This contribution deals with a computational study of hole transfer (HT) and excess electron transfer (EET) in complexes of a buckyball and a molecular catcher having two concave buckybowls as described by Sygula et al. (J. Am. Chem. Soc. 2007, 129, 3842). Three systems are considered: (1) the inclusion complex consisting of the fullerene and catcher subunits, (2) a system formed by two catchers, and (3) a supermolecular system consisting of two fullerene and two catcher molecules. Such a type of organic system is of potential interest in the design of nanoelectronic devices. HT and EET electronic couplings of the subunits in the systems are calculated using the HF/6-31G* method and the semiempirical INDO/S scheme; the calculation of the reorganization energy is carried out within the B3LYP/6-31G* method. On the basis of the computed values of electronic couplings and reorganization energies, we predict that excess charge (hole or electron) should be strongly confined to a single subunit in the complexes. Then, we suggest that excess charge propagation within the fullerene-catcher system in the solid state occurs as superexchange mediated hopping; in this process, fullerene molecules function as stepping stones, while the catcher effectively mediates the charge transport between buckyballs. The properties of the buckycatcher, acting as a charge-transfer mediator from and to fullerenes, are found to be quite different for electron- and hole-transfer processes. We estimate the absolute rate of the hole and the excess electron hopping between fullerenes, $k_{HT} = 1.28 \times 10^{12} \text{ s}^{-1}$, while $k_{EET} = 1.07 \times 10^9 \text{ s}^{-1}$ and find that the HT is much faster than the EET because of (1) the stronger HT coupling between neighboring buckybowls of the catchers and (2) the smaller HT reorganization energy relative to that for EET.

**Introduction**

Recently, a rather stable inclusion complex (Figure 1) has been reported between C$_{60}$ and a catcher, namely, a bowl-shaped polycyclic hydrocarbon. This complex is formed because of the $\pi-\pi$ interaction between the convex face of the fullerene and the concave faces of the corannulene subunits of the buckycatcher. Among various interesting applications of such systems, one may imagine their use as building elements in molecular electronics. Actually, fullerenes and their derivatives are already widely employed in solar cells (photovoltaic devices) and may also be key elements for different molecular electronic systems, one may imagine their use as building elements in molecular electronics. Actually, fullerenes and their derivatives are already widely employed in solar cells (photovoltaic devices) and may also be key elements for different molecular electronic devices. For organic systems, photochemical or electrochemical doping is used to introduce charge carriers; depending on the injected charge, two types of charge transfer (CT) can be activated: (i) a positive charge or hole transfer (HT), when a radical-cation state migrates within a system and (ii) an excess electron transfer (EET), which is associated with migration of a radical-anion state.

The last 20 years have been very important for understanding CT mechanisms underlying in molecular electronics. The performance of a molecular device depends critically on the efficiency of charge transfer between its subunits, which in turn is determined by the electronic interactions present in the system. In particular, delocalization of an excess charge over the system is directly associated with CT properties and electron transport mechanisms. Recently, it has been shown that the mobility of charge carriers within a device is closely related to the CT rate.

A detailed discussion of how these CT processes can be described at the molecular level is given in excellent reviews. Three key parameters, (a) the donor–acceptor energy gap, (b) the electronic coupling, and (c) the reorganization energy associated with charge migration, determine the probability of electron transfer in the nonadiabatic regime. Because the CT efficiency is related to the electronic coupling, $V_{DA}$ of donor and acceptor states (it is proportional to $V_{DA}^2$), the quantum chemical calculation of $V_{DA}$ provides valuable information about the electronic effects in the charge-transfer process. The computational aspects of estimating electronic coupling have already been considered in detail in several reviews. The effects of structural and dynamical disorder on charge transfer in $\pi$-stacked arrays of conjugated organic molecules have also been considered in detail.

In the present paper, we calculate CT parameters for three key systems: the buckyball-catcher inclusion complex, catcher–catcher dyad, and the supermolecular system consisting of two fullerene and two catcher units. Both the hole transfer and excess electron transfer are considered. Comparison of the EET and HT parameters provides useful insight into the electronic interactions in the systems.

**Computational Details**

Application of quantum chemical calculations to study conductivity in a $\pi$-stacked system (polyacetylene) was considered by Rodriguez-Monge and Larsson. In particular, they...
DNA π stacks, we also used this scheme for calculations of the charge-transfer parameters for complexes 1–3.

**Estimation of Electronic Couplings.** Two methods were employed to calculate electronic couplings (1) the generalized Mulliken–Hush (GMH) method, and the fragment-charge model (FCM). We used two- and multistate variants of these methods. When applying the two-state approach, particular attention has been given to properly select one-electron states corresponding to the “+” and “−” combinations of the donor and acceptor states. Within the two-state GMH approach, the electronic coupling $V_{da}$ is expressed via the energy and dipole moment differences for adiabatic states $\Delta E = E_2 - E_1$, $\Delta \mu = \mu_2 - \mu_1$ and the transition dipole moment $\mu_{12}$. 

$$V_{da} = \frac{\Delta E|\mu_{12}|}{\sqrt{\Delta \mu^2 + 4\mu_{12}^2}} \quad (1)$$

A very useful characteristic of determining the donor and acceptor states is the effective donor–acceptor distance, which can be derived from the difference of the diabatic dipole moment, $R_{da} = R_{da}^{(1)} - R_{da}^{(2)}$. Comparison of $R_{da}$ with a distance between the donor and acceptor sites estimated from the structural parameters of the system provides a simple way to discriminate the diabatic states of interest. Because of symmetry (we assume that complex 1 has $C_{2v}$ geometry, while complexes 2 and 3 have $C_{2h}$ symmetry), the electronic coupling is nonzero only when states of the same symmetry are considered. The computational procedure to derive electronic couplings has already been described in detail elsewhere.

**Internal Reorganization Energy.** The internal reorganization energy $\lambda_i$ was calculated at the B3LYP/6-31G* level; for the radical-anion and radical-cation states, the unrestricted Kohn–Sham method was applied. By definition, $\lambda_i$ for the EET reaction in complex 1, $C_{60} + \text{Catcher} \rightarrow C_{60} + \text{Catcher}^-$, turns out to be a sum of the reorganization energies of the subunits, $\lambda_i = \lambda_i(C_{60}) + \lambda_i(\text{Catcher})$. If we consider the charge transfer between identical donor and acceptor, for example, between $C_{60}$ subunits in complex 3, then $\lambda_i = 2\lambda_i(C_{60})$. To estimate $\lambda_i$ for a molecule X (X = C60, Catcher), we computed the following terms: (1) the energy $E_0(X)$ of neutral X at the optimized geometry, (2) the energy $E_-(X^-)$ of the corresponding anion radical at the optimized geometry, (3) the energy $E_+(X^+)$ of neutral X calculated at the geometry of the anion radical $X^-$, and (4) the energy $E_0(X^-)$ of the radical-anion state at the geometry of corresponding neutral molecule X. Thus, the reorganization energy $\lambda_i(X)$ becomes

$$\lambda_i(X) = \frac{1}{2} [E_+(X) - E_-(X^-) + E_0(X^-) - E_0(X)] \quad (2)$$

A similar approach was used to calculate the reorganization energy for the HT process.

**Geometries.** As starting point for geometry optimization of 1, we used the atomic coordinates of the complex arising from X-ray data. Optimizations were carried out within the modified tight-binding model (MTB), which provides very accurate energetic and structural parameters for hydrocarbons. The mutual position of the catcher subunits in 2 and 3 are taken from structural data. Note that the $\pi-\pi$ interaction between the fullerene and the catcher depends on the contact distances between the subunits, which in turn are determined mainly by the two parameters $r$ and $\alpha$ shown in Figure 1.
TABLE 1: Electronic Couplings of Excess Electron Transfer for Various Geometries of Complex 1

<table>
<thead>
<tr>
<th>geometry</th>
<th>R_C-C</th>
<th>R_min</th>
<th>transition</th>
<th>ΔE</th>
<th>Δμ△q</th>
<th>GMH</th>
<th>FCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a: r = 5 Å, α = 85.4°</td>
<td>3.56</td>
<td>3.26</td>
<td>L+1 → L+5</td>
<td>1.64</td>
<td>17.7</td>
<td>0.096</td>
<td>0.090</td>
</tr>
<tr>
<td>1b: r = 5 Å, α = 85.4°</td>
<td>3.48</td>
<td>2.85</td>
<td>L+2 → L+8</td>
<td>1.805</td>
<td>20.0</td>
<td>0.140</td>
<td>0.132</td>
</tr>
<tr>
<td>1c: r = 5 Å, α = 80°</td>
<td>3.62</td>
<td>3.42</td>
<td>L+1 → L+5</td>
<td>1.69</td>
<td>18.3</td>
<td>0.134</td>
<td>0.104</td>
</tr>
<tr>
<td>1d: r = 6 Å, α = 85.4°</td>
<td>3.64</td>
<td>3.49</td>
<td>L+2 → L+8</td>
<td>2.00</td>
<td>24.3</td>
<td>0.111</td>
<td>0.072</td>
</tr>
<tr>
<td>1e: r = 7 Å, α = 85.4°</td>
<td>3.83</td>
<td>3.83</td>
<td>L → L+6</td>
<td>1.83</td>
<td>26.7</td>
<td>0.032</td>
<td>0.021</td>
</tr>
</tbody>
</table>

* R_C-C: average contact distance in Å; R_min: C-C separation for shortest contacts in Å; ΔE: excitation energy in eV; Δμ△q: difference of the diabatic dipole moment in D; V, electronic coupling in eV.

Results and Discussion

First, we consider the electronic interaction between fullerene and its catcher in complex 1; then, we focus on the electronic coupling between buckybowls of neighboring catchers (complex 2), and finally, we consider the charge transfer in supermolecular system 3.

Fullerene–Catcher electronic Interaction. Intersurface Contacts. Usually, one assumes that two carbon atoms belonging to different subunits are in contact when their distance is shorter than 3.80 Å.28 This distance was also taken here as the criterion to suggest contacts between the buckyball and the catcher. In the reference structure, r = 5 Å and α = 85.4° (complex 1a in Table 1) there are 112 contacts between the two subunits; the average distance between contacting carbon atoms is 3.55 Å; in the shortest contacts, the C-C separation is found to be ca. 3.20 Å. According to MTB calculations, a small decrease of angle α (Figure 1), from 85.4° to 80.0°, is accompanied by remarkable shortening (by ~0.4 Å) of closest contacts 1b (Table 1), which leads to repulsion between subunits: the energy of the system increases by ca. 6 kcal/mol. However, no meaningful change in the total energy is found when increasing the angle by going from the reference geometry to structure 1c (Table 1); the structural changes bring about a small increase of contact distances. As expected, the separation between the subunits increases rapidly with the value of r (geometries 1a, 1d, and 1e in Table 1). In particular, when r = 7 Å and α = 85.4° the shortest distance between subunits, 3.83 Å, falls out of the range of the C-C contact (3.80 Å).

Excess Electron Transfer. Injection of an excess electron into the complex yields a radical-anion system. Three lowest-energy states of the system correspond to the threefold degenerate T1u level of C60; due to the π–π interaction with the buckycatcher, these states are slightly split, within 0.07 eV. According to our calculations, the excess charge in the anion radical is almost completely localized (99%) on the fullerene (Figure 2A, Table 2). The lowest excited state, where the excess electron is confined mainly to the catcher, lies ca.1.6 eV higher than the ground state of the radical anion (Table 2) and thus cannot be thermally populated. Table 1 lists adiabatic parameters.

Coupling values derived using the fragment-charge model are also given in Table 1. In all cases, the GMH and FCM values agree quite well. For geometries 1a and 1c, the coupling is calculated to be 0.1 eV. When the catcher clasps its jaws (structure 1b in Table 1) the coupling increases significantly. However, as noted above, this structure lies 6 kcal/mol higher in energy than the reference system 1a, and therefore it cannot contribute to the CT probability substantially. In the complex with r = 7 Å (structure 1e), the coupling decreases by a factor of ~2.5 as compared to the reference system.

Overall, the coupling of the fullerene and the catcher is quite effective and not very sensitive to the parameters r and α. However, because the energy gap between the relevant diabatic states is quite large (1.5 eV), the catcher does not provide intermediate states where an excess electron can reside during charge transfer from/to fullerene. Thus, the catcher may mediate EET only via superexchange. As can be seen from Figure 2A, the wave function LUMO+5 is not uniformly delocalized over the Fullerene–Catcher system X in the C60−catheter–X system X should be bound to the corannulene fragments that contribute most to the adiabatic state.

Our calculations show that the INDO/S method is of limited use for calculations of EET electronic couplings. The INDO/S coupling matrix elements calculated for structures 1a–1e are by a factor of 2–4 smaller than the corresponding HF values, and therefore this method cannot be employed to derive the
TABLE 3: Hole Transfer Electronic Couplings Calculated for Several Geometries of Complex 1a

<table>
<thead>
<tr>
<th>geometryb</th>
<th>transitionc</th>
<th>ΔE</th>
<th>Δµda</th>
<th>Rdac</th>
<th>[V], HF/6-31G*</th>
<th>[V], INDO/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a H → H− 5</td>
<td>0.254</td>
<td>22.3</td>
<td>0.096</td>
<td>0.104</td>
<td>0.080</td>
<td>0.123</td>
</tr>
<tr>
<td>1b H−1 → H− 5</td>
<td>0.432</td>
<td>22.2</td>
<td>0.148</td>
<td>0.166</td>
<td>0.123</td>
<td></td>
</tr>
<tr>
<td>1c H−1 → H− 5</td>
<td>0.149</td>
<td>22.4</td>
<td>0.063</td>
<td>0.065</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>1d H−1 → H− 5</td>
<td>0.107</td>
<td>26.3</td>
<td>0.053</td>
<td>0.054</td>
<td>0.036</td>
<td></td>
</tr>
<tr>
<td>1e H−1 → H− 4</td>
<td>0.139</td>
<td>28.9</td>
<td>0.043</td>
<td>0.038</td>
<td>0.024</td>
<td></td>
</tr>
</tbody>
</table>

a ΔE, excitation energy in eV; Δµ, dipole moment difference in D; V, electronic coupling in eV. b Geometric parameters are given in Table 1. c H−K labels one-electron states of the cation radical with a hole on HOMO−K of the neutral system.

TABLE 4: HT and EET Electronic Couplings V (eV), Diabatic Dipole Moment Difference Δµda (D), and Effective Donor−Accepter Separation Rdac (Å) Calculated for the Catcher Dimer

<table>
<thead>
<tr>
<th>model</th>
<th>transitiond</th>
<th>ΔE</th>
<th>Δµda</th>
<th>Rdac</th>
<th>[V], GMH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT HF/6-31G*</td>
<td>H → H− 3</td>
<td>0.39</td>
<td>16.48</td>
<td>3.4</td>
<td>0.195</td>
</tr>
<tr>
<td>INDO/S</td>
<td>H → H− 3</td>
<td>0.35</td>
<td>19.69</td>
<td>4.1</td>
<td>0.176</td>
</tr>
<tr>
<td>EET HF/6-31G*</td>
<td>L → L+3</td>
<td>0.13</td>
<td>23.62</td>
<td>4.9</td>
<td>0.064</td>
</tr>
</tbody>
</table>

EET parameters for the systems under study. On the contrary, as shown below, INDO/S provides very good estimates for HT couplings.

Hole Transfer. The calculated HT parameters for different geometries of complex 1 are gathered in Table 3. Loss of an electron by the complex leads to the formation of a radical. C₆₀ has fivefold degenerate highest occupied MOs of H₄ symmetry. In the complex, five low-energy electronic states originate from the H₄ state of C₆₀ and found to be of similar energy; the total splitting calculated with HF/6-31G* is ca. 0.19 eV (Table 3). Although in these states the hole is localized mostly on the fullerene, an admixture of catcher orbitals can be seen clearly (Figure 2B, Table 2). According to our calculations, in the ground state of the radical cation (a hole in the HOMO of the neutral complex) 78% and 22% of the hole is localized on the fullerene and the catcher, respectively. The second relevant adiabatic state (the hole in the HOMO-5) exhibits inverse hole distribution, namely, 21% and 79%, and lies only 0.25 eV higher in energy than the ground state (Table 2).

The HT electronic coupling of 0.10 eV is very similar to that calculated for EET. These results reflect the similar nature of the EET and HT diabatic states, (a hole in the HOMO-5), INDO/S predicts Δµda = 23.6 D. Accordingly, the electronic coupling is substantially smaller, V = 0.062 eV. Thus, one can expect that HT should be more effectively mediated by the catchers than the EET.

Charge Hopping between Fullerenes. Let us consider here INDO/S computational results for supermolecule 3. Because the calculations are performed for the entire system, the model explicitly accounts for the contributions from all possible superexchange pathways for the charge transfer. In system 3, the 10 highest occupied MO, arising from the H₄ electronic level of the fullerene subunits, lie within a narrow interval of 0.11 eV. One-electron states localized on the catchers are ca. 1 eV higher in energy than the ground state of the radical cation. HOMO-10 and HOMO-13 localized on adjacent buckybowls are very similar to the states shown in Figure 3A. The energies of these states (relative to the ground state of the radical cation) are 0.52 and 1.04 eV, respectively. The shortest distance between carbon atoms, which belong to different fullerene subunits, is 9.8 Å. (geometrical centers of the fullerenes are separated by 16.6 Å). The electronic coupling derived from one-electron states HOMO and HOMO-3 (Figure 4A) is 6.85 × 10⁻³ eV. The difference of the diabatic dipole moments, Δµda, is calculated to be 54.0 D, which corresponds to the effective donor−acceptor distance of 11.3 Å. This indicates that the centers of the diabatic states are shifted toward each other. Another pair of diabatic states derived from HOMO-1 and HOMO-2 (Figure 4B) is coupled much weaker, 1.25 × 10⁻³ eV. The difference of the diabatic dipole moments in this case is 79.4 D, corresponding to Rdac = 16.5 Å, which agrees very closely with the C₆₀−C₆₀ distance of 16.6 Å.

Overall, the HT coupling of fullerene subunits in 3 can be estimated as 7 × 10⁻³ eV. This coupling value corresponds to the nondiabatic regime for the hole transfer, which occurs as superexchange mediated hopping between fullerene subunits functioning as stepping stones.

It is interesting to compare the calculated coupling value with an estimate derived from the superexchange model. In a system d−b₁−b₂−a, where the donor and acceptor are separated by two consecutive bridges, the coupling is

\[ V_{da}^{SE} = \frac{V_{d-b_1} V_{b_1-b_2} V_{b_2-a}}{\Delta^2} \] (3)
where $\Delta$ is the energy gap between donor and bridge levels. In eq 3, the effect of the direct coupling (through-space interaction of the fullerene units is negligibly weak). Taking into account that INDO/S value of $V_{d-b_1} = V_{b_1-a}$ is 0.08 eV (Table 3) and $V_{b_1-b_2}$ is of 0.18 eV (Table 4) and $\Delta \sim 0.8$ eV, we obtain $V_{da}^{SE} \sim 1.8 \times 10^{-3}$ eV. This value is by a factor of 4 smaller than the $V = 6.85 \times 10^{-3}$ eV calculated for the supermolecular system.

Using the HF data for systems 1 and 2, one can estimate the coupling for hole and excess electron transfer within superexchange model. For HT, insertion of $V_{d-b_1} = V_{b_1-a} = 0.1$ eV,
$V_{b_2-b_1} = 0.2 \text{ eV}, \Delta \sim 0.4 \text{ eV}$ into eq 3 gives $V_{d_{b_1}}^{SE} (HT) = 12.5 \times 10^{-3} \text{ eV}$. For EET, with $V_{d-b_1} = V_{b_1-a} = 0.14 \text{ eV}, V_{b_1-b_2} = 0.06 \text{ eV}, \Delta \approx 1.2 \text{ eV}$ (difference of vertical electron affinities calculated using B3LYP/6-31G*), we get $V_{d_{b_1}}^{SE} (EET) = 0.82 \times 10^{-3} \text{ eV}$. Because the rate for the nonadiabatic charge transfer is proportional to the coupling squared, we may conclude that the hole hopping between fullerene subunits should be faster by at least 2 orders of magnitude than the excess electron transfer.

**Reorganization Energy.** The internal reorganization energy was calculated at the B3LYP/6-31G* level for the catcher and $C_{60}$ molecules using eq 2. For the fullerene, we found that electron attachment is associated with a reorganization energy of ca. 0.15 eV, whereas when an electron is removed, the reorganization energy is significantly smaller, namely 0.04 eV. Thus, the reorganization energy for EET and HT between the fullerene subunits amounts to 0.30 and 0.08 eV, respectively. Note that the smaller reorganization energy for HT should lead to more efficient hole hopping relative to EET.

**Excess Charge Delocalization.** Excess charge delocalization depends strongly on the relative magnitudes of the electronic coupling, the energy gap and the reorganization energy. Within a two-state model, the difference of the excess charges $q_1$ and $q_2$ on subunits 1 and 2, $\Delta q = q_2 - q_1$, is determined by

$$\Delta q = \frac{\Delta e^0 + \lambda \Delta q}{\sqrt{(\Delta e^0 + \lambda \Delta q)^2 + 4V_{12}^2}}$$  \hspace{1cm} (4)

where $V_{12}$ is the electronic coupling, $\Delta e^0$ is the difference between diabatic energies, and $\lambda$ stands for the reorganization energy. If the donor and acceptor are identical, then $\Delta e^0 = 0$ and the ratio of the reorganization energy and the coupling determines the charge distribution. From eq 4, we can derive that when $|\lambda/V_{12}| > 5 \, 95\%$ of excess charge will be confined to one of the subunits. Obviously, the charge localization will increase with $|\Delta e^0|$. When $|\lambda/V_{12}| \leq 2$, the charge is delocalized over both sites. Because in the supermolecular system the ratio $|\lambda/V_{12}|$ is estimated to be greater than 6, the excess charge should be confined to a single fullerene for both HT and EET.

**Absolute Hopping Rates.** We estimate the absolute rate for hole and excess electron hopping using Marcus’ formula for the nonadiabatic reaction

$$k = \frac{2\pi}{\hbar} \frac{|V|^2}{4\pi\lambda k_BT} \exp \left[ -\frac{(\Delta G + \lambda)^2}{4\lambda k_BT} \right]$$  \hspace{1cm} (5)

Because the charge transfer occurs among an identical donor and acceptor, the free energy for the HT and EET reactions is zero. Inserting the calculated parameters ($V(HT) = 6.85 \times 10^{-3} \text{ eV}, \lambda(HT) = 0.08 \text{ eV}; V(EET) = 0.8 \times 10^{-3} \text{ eV}, \lambda(EET) = 0.30 \text{ eV}$) into eq 5, we obtain $k_{HT} = 1.28 \times 10^{12} \text{ s}^{-1}$ while $k_{EET} = 1.07 \times 10^9 \text{ s}^{-1}$. Thus, we predict HT to be much more feasible in comparison to EET, $k_{HT}/k_{EET} = 1200$.

**Concluding Remarks.** In the present paper, we consider the charge-transfer properties of the molecular complex between the buckyball and the catcher described recently by Sygula et al. We estimated the electronic couplings for hole and excess electron transfer in a supermolecular system consisting of two fullerene and two catcher subunits. It has been found that the INDO/S method gives reliable coupling matrix elements for HT, whereas it seems to be of limited use to study EET in $\pi$-stacked hydrocarbon systems. The reorganization energies for both excess electron transfer and hole transfer were calculated using the B3LYP/6-31G* level of theory.

On the basis of the computed values of electronic couplings and reorganization energies, we predict that excess charge (hole or electron) should be strongly confined to single subunit in the complexes. Then, we suggest that excess charge propagation within the fullerene—catcher system in the solid state occurs as superexchange mediated hopping; in the process, fullerene molecules function as stepping stones, while the catcher effectively mediates the charge transport between buckyballs.

The hole transfer is found to be much faster than the excess electron transfer, $k_{HT} = 1.28 \times 10^{12} \text{ s}^{-1}$ while $k_{EET} = 1.07 \times 10^9 \text{ s}^{-1}$, despite the fact that the EET and HT electronic couplings between the fullerene and the catcher are very similar, ca. 0.1 eV. The fast hole transport is due mainly to the stronger HT coupling between neighboring buckyballs of the catchers and the smaller donor—bridge energy gap as compared to the corresponding parameters for EET. Also, the smaller HT reorganization energy (relative to that for EET) favors the hole transport.

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**References and Notes**

