Intramolecular charge transfer of π-conjugated push–pull systems in terms of polarizability and electronegativity

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Intramolecular charge transfer of $\pi$-conjugated push–pull systems in terms of polarizability and electronegativity

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We have derived a simple expression to evaluate the amount of intramolecular charge transfer (ICT) of $\pi$-conjugate push–pull systems from the properties of electronegativity ($\chi$) and polarizability ($\alpha$) of the corresponding push and pull systems. This simple model is verified from ab initio calculations of disubstituted benzenes, stilbenes, and butadienes (push–pull systems) and their monosubstituted (push or pull) systems with various donors and acceptors. The bond length alternation (BLA) is often used as a good structural parameter to describe the amount of ICT; however, it is not a complete parameter because the amounts of ICT for the same sets of donor/acceptor pairs are different for different bridge systems. Here, we report a parameter composed of polarizability and electronegativity to give a consistent amount of ICT for different bridge systems. In particular, when a highly electropositive donor is used, the polarizability of an acceptor is the most determining factor for ICT. On the basis of this model, we find a very strong acceptor with large polarization effect, CH$_2$C$_2$H$_2$, which gives a large nonlinear optical (NLO) response when a highly electropositive donor is used. The model would be a very useful utility to design various types of new functional molecular systems involving ICT optimization. © 2001 American Institute of Physics. [DOI: 10.1063/1.1413986]

I. INTRODUCTION

Charge transfer (CT) is an important subject in many chemical and biological problems. In particular, how to optimize the amount of CT in a $\pi$-conjugated push–pull system is a critical issue for practical applications such as design of nonlinear optical (NLO) materials. Materials exhibiting a large NLO response are of great interest for opto-electronic and photonic applications. Conjugated organic compounds have been the focus of many experimental and theoretical investigations, because CT is important for NLO response and their delocalized $\pi$-system is considered to be a good bridge for CT from donor to acceptor. Thus, such several $\pi$-conjugated systems as benzene, stilbene, thiophene, polyene, and polyyne have been studied extensively. Recently, we reported that the polyenic chain is a better bridge for long path while the polyenic chain is better for short bridge mainly due to the mobility of the $\pi$-electrons. The rate of CT through insulating molecular spacers is reported to depend strongly on the nature of chemical bonding of spacer. Sachs et al. measured the rate of interfacial CT between a gold electrode and a ferrocene group covalently connected to gold by $\pi$-conjugated spacer and trans alkane spacer. The values of rate constant for CT is observed to be orders of magnitude larger for the $\pi$-conjugated spacer than the trans alkane one.

Oudar and Chemla employed the equivalent internal field (EIF) model to understand nonlinear optical responses in monosubstituted systems. In the EIF model, the major part of the quadratic hyperpolarizability of a monosubstituted conjugated molecule is attributed to the distortion of the bridge system by the substituent radical. The action of the substituent on the $\pi$-electrons of the bridge is described by an equivalent internal field. The presence of both donor and acceptor at opposite ends of the bridge results in an additional contribution due to intramolecular charge transfer (ICT). For a donor–bridge–acceptor (D–B–A) system, the ICT is influenced by the bridge as well as the substituents. As an extension of the EIF method, the additivity model was proposed to deal with disubstituted derivatives.

To design a new electro-optic material, the amount of ICT should be optimized because the hyperpolarizability is found to decrease when the strengths of both donor and acceptor are too strong. This phenomenon has been understood from a two-state approximation because the CT-excited-state term dominates the perturbation sum for the value of hyperpolarizability. The dipole moment due to ICT ($\mu_{\text{ICT}}$) is often used as a parameter. The amount of ICT has been roughly approximated from the measurement of structural distortion associated with it, in particular for the $\pi$-conjugated systems. The bond length alternation (BLA) is
considered to be a good indicator for ICT in many related \( \pi \)-conjugated systems. \(^{10}\) Balakina et al. investigated the nonlinear optical responses by varying the degree of the ground-state polarization via the application of an external electric field in acceptor substituted carotenoids.\(^{11}\) They observed a state polarization via the application of an external electric field on the amount of ICT from the properties of electronegativity push–pull systems, and derive a simple expression to evaluate \( \gamma \) and polarizability \( \alpha \) of atoms from the electronegativity equalization approximation (EEA)\(^{12}\)

\[
Q_{AB} = (\chi_B - \chi_A)/(\eta_A + \eta_B - 2\gamma_{AB}) = \Delta\chi_{AB}/\Gamma_{AB},
\]

(1)

\[
\alpha_{AB} = R_{AB}^2/\Gamma_{AB},
\]

(2)

\[
\Gamma_{AB} = \eta_A + \eta_B - 2\gamma_{AB},
\]

(3)

where \( \eta \) is twice the hardness of each atom; \( \gamma_{AB} \) is related to the electrostatic interaction between two sites; \( R_{AB} \) is the distance between \( A \) and \( B \).

Previously, it was reported that the physical properties originated from ICT can be obtained from the superposition approximation.\(^{13}\) Applying the superposition approximation, the amount of ICT \( Q_{CT} \) in a push–pull system can be defined as

\[
Q_{CT} = (Q_{DA} + Q_{HH}) - (Q_{HA} + Q_{DH}),
\]

(4)

where the subscripts DA (push–pull system), DH (push system), HA (pull system), and HH represent the system with donor and acceptor, the system with donor, the system with acceptor, and the system only with H atoms, respectively. Using the relationship of \( Q_{AB} \) from EEA [combining Eqs. (1), (2), and (4)], \( Q_{CT} \) can be reexpressed in push–pull systems as

\[
Q_{CT} = \Delta\chi_{DA}/\Gamma_{DA} - (\Delta\chi_{HA}/\Gamma_{HA} + \Delta\chi_{DH}/\Gamma_{DH}),
\]

(5)

\[
Q_{CT} = \Delta\chi_{DA}\alpha_{DA}/R_{DA}^2 - (\Delta\chi_{HA}\alpha_{HA}/R_{HA}^2 + \Delta\chi_{DH}\alpha_{DH}/R_{DH}^2),
\]

(6)

### II. THEORETICAL APPROACHES

It is known that for a diatomic molecule \( AB \), the equilibrium charge \( Q_{AB} \): the amount of charge separation at the equilibrium geometry; \( q_A = Q_{AB} \) and \( q_B = -Q_{AB} \) and polarizability \( \alpha_{AB} \) are related to electronegativities \( \chi_A \) and \( \chi_B \) of the X–B system (B = stilbene, butadiene, and benzene).

<table>
<thead>
<tr>
<th>( \chi )</th>
<th>Stilbene</th>
<th>Butadiene</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi )</td>
<td>0.105</td>
<td>0.080</td>
<td>0.087</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>356.0</td>
<td>101.1</td>
<td>92.1</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>353.4</td>
<td>111.0</td>
<td>100.3</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>324.7</td>
<td>88.3</td>
<td>81.4</td>
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<td>380.7</td>
<td>113.4</td>
<td>101.6</td>
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<td>346.7</td>
<td>103.1</td>
<td>97.8</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>376.0</td>
<td>117.1</td>
<td>103.2</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>300.8</td>
<td>71.4</td>
<td>77.3</td>
</tr>
</tbody>
</table>

### FIG. 1. Comparison of \( \mu_{CT} \) (a.u.) for different bridge systems (D–B–A) with D=NH\(_2\), OMe, OH, A=NO\(_2\), Cl, CHO, and B=butadiene, benzene, and stilbene.

### FIG. 2. Dependence of \( \mu_{CT} \) (a.u.) on the BLA (Å) of D–B–A systems (D=NH\(_2\), OMe, OH, A=NO\(_2\), Cl, CHO, and B=butadiene, benzene, and stilbene).

### TABLE I. B3LYP/6-31G\(^*\) predicted polarizability \( \alpha \) and electronegativity \( \chi \) of the X–B system (B = stilbene, butadiene, and benzene). All units are in a.u.
where $\Delta\chi_{DA} = \Delta\chi_{DH} + \Delta\chi_{HA}$. $\Delta\chi_{OH}$ is equal to zero because it is homodiatomic. The distances $R_{DA}(=R)$ are similar for all systems of the benzene, stilbene, and butadiene derivatives investigated. As $R$ is nearly constant, we can further simplify the equation

$$Q^{CT} = [\Delta\chi_{DH}(\alpha^{CT} + \alpha_{HA} - \alpha_{HH})] + [\Delta\chi_{HA}(\alpha^{CT} + \alpha_{DH} - \alpha_{HH})]/R^2. \quad (7)$$

In the systems investigated here, the ICT-induced polarizability is very small; hence, $Q^{CT}$ can be approximated as

$$Q^{CT} = [\Delta\chi_{DH}(\alpha_{HA} - \alpha_{HH})] + [\Delta\chi_{HA}(\alpha_{DH} - \alpha_{HH})]/R^2. \quad (8)$$

### III. Calculation Methods

To verify the above linear relationship in push–pull systems, we calculated $\mu^{CT}(=\Sigma_{r_i}\Delta q_i)$ using $\Delta q_i = q_i(DA) - q_i(DH) - q_i(HA) + q_i(HH)$, where $r_i$ and $q_i$ denote the position and the charge of the ith atom in push–pull systems, respectively. The charges were obtained from the dipole moment derivatives, which are known to give reasonable values. As pointed out previously, in planar systems all perpendicular charge fluxes, and in fact, the perpendicular fluxes of any in-plane moment, are zero. Thus, for a planar molecule in the $x$–$y$ plane we have $qA_{x}/\partial A_{x}=0$ by symmetry. Then, the static point charges are obtained from $q_{A}=\partial\mu_{x}/\partial A_{x}$. This force-related atomic charge exactly reproduces the molecular dipole moments of planar molecules. The electronegativity was shown by Mulliken to be $\chi = (I + A)/2$, where $I$ and $A$ are the ionization energy and electron affinity, respectively. From the Koopmans’ theorem, the $I$ and $A$ are obtained from HOMO and LUMO energies, respectively. Hence, we obtain the electronegativity using $\chi = -(E_{HOMO} + E_{LUMO})/2$.

First, we verify Eq. (8) for different bridge systems (butadiene, benzene, and stilbene) with typical donors of NH$_2$, OMe, and OH, and typical acceptors of NO$_2$, Cl, and CHO. Then, we have studied benzene derivatives (D–C$_2$H$_4$–A) with diverse donor–acceptor pairs, where D=O, NMe$_2$, or NH$_2$, and A=N$_2^+$, NO$_2$, BC1$_2$, BH$_2$, BF$_2$, CN, or NC. All the values (dipole derivatives, orbital energies, and polarizabilities) were calculated using the Becke–3–Lee–Yang–Parr density functional theory (B3LYP) with 6–31G* and 6–31+G* basis sets. The density functional theory is widely used to obtain $\chi$ and $I$ of a molecule, and is considered to give reasonable values.

### IV. Results and Discussion

In push–pull systems, some physical properties are non-additive (i.e., properties of donor–acceptor pair are larger than the sum of those of donor and acceptor properties), and this is mainly due to ICT. Owing to the complexity of the origin of ICT, it has been difficult to obtain the amount of ICT in various systems. Recently, Mhin et al. investigated the relationship between $\mu^{CT}$ and the effective conjugate coordinate (ECC), which is equivalent to BLA in disubstituted benzenes. Though the ECC has a good relationship with the $\mu^{CT}$, the proportional constant highly depends on the donor group (in particular, polarizability of donor group), implying that ECC alone cannot properly describe the ICT. We investigated $\mu^{CT}$ for different bridge systems with the same donor and acceptor sets.

Figure 1 shows the relationship of $\mu^{CT}$ for various bridge systems with nine different D/A pairs. The $\mu^{CT}$ of benzene is given in both the $x$- and $y$ axis as the reference because the D/A pair cannot be quantified. It should be noted that for the same D/A pairs, different backbone systems give different amounts of ICT, which can be noted from the significant difference in proportional constant ($\mu^{CT}_{benzene}{\approx}1.4\mu^{CT}_{stilbene}$ and $\mu^{CT}_{butadiene}{\approx}0.5\mu^{CT}_{benzene}$). This is because the charge transfer is affected by the characteristics of π-electrons depending on different bridges as well as D/A pairs.

Figure 2 shows the variation of $\mu^{CT}$ with the BLA for different linker systems. This also clearly shows that the amount of ICT is highly dependent on the bridge system, and cannot be in a single straight line. Within each bridge system, the amount of ICT has a good linear relationship with BLA. For stronger D/A pairs, the BLA is larger in the benzene bridge system, while it is smaller in the stilbene and butadiene bridge systems. This can be understood from the two-state (ground- and CT-excited states) model. For the ground state, the BLA is zero in the benzene system, but it is nonzero in the stilbene and butadiene systems. On the other hand, for the CT-excited state, the situation is reversed; the BLA approaches nonzero in the benzene system, while it approaches zero in the stilbene and butadiene systems. For the push–pull system (D/A pair system), there is a certain amount of ICT; thus, the $\mu^{CT}$’s of butadiene, benzene, and stilbene systems show different trends with respect to BLA. In fact, the BLA has often been used to optimize structures to obtain the maximum hyperpolarizability for the same type of bridge system; however, optimization conditions leading to the maximum molecular polarizabilities have been tricky.
Thus, it is of importance to derive a simple and useful expression to obtain the amount of ICT (which is independent of backbone bridges) in push–pull systems. From the electronegativity equalization, we obtained an expression of the amount of ICT in terms of polarizabilities and electronegativities, as shown in the previous section. The induced dipole moment is proportional to the amount of ICT, that is, $\mu^\text{CT} = RQ^\text{CT}$. This indicates that $\mu^\text{CT}$ has a linear relationship with $[\Delta \chi_D(\alpha_{HA} - \alpha_{HH}) + \Delta \chi_A(\alpha_{DH} - \alpha_{AH})]/R$ from Eq. (8), implying that the ICT has two origins: electronegativity and polarizability. The first term arises from the electronegativity of a donor system and the polarizability of an acceptor system, while the second term stems from the electronegativity of an acceptor system and the polarizability of a donor system. Hence, the ICT of a push–pull system can be estimated from the cross correlation of electronegativities and polarizabilities of push (DH) and pull (HA) systems.

Table I lists the B3LYP/6-31G* predicted polarizabilities and electronegativities of X–B, where X=NH$_2$, OMe, OH, NO$_2$, Cl, CHO, and H, and B=butadiene, benzene, and stilbene. In all bridge (B) cases, the electronegativities of donor systems are smaller than that of the X=H system, while those of acceptor systems are larger than that of the X=H system. These results are consistent with the fundamental concept of donor and acceptor. Thus, the B3LYP results are reasonable, and often used for the calculation of orbital energies, ionization potential, and electron affinity. The value of electronegativity decreases with electron donation strength, and increases with the acceptance strength.

Table II lists the $\mu^\text{CT}$ and $R$ obtained from B3LYP/6-31G* for push–pull butadiene, benzene, and stilbene systems with typical donors of NH$_2$, OMe, and OH, and acceptors of NO$_2$, Cl, and CHO. The distances between donor and acceptor for a given bridge system are only within a small variation, and can be considered to be constant as approximated in Eq. (7). Figure 3 shows a good linear relationship between $\mu^\text{CT}$ and $[\Delta \chi_D(\alpha_{HA} - \alpha_{HH}) + \Delta \chi_A(\alpha_{DH} - \alpha_{AH})]/R$. This confirms that our expression is valid, and indicates that the amount of ICT can be estimated from the electronegativities and polarizabilities of push and pull systems, because the polarizability or electronegativity of push and pull systems includes the characteristic backbone polarization of each bridge system. It is very important that the $\mu^\text{CT}$ gives a good linear relationship with $[\Delta \chi_D(\alpha_{HA} - \alpha_{HH}) + \Delta \chi_A(\alpha_{DH} - \alpha_{AH})]/R$ for all the different $\pi$-conjugated bridge systems. Hence, for any kind of bridge systems, the amount of ICT in push–pull systems can be estimated from the polarizabilities and electronegativities of the push and pull systems.

We have studied benzene derivatives (D–C$_6$H$_4$–A) with highly effective donor–acceptor pairs using 6-31+G* basis sets, where D=O$^-$, NMe$_2$, or NH$_2$, and A=N$_2$, NO$_2$, BCl$_2$, BH$_2$, BF$_2$, CN, or NC. Along with the values of $\alpha$ and $\chi$ for X–C$_6$H$_5$ in Table III, the obtained ICT-driven dipole moments and path lengths are listed in Table IV. The negative electronegativity of C$_6$H$_5$O$^-$ (−0.060 a.u.) implies that it is highly electropositive and becomes unstable when an electron is attached, and O$^-$ acts as a very strong electron donating group. Based on the electronegativity, electron donating power is on the order O$^->$NMe$_2$>NH$_2$, and electron withdrawing power is on the order N$_2^->$NO$_2$>BCl$_2$>BH$_2$>CN>BF$_2$>NC. Thus, the $\mu^\text{CT}$ for NO$_2$ is expected to be larger than that for BCl$_2$; however, in all donor systems the $\mu^\text{CT}$ values give the opposite trend. This is due to the larger polarizability of BCl$_2$ (145.3 a.u.) than NO$_2$ (113.5 a.u.), as seen in Eq. (8). This is more evident when the change of $\mu^\text{CT}$ is investigated for three different donor systems. The values of $\mu^\text{CT}$ for A=NO$_2$/BCl$_2$ of D–benzene–A are 1.701/2.057, 0.638/0.681, and 0.457/0.531 for D=O$^-$, NMe$_2$, and NH$_2$, respectively. For a given donor, the second term of Eq. (8) for NO$_2$ is larger than that for BCl$_2$ because the electronegativity

### Table III. B3LYP/6-31+G* predicted polarizability ($\alpha$) and electronegativity ($\chi$) of the X–C$_6$H$_5$ system. All units are in a.u.

<table>
<thead>
<tr>
<th>X</th>
<th>O$^-$</th>
<th>NMe$_2$</th>
<th>NH$_2$</th>
<th>N$_2$</th>
<th>NO$_2$</th>
<th>BCl$_2$</th>
<th>BH$_2$</th>
<th>BF$_2$</th>
<th>CN</th>
<th>NC</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>117.6</td>
<td>138.1</td>
<td>102.2</td>
<td>123.2</td>
<td>113.5</td>
<td>145.3</td>
<td>114.6</td>
<td>104.0</td>
<td>122.4</td>
<td>125.1</td>
<td>78.6</td>
</tr>
<tr>
<td>$\chi$</td>
<td>-0.060</td>
<td>0.098</td>
<td>0.104</td>
<td>0.381</td>
<td>0.199</td>
<td>0.180</td>
<td>0.173</td>
<td>0.168</td>
<td>0.172</td>
<td>0.163</td>
<td>0.136</td>
</tr>
</tbody>
</table>

### Table IV. B3LYP/6-31+G* predicted ICT-driven dipole moments ($\mu^\text{CT}$) and path length ($R$) in the D–C$_6$H$_4$–A system.

<table>
<thead>
<tr>
<th></th>
<th>N$_2$</th>
<th>NO$_2$</th>
<th>BCl$_2$</th>
<th>BH$_2$</th>
<th>BF$_2$</th>
<th>CN</th>
<th>NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^\text{CT}$</td>
<td>2.375</td>
<td>1.701</td>
<td>2.057</td>
<td>1.410</td>
<td>1.118</td>
<td>1.056</td>
<td>1.034</td>
</tr>
<tr>
<td>O$^-$</td>
<td>2.034</td>
<td>0.638</td>
<td>0.681</td>
<td>0.521</td>
<td>0.421</td>
<td>0.423</td>
<td>0.338</td>
</tr>
<tr>
<td>NMe$_2$</td>
<td>1.246</td>
<td>0.457</td>
<td>0.531</td>
<td>0.413</td>
<td>0.323</td>
<td>0.301</td>
<td>0.241</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>10.22</td>
<td>10.48</td>
<td>10.73</td>
<td>10.77</td>
<td>10.75</td>
<td>10.56</td>
<td>10.48</td>
</tr>
<tr>
<td>R</td>
<td>10.40</td>
<td>10.67</td>
<td>10.92</td>
<td>10.92</td>
<td>10.91</td>
<td>10.68</td>
<td>10.59</td>
</tr>
<tr>
<td>NMe$_2$</td>
<td>10.35</td>
<td>10.63</td>
<td>10.87</td>
<td>10.87</td>
<td>10.87</td>
<td>10.64</td>
<td>10.55</td>
</tr>
</tbody>
</table>

### FIG. 3. Relationship between $\mu^\text{CT}$ (a.u.) and $[\Delta \chi_D(\alpha_{HA} - \alpha_{HH}) + \Delta \chi_A(\alpha_{DH} - \alpha_{AH})]/R$ (a.u.) for D–B–A with D=NH$_2$, OMe, OH, A=NO$_2$, Cl, CHO, and B=butadiene, benzene, and stilbene.
activity and polarizability of monosubstituted systems can lead to highly electropositive donor systems. Indeed, the values of $\Delta \chi_{DH}$ are 3.656 and 0.801 a.u. for O–C$_6$H$_4$–CH=CH$_2$ and H$_2$N–C$_8$H$_4$–CH=CH$_2$, respectively. We found that the first hyperpolarizability of O–C$_6$H$_4$–CH=CH$_2$ is highly enhanced (about five times the value of NH$_2$/NO$_2$), due to the large ICT by high polarization of C$_5$H$_5$–CH=CH$_2$ and highly electropositive effect of O–C$_6$H$_5$.

V. CONCLUSION

We have elucidated the origin of ICT in push–pull systems, and described a simple model to estimate the amount of ICT for various systems as a function of the properties of monosubstituted systems. The model has been verified from the studies of various push–pull bridge systems of butadiene, benzene, and stilbene, with various donor and acceptors. We have found that the amount of ICT for a push–pull system can be estimated by the electronegativities and polarizabilities of push and pull systems. In particular, when the donor is highly electropositive ($\Delta \chi_{DH}$ is very large), the polarizability ($\alpha_{HA}$) of the acceptor group becomes a critical factor to determine the amount of ICT. In this way, we have predicted that a fulvene is a very powerful electron acceptor. The main reason that the fulvene can be a good acceptor group is not electronegativity but polarizability. Indeed, it is demonstrated from ab initio calculations that the first hyperpolarizability of O–C$_6$H$_5$–CH=CH$_2$ is highly enhanced (about five times the value of NH$_2$/NO$_2$), due to the large ICT by high polarization of C$_5$H$_5$–CH=CH$_2$ and highly electropositive effect of O–C$_6$H$_5$. Thus, the present CT-optimization model would be a very useful utility to design various types of new functional molecular systems involving ICT.

ACKNOWLEDGMENT

This work was supported by Korea Institute of Science and Technology Evaluation and Planning (2000).


We find that, on the basis of our present and previous \cite{15} ab initio calculations, charge transferred polarizabilities of various push–pull systems are found to be less than 10% the total polarizabilities.


\cite{20} M. J. Frisch, G. W. Trucks, H. B. Schlegel \textit{et al.}, \textit{GAUSSIAN 98} Revision A (Gaussian, Inc., Pittsburgh, PA), 1999.
