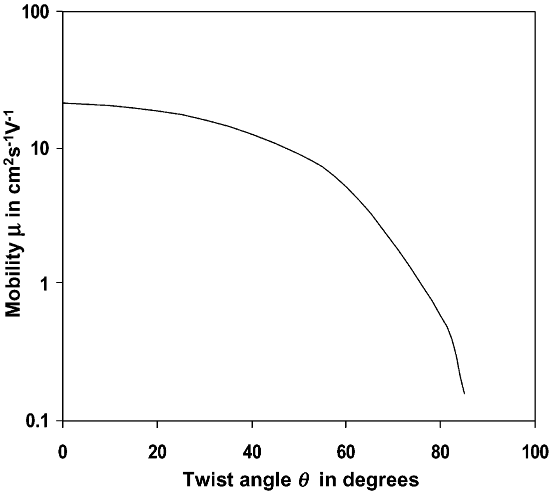

Figure 5. Mobility of holes, *μ*, as a function of the angle *θ* between the planes of the benzene rings attached to the ends of the BCP cage. Calculations were performed for room temperature using eqs 2 and 4 with $\lambda = 0.29$ eV as indicated in Table 1. The angular dependence of the electron-transfer matrix element *V* computed at the UHF/STO-3G level was taken from ref 24.

TABLE 3: Upper Bound for the Diffusion Coefficient *D* and the Drift Mobility *μ* of Electons in Molecular Wires at 290 K with Various Alternating *π*-Conjugated and *σ*-Bonded Structural Units[a]

molecular wire			
π-conjugated fragment	*σ*-bonded spacers	diffusion coefficient ($cm^2\ s^{-1}$)	drift mobility ($cm^2\ s^{-1}\ V^{-1}$)
benzene ring	BCP	0.25	10.1
	CUB	0.002	0.07
	BCO	0.023	0.90
3-methylbiphenyl unit	BCP	0.039	1.56
	CUB	0.0003	0.01
	BCO	0.003	0.14
DMPP	BCP	0.20	8.10
	CUB	0.001	0.06
	BCO	0.018	0.72
SPPDMP	BCP	0.99	39.8
	CUB	0.007	0.28
	BCO	0.088	3.54

[a] Estimated from eqs 2−4 for room temperature. Parameters *L* are taken from ref 24. The electronic coupling matrix element *V* matrix elements are taken from Table 4.

The diffusion coefficient *D* and the mobility *μ* of electrons undergoing hopping motion along various molecular wires of general structure $-(CS)_n-$ are given in Table 3. The above considerations concerning the influence of the orientation of the aromatic rings on the electron-transfer matrix element again apply.

The results described above support our earlier conclusion[8c,14j] that transport properties are determined not only by the structure

TABLE 4: Electronic Coupling Matrix Element V for Hole and Electron Transfer Calculated for Alkyl Cages Spacers (eV)

	hole transfer		electron transfer
spacer	Marcus−Hush two-state model[a]	$^1/_2\Delta E$(UMP2)[b]	$^1/_2\Delta E$(UMP2)[b]
BCP	0.54	0.49	0.50
CUB	0.26	0.23	0.04
BCO	0.07	0.01	0.12

[a] V evaluated at the UHF/DZP level, ref 24. [b] Estimated in this work. Triplet diradical CH_2-S-CH_2 was optimized at the UB3LYP/6-31G* level first, with C_{2v} (BCP and BCO) or C_{2h} (CUB) symmetry constraints. Symmetry requirements prevented twisting of the two methylene centers. Next, half of the difference of energy between the two appropriate states[21j,k] of cation radical (hole transfer) or anion radical (electron transfer) calculated at the UMP2 6-31G* level was taken as an approximate value of V. Replacement of the conjugated fragments of the wire by the methylene groups, CH_2, can result in overestimated values of V.[36]

of the molecular units comprising the wire, but also by their conformations. As in other molecular systems,[37] conformational changes in wires composed of alternating π-conjugated and σ-bonded units can affect the electronic coupling between charge-transfer states and, hence, the rates of hole and electron hopping. Therefore, more rigorous calculations of charge mobility require information about the equilibrium values of the twist angle, θ_{eq}, and fluctuations of θ within the wire.

The time scale of these fluctuations, τ_F, is of particular importance for accurate evaluations of the drift mobility. If fluctuations are slow in comparison with the rate W of electron-transfer reactions 1 so that $\tau_F W \gg 1$, some π-conjugated units visited by a moving charge will be in nonequilibrium conformations with large deviations of twist angles θ from their equilibrium values θ_{eq}. Although the number of such units might be small, they represent a bottleneck for the transport process, as follows from the angular dependence of μ (see Figure 5). Consequently, in this limit, the genuine drift mobility of the charge carriers will be much lower than μ estimated for completely equilibrated wire with $\theta = \theta_{eq}$.[38] By contrast, in the limit of fast fluctuations ($\tau_F W \ll 1$), the drift mobility will be determined by the distribution of θ values at equilibrium and by the statistical weight of these orientations, as can be shown using simple probabilistic argument. This underscores the idea that conformational dynamics can strongly affect transport properties of molecular wires, especially if the rates of electron-transfer reactions 1a and 1b are high. Calculated values of the reorganization energy and the electronic transfer matrix element suggest that the latter condition is satisfied for the wires with BCP and CUB spacers. As a consequence, theoretical results that neglect the dynamics of conformation changes can significantly overestimate the drift mobility of charge carriers in these systems.

To verify this conclusion, we evaluated the lower bound of μ for the molecular wires listed in Table 2. Our calculations rely on the experimental V values that have been estimated from the measured rate of electron transfer between π-conjugated donor and acceptor pairs linked by single CUB and BCO moieties.[21g,j] Because the measurements were performed in solution, the quantity deduced from experiment should actually be considered as the effective electron-transfer matrix element V_{eff}, which takes conformational dynamics into account implicitly. Therefore, if the effect of conformational changes on electron coupling is essential, the difference between the lower bounds of hole mobility in benzene/CUB and benzene/BCO wires will be much smaller than the difference between the upper bounds. The results obtained support our expectations. For both systems, the estimated lower limits of μ are found to be close to 0.1 $cm^2\ V^{-1}\ s^{-1}$, whereas the upper limits differ by 2 orders of magnitude (see Table 2). A similar situation occurs for 3-methylbiphenyl/CUB and 3-methylbiphenyl/BCO wires, although the lower limit of hole mobility in these systems reduces to 0.05 $cm^2\ V^{-1}\ s^{-1}$. This implies that, in many cases, information about static electronic coupling is insufficient for reliable conclusions concerning applications of a particular wire in molecular circuits; such conclusions might be illusory without careful consideration of dynamic effects.[39] In fact, the situation can become more complex depending on the symmetry of the bridge. For a benzene spacer, the geometric variation of V_{eff} with twist angle is simple, with maxima expected for coplanar arrangements ($\theta = 0°, 180°$) and minima corresponding to perpendicular ones ($\theta = 90°, 270°$). For the BCP and CUB spacers, there are three minima at $\theta = 0°$, 120°, and 240°. For BCO, there are again three minima, close to $\theta = 15°$, 135°, and 255°. For each of these situations, the same considerations concerning which geometry (equilibrium or locally trapped) dominates the transport will hold. If the barrier heights are small compared to thermal energies (about 0.025 eV at room temperature), the rotation should be nearly free, and averaging can be directly done over the angle.

4. Conclusions

The necessary condition for nanostructures connected between two reservoirs of charge carriers to be considered as molecular wires is the requirement that their spatial configuration, energetics, and nuclear and electronic dynamics promote one-dimensional long-range charge transport. Taking this requirement into consideration, we have considered the class of molecular systems composed of alternating π-conjugated and σ-bonded units. Because of the differences in ionization potentials and/or electron affinities, charge carriers are able to move along such wires undergoing a series of hops between the units with proper energetics. It is assumed that each step of this hopping motion can be treated as an electron-transfer reaction, with the rate depending on the internal reorganization energy λ of molecular units visited by moving charges and on the electronic coupling between them.

To calculate the diffusion coefficient and the drift mobility within this mechanistic picture, we have optimized neutral and ionic geometries of benzene, 3-methylbiphenyl, DMPP, and SPPDMP molecules selected as candidates for π-conjugated units of the wire. Using UHF and UDFT-B3LYP methods with the 6-31G* basis set, we show that localization of charge on these molecules has several consequences for their primary structure. These include changes in bond lengths and bond angles, as well as a shift in geometry toward planarity in the case of 3-methylbiphenyl, DMPP (reduced structure), and SPPDMP (reduced structure; the dihedral angle between the pyridinium rings decreases, but the sufhydrylphenyl−pyridinium dihedral angle increases). Calculations of energies that refer to the primary electronic configuration and two configurations with extra positive and negative charge in neutral and ionic geometries enable us to evaluate energy parameters of states involved in electron and hole transfer. The computational procedure proposed turns out to be particularly useful for estimations of the vertical ionization potential I, electron affinity, and internal reorganization energy λ. Comparison of our theoretical findings with the available experimental data demonstrates that UHF calculation and subsequent application of the Koopmans' theorem overestimate I, whereas the results obtained with the

UDFT method are in reasonable agreement with the measured values. Reorganization energies evaluated at the UHF/6-31G* level are also found to be larger than UDFT estimates. The disagreement between the predictions of the UHF and UDFT methods is explained by the fact that the former does not include electron correlations.

The reorganization energies computed at the UDFT-B3LYP level and data for electronic coupling reported by other groups were exploited to calculate the upper and lower limits of the drift mobility of holes and electrons undergoing consecutive transitions between neighboring benzene or 3-methylbiphenyl units linked by σ-bonded molecular cages. On the basis of numerical results, we infer that the upper limit of hole mobility corresponds to the situation where aromatic rings attached to cage termini are coplanar along the entire system. In this case, electron coupling turns out to be most efficient, and the upper limit of hole mobility depends exclusively on the reorganization energy and on the value of the electron-transfer matrix element at zero twist angle. Because both quantities strongly vary from system to system, the maximum value of mobility also changes. For benzene/CUB and benzene/BCO wires, for instance, the upper limits of hole mobility differ by 2 orders of magnitude and are equal to 14.8 and 0.2 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$, respectively. For the benzene and 3-methylbiphenyl systems, the reorganization energies for electron transfer are higher than the reorganization energies for hole transfer. As a result, the combination of these units with BCP or CUB spacers (comparable or smaller value of V for electron transfer vs V for hole transfer) produces wires with lower electron mobilty as compared to hole mobility (Table 2, numbers in parentheses; Table 3). Interestingly, the calculated value of V for electron transfer for BCO spacer is 1 order of magnitude larger than the V value calculated for hole transfer for the same spacer (2 orders of magnitude difference in V^2). The functional dependence of rate transfer on V (second power) and reorganization energy (exponential) makes reliable predictions of mobility parameters difficult, as small errors in estimates of V and λ will lead to significant errors in calculated transfer rates, diffusion coefficients, and drift mobilities.

Thermally induced twisting of aromatic rings can destroy the planar configuration, and the efficiency of electron coupling will decrease. As a result, the hole/electron mobility reduces to a much smaller value determined by conformational changes mentioned above. As follows from our estimates, the lower limit imposed on hole mobility by this dynamic effect is expected to be about 0.1 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$ for benzene/CUB and benzene/BCO wires. Thus, care must be exercised when trying to predict transport properties of molecular wires on the basis of information about static electron coupling; a proper theoretical treatment must explicitly take into account the dynamic behavior of the structural units comprising these one-dimensional systems.

Acknowledgment. This research is supported by funding from the DoD/MURI and DARPA Moletronics programs.

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(39) The lower bound for hole mobility allows for a simple estimation of the conductance Λ_h associated with the hopping motion of a single charge carrier along a molecular wire with alternating π-conjugated and σ-bonded units. Assuming that the wire has the form of a cylinder with cross section S and length l, this conductance can be expressed in terms of the hole mobility μ as $\Lambda_h = e\mu/l^2$. Because the lower bound for μ at room temperature is $\sim$0.1 $cm^2\ V^{-1}\ s^{-1}$, a wire 2 nm long is expected to have a "hopping" conductance of $\sim$1 $M\Omega^{-1}$. This suggests that Λ_h is much larger than the "molecular" conductance Λ_M of BCP, CUB, and BCO spacers (5×10^{-6}, 1.3×10^{-6}, and 4×10^{-7} $M\Omega^{-1}$, respectively[24]) obtained from Landauer's formula.[2b]