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Correlation of Substituent Parameter Values to Electronic Properties of Molecules

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ABSTRACT

There are a vast number of organic compounds that could be considered for use in molecular electronics. Because of this, the need for efficient and economical screening tools has emerged. We have demonstrated that the substituent parameter values (σ), commonly found in advanced organic chemistry textbooks, correlate very strongly with features of the charge migration process. This result supports the use of the σ values as a low cost time saving tool in the selection of compounds for use in molecular electronic devices.

INTRODUCTION

The development of single molecule electronic devices is a challenging goal, that if realized could revolutionize computation, remote sensing, medicine etc. Recently there has been considerable effort to both measure the electrical properties of single molecules [1-4] and to describe these properties theoretically [5,6]. The development of molecular electronics technology could be greatly accelerated with a technique for selecting appropriate molecular species from the vast catalog of potential compounds.

For various applications, a property termed negative differential resistance (NDR) is particularly desirable. In devices exhibiting NDR, the current as a function of applied voltage is not linear as is the case with classical conductors. Within some range, increasing the applied potential leads to a drop in current. This is known as negative differential resistance (NDR) and can lead to peaks in the I/V characteristic [2,5,7].

It has been experimentally observed that self-assembled monolayers (SAMs) of certain conjugated organic molecules exhibit NDR upon application of a potential difference perpendicular to the SAM [1-2]. As reported, key to NDR is the presence of a nitro substituent ($\sim\text{NO}_2$), such as in the molecule 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiolate and similar $\sim\text{NO}_2$ containing molecules. The advantages of using organic compounds as possible molecular wires and nanoelectronic components are a low resistance to electron transfer due to delocalized pi-molecular orbitals [4,8,9], and biocompatibility for bioelectronic devices [10].

The obvious dependence of NDR on the chemical nature of a substituent group present in a molecule, suggested we investigate substituent parameter (σ) values as a possible marker of molecular electronic properties. Historically, it has been observed that substituents influence the chemical behavior of a compound and the σ values were developed to quantify the substituent effect. In the 1930s, Hammett [11] noted that substituents systematically change the free energy of proton dissociation of benzoic acid derivatives and the free energy of hydrolysis of ethyl benzoate derivatives [12]. By plotting the substituent induced changes in these chemical processes on orthogonal axes, a linear trend is revealed, which is termed a linear free energy

relationship (LFER). From the correlation, Hammett developed a set of σ values, which may be used as a tool to predict the reaction properties of other substituted aromatic compounds [12]. Upon examination of a table of σ values, it is evident that they correlate with qualitative ideas about the electron withdrawing and donating effects of substituents. For example, the strongly electron withdrawing group $\sim\text{NO}_2$ has a $\sigma = 0.81$, as opposed to the electron donating $\sim\text{CH}_3$ with a $\sigma = -0.14$ [12].

The implicit electronic structure information contained within the σ values supports their use as descriptors of charge transfer properties in conjugated organic molecules. Here we correlate the σ values with energies involved in the charge transfer process, and with explicit calculations of charge transfer, the ultimate goal being the employment of the σ values as a convenient and accessible tool for the *a priori* selection of organic compounds with a suitable set of electron transfer properties for a particular molecular electronic device.

THEORETICAL MODELS

NDR and electron transport model

A model proposed to explain the mechanism of the substituent effect of NDR in molecules is the double barrier electron-tunneling model [5]. In this model, molecules exhibiting NDR display a barrier-well-barrier potential energy profile along the electron transport coordinate. The well supports quantum resonance leading to resonant enhanced tunneling. The origin of the double barrier potential may be described in terms of the electron transport process in the molecular device. Starting with a neutral molecule, an electron from the donating electrode reduces the neutral species. The energy cost associated with placing the electron on a neutral molecule is the vertical attachment energy denoted E_v . The reduced species then relaxes, allowing the molecular orbitals to respond to the negative charge, into the radical anion. The energy difference between the relaxed radical anion and the neutral species is the adiabatic attachment energy denoted E_a . As the electron moves from the junction to the accepting electrode, reneutralization occurs from the relaxed radical anion geometry. The energy cost of this process is the vertical detachment energy denoted E_n . According to experimental and theoretical evidence, the chemical nature of a substituent can alter the potential energy profile along the electron transport coordinate [5]. In the present work, all calculations of E_a , E_v , and E_n were carried out at the HF/6-31G⁺⁺ level of theory with the GAMESS code [13].

Charge transfer model

Gonzales and Morales [6] have developed a method for extracting information about the electron transport properties of a molecule from semi-empirical ZINDO/S-CI calculations of its ground electronic state and charge transfer state (CTS). They performed calculations on donor-bridge-acceptor (D-P_n-A) systems, i.e. $\text{CH}_3\text{-(CH=CH)}_n\text{-CHO}$ where $n=1$ to 10, D = $\sim\text{CH}_3$, A = $\sim\text{CHO}$, and P_n = $(\text{CH=CH})_n$ is the acetylenic bridge. In these systems, placing electron donor and acceptor groups on opposite sides of the molecule mimics the applied potential field imposed by electrodes in the experimental situation.

After identifying the CTS, the charge transfer (Q_a) was obtained from orbital analysis of the carbonyl group (CO) in the acceptor portion of the molecule. Gonzales and Morales calculated charge transfer Q_a^n by monitoring the change in the CO charge between the ground and charge transfer states for the molecules ($n=1$ to 10) in the series. They then calculated the normalized

charge transfer (Q_r^n) by dividing all Q_a^n by the charge transfer Q_a^0 of a hypothetical base molecule ($\text{CH}_3\text{-(CH=CH)}_n\text{-CHO}$ where $n=0$) derived by extrapolation.

We have developed an *ab initio* implementation of the Gonzales and Morales semiempirical method in order to calculate the Q_a to CO from the ground to the charge transfer state during excitation. The charge transfer state (CTS) is an excited state with the dominant electron configuration state function (CSF) describing a $\pi \rightarrow \pi$ transition, which can be identified by examining the expansion coefficients of the configuration interaction. For example, if a CSF has the occupancy vector $\bar{v} = (2,2,2,2,2,0,0,0,0)$, it implies a ground electronic state with 10 molecular orbitals of which 5 are doubly occupied. On the other hand, if a dominant CSF for an electronic state has the occupancy vector $\bar{v}_{\text{CTS}} = (2,2,2,2,1,1,0,0,0)$, a HOMO electron has been excited to the LUMO. Charge transfers are not always the HOMO \rightarrow LUMO transition, especially in molecules that are not as highly conjugated. To ensure $\pi \rightarrow \pi$ character, the orbital eigenvectors are inspected to identify those with the largest contributions from p atomic orbitals perpendicular to the plane of the molecule.

To calculate Q_r , the density matrix (\mathbf{P}) is calculated for the ground and CTS from molecular orbital expansion coefficients ($\bar{\mathbf{C}}$) and overlap matrix (\mathbf{S}) extracted from standard quantum chemical code output and an occupancy vector ($\bar{\mathbf{v}}$) for the state(s) in question [13, 14]. The general density matrix expression can be written in terms of the occupancy vector as

$$P_{\mu\nu} = \sum_{i=1}^M v_i C_{\mu i} C_{\nu i}^* , \quad (1)$$

where M is the number of molecular orbitals, v_i guarantees that only the nonzero occupancy orbitals are integrated into \mathbf{P} , and $C_{\mu i}$ is the matrix of occupied molecular orbital eigenvectors.

Multiplying the ground or excited state $P_{\mu\nu}$ elements by the $S_{\mu\nu}$ elements, one arrives at a Mulliken population (ρ) for all atoms. For atom A this is

$$\rho_A = \sum_{\mu \in A}^L \sum_{\nu}^L P_{\mu\nu} S_{\mu\nu} , \quad (2)$$

where L is the number of expansion coefficients (atomic orbitals) and the μ index includes only those L centered on atom A . The charge transferred (Q_a) could be determined by taking the difference in electronic population on the carbonyl group acceptor atoms (CO) between the ground and CTS

$$Q_a = \rho_{\text{CO,CTS}} - \rho_{\text{CO,ground}} . \quad (3)$$

All geometry optimizations, configuration interaction calculations (CI) and charge transfer calculations were carried out at the HF/STO-6G level of theory. We adopt Mulliken population analysis for our charge distribution calculations. After the geometry optimizations, the next step was to perform configuration interaction (CI) calculations, including all possible single excitation configuration state functions (CSF) from valence to virtual orbitals. These were carried out as single point energy calculations on HF/STO-6G optimized geometries.

RESULTS AND CONCLUSION

Correlation of substituent parameter values to electron transport energies

To explore the substituent effect on electron transport we performed a series of calculations on 16 substituted benzenes with substituents for which parameter values were available. In order

to simulate the electron transport events, each molecule in the study underwent four total energy calculations. **E_I**) An initial geometry optimization of the neutral species was performed, followed by **E_{II}**) a single point energy calculation of the 1-electron reduced molecule at the optimized neutral geometry. **E_{III}**) The 1-electron reduced species was geometry optimized to obtain the most stable radical anion structure, and finally, **E_{IV}**) a single point energy was calculated for the neutral species at the optimized radical anion geometry. The three electron transport energies were obtained as follows: $E_v = E_{II} - E_I$, $E_a = E_{III} - E_I$, and $E_n = E_{IV} - E_{III}$. The electron transport energy that correlated the best to σ values is the vertical detachment energy E_v with an R^2 value of 0.595. Figure 1 shows the E_v vs. σ data and the elliptical 95.5% confidence interval.

Correlation of substituent parameter values to normalized charge transfer

The electron transfer energies describe the energetic profile experienced by a charge being transmitted across a molecule; therefore they implicitly contain information on the electronic properties of a compound. It would be desirable to correlate the σ values to a more explicit measure of electronic transport properties. We have selected the normalized charge transfer (Q_r) as estimated by the method of Gonzales and Morales and implemented based on *ab initio* calculations.

To validate our *ab initio* implementation of the Gonzales and Morales semiempirical method, we reproduced their Q_r^n results. For this procedure we used their $\text{CH}_3\text{-(HC=CH)}_n\text{-COH}$ with $n = 1$ to 10 series. Figure 2 shows the graphical comparison that confirmed our method.

The charge transfer procedure was next applied to the base molecule 5-(4-Penta-1,3-dienyl-phenyl)-penta-2,4-dienal, and to all the molecules resulting from the placement of 16 different substituents on the x site. Figure 3 shows the base molecule and the x site. The Q_r calculations on the 16 substituted resulted in the best correlation to the σ values with an $R^2=0.863$, which is illustrated in Figure 4. This correlation excludes the $\sim\text{NO}_2$ substituent because it is an outlier at 95.5% confidence. Evidently the electron transport properties introduced by the $\sim\text{NO}_2$ substituent are not fully captured in its σ value.

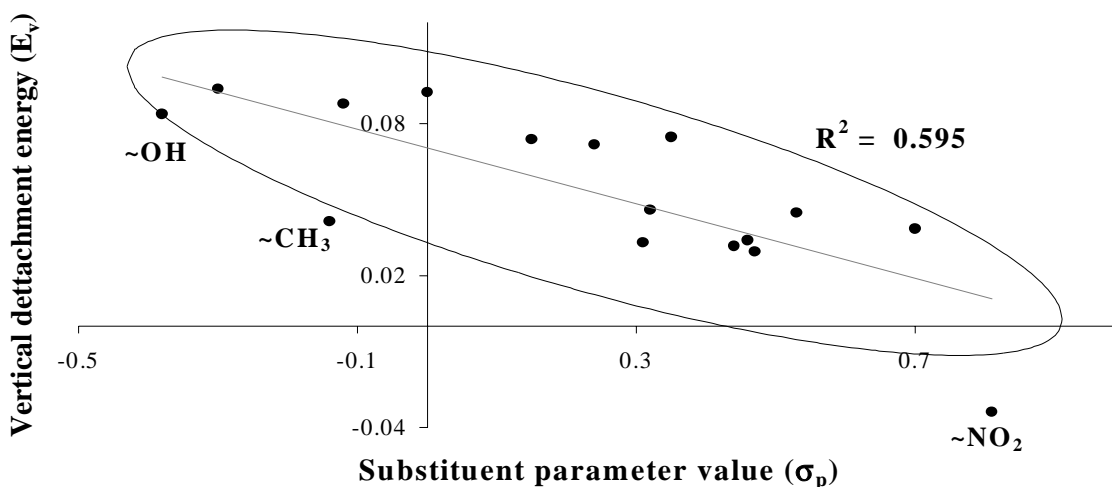


Figure 1 – Correlation of vertical detachment energy (E_v) to substituent parameter values (σ). The ellipse represents the 95.5% confidence interval.

In conclusion, the *a priori* selection of a molecule for its use in an electronic device will require screening tools because of the number of organic molecules that could be used is very large. We have demonstrated that the normalized charge transfer correlates with substituent parameter values. This suggests that the substituent parameters have utility as a cost-free predictor of electron transport properties.

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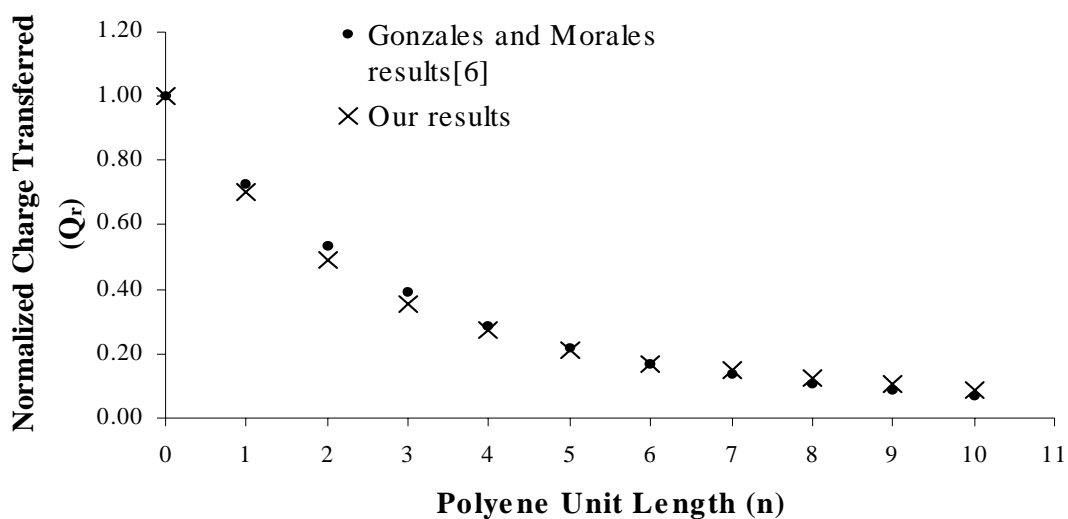


Figure 2 – Graphical comparison of normalized charge transferred calculations between the Gonzales and Morales result and our ab initio implementation.

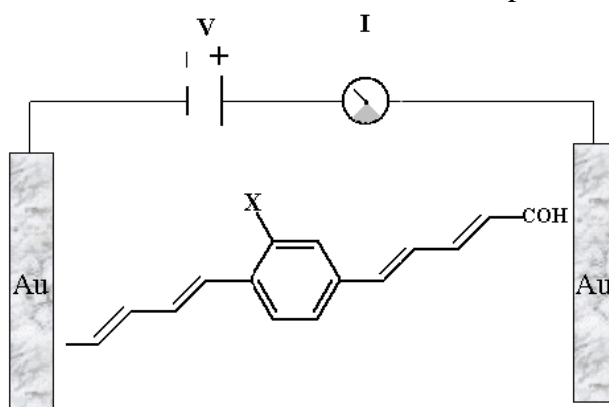


Figure 3 – The base molecule used in the normalized charge transfer (Q_r). The x site was replaced with the substituents $\sim\text{OH}$, $\sim\text{NH}_2$, $\sim\text{CH}_3$, $\sim\text{OCH}_3$, $\sim\text{H}$, $\sim\text{F}$, $\sim\text{Cl}$, $\sim\text{O}_2\text{CCH}_3$, $\sim\text{CHCl}_2$, $\sim\text{CHF}_2$, $\sim\text{CO}_2\text{H}$, $\sim\text{CCl}_3$, $\sim\text{OCCH}_3$, $\sim\text{CF}_3$, $\sim\text{CN}$, and $\sim\text{NO}_2$.

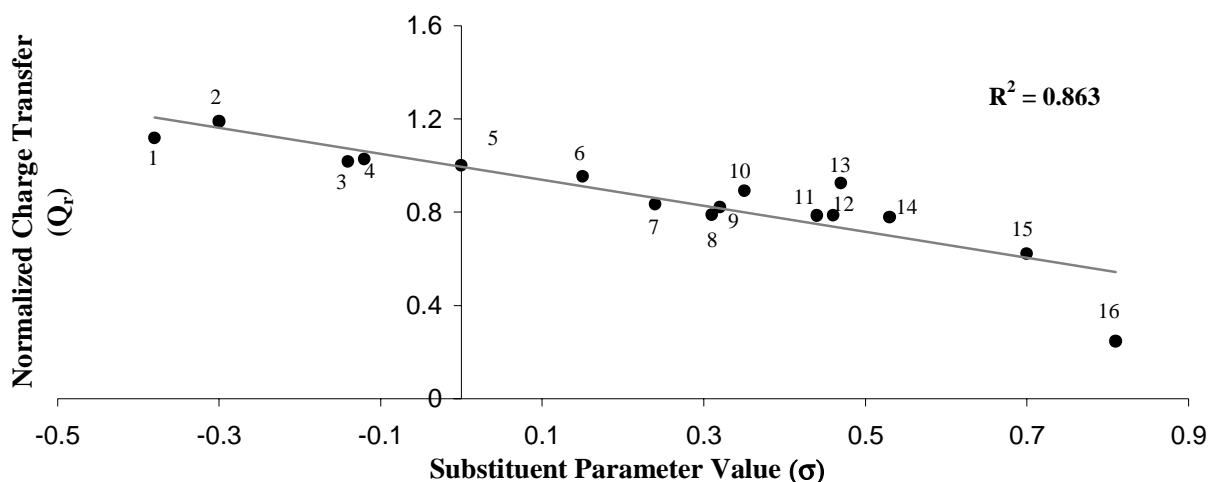


Figure 4 - Correlation of Normalized Charge Transferred (Q_r) to substituent parameter values (σ). The substituents are: 1= \sim OH, 2= \sim NH₂, 3= \sim CH₃, 4= \sim OCH₃, 5= \sim H, 6= \sim F, 7= \sim Cl, 8= \sim O₂CCH₃, 9= \sim CHCl₂, 10= \sim CHF₂, 11= \sim CO₂H, 12= \sim CCl₃, 13= \sim OCCH₃, 14= \sim CF₃, 15= \sim CN, 16= \sim NO₂.

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