

Intermolecular Interaction and Molecular Structure Deformation Effects on Hole Mobility in Molecular Doped Polymers

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Abstract

We tried to refine our previous method, which suggests a guideline to design new high mobility hole carrier transport molecules (CTMs) from polarizability and dipole moment of CTM, by considering intermolecular interaction and molecular deformation effects as well as polarizability and dipole moment of CTM. The molecular structure differences between neutral CTMs and their cations were investigated by using semiempirical molecular orbital theory. Semiempirical molecular orbital theory was also used to analyze intermolecular interactions of CTM dimers, where the structures of CTM dimers were optimized by molecular mechanics and semiempirical molecular orbital calculations. Intermolecular interactions of CTM dimers and the molecular structure deformation effect were analyzed to consider how these factors affected hole mobility in molecularly doped polymers. Our results suggested that the effects of intramolecular reorganization and intermolecular interaction between neighboring CTMs upon hole mobility were smaller than those of the electronic cloud extension and dipole moment of CTM.

Introduction

Hole transport phenomena in molecularly doped polymers (MDPs) have been widely discussed as the one of the most important research issues to develop new organic photoreceptor's materials. Since hole transport molecules in MDPs interact very weakly and the MDPs do not have any ordered structures usually, the charge carriers (holes) would be localized on some hopping sites with energetic and positional disorder.

The small polaron hopping theory¹⁻⁴ and the disorder theory⁵⁻⁸ have been accepted as the plausible explanations for the hole transport properties in such MDP systems. It is very useful for development of new CTMs to investigate relationship between parameters used in these theories and physical properties of hole transport molecules. Several experimental data indicate that increasing the polarity of the transport molecule has decreased the hole mobility in doped polymers⁹⁻¹¹ and in vapor-deposited molecular glasses¹²⁻¹³.

Recent disorder model's studies^{9,14-17} have been shown the energetic disorder parameter depends on dipole moment of hole transport molecules in MDPs.

Pacansky¹⁸ and Sakanoue et al¹⁹ have investigated intramolecular reorganization energies of hole transport molecules by using molecular orbital calculations. Sakanoue et al¹⁹ have shown that hole mobility has increased with decreasing intramolecular reorganization energy of CTM.

In our previous work²⁰⁻²¹, we have shown that smaller dipole moment and larger polarizability of hole transport molecules are preferable properties for hole transport. These results have suggested that the extension of electronic cloud of CTM and the smallness of dipole moment of CTM are important for hole mobility. In this paper, we study the effect of the intramolecular reorganization energy, which is caused by geometry change between a neutral CTM and the CTM cation, upon hole mobility. We also study the effect of intermolecular interaction between two homogeneous CTM dimer upon hole mobility.

Computational Methods

Hole transport phenomena in MDPs is expressed by a sequence of charge transfer reaction between a cation of CTM and a nearest neutral CTM. Through a sequence of charge transfer reactions, the MDPs are reorganized to obtained free energy lowering of whole system. The reorganization energy (λ) could be considered to composite from the contribution of medium reorganization energy and intramolecular organization energy. In this work, we estimated the intramolecular reorganization energy ($\lambda_{\text{intramolecular}}$) using semiempirical molecular orbital calculation. The intramolecular reorganization energy can be divided two components as shown in Figure 1. The first is the energy difference between neutral CTM's energy at the structure optimized for neutral CTM and that at the structure optimized for the cation of CTM. The first term is shown as λ_{neutral} in this work. The second is the energy difference between the cation's energy at the structure optimized for the neutral CTM and that at the structure optimized for the cation of CTM. The second term is shown as λ_{cation} . The program MOPAC93²² was used to carry out

the restricted Hartree-Fock (RHF) calculation based on the Parametric Method number 3 (PM3)²³ method of the Modified Neglect of Diatomic Overlap (MNDO) for all neutral CTMs shown in Figure 2 and to carry out the half-electron method based on PM3 for the cation systems. Molecular structures of all CTMs and the cations were optimized by the Eigenvector Following (EF)²² technique.

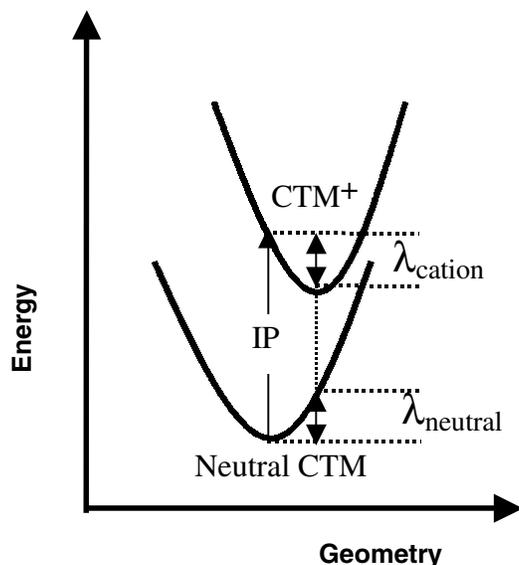


Figure 1. Intramolecular reorganization energy between neutral CTM and the cation of CTM.

Intermolecular interactions among CTMs are also important for hole transport phenomena in MDPs, because intermolecular interaction would derive aggregation of CTM molecules in the coating process of MDP layer and give the distribution of inter hopping site distances which is related to energetic and positional disorder of MDP systems. We estimated the magnitude of intermolecular interaction among CTM molecules in MDP by calculating dimerization energy of CTM molecules. Dimerization energies of CTMs (CTM3, CTM4, and CTM9 in Figure 2) were carried out as following scheme;

- 1) The CTM monomer was calculated to obtain electrostatic potential (ESP) charges²² as coulomb potential parameters and CTM monomer's energy by using semiempirical MO calculation based on the PM3 method. The MOPAC93 was used in these calculations.

- 2) The initial dimer structures with several intermolecular distances and several molecular intermolecular orientations were created by the scheme shown in Figure 3.
- 3) Molecular mechanics calculations were carried out with Biosym's Lennard-Jones type (12-6) potential parameters²⁴ and the ESP coulomb obtained in the step 1) under rigid body approximation of molecular structure. The program PCK91²⁵ was used in these calculations.
- 4) The ten lowest energy dimers obtained in the step 3) were submitted for geometry optimization with flexible molecular structure treatment by using semiempirical MO calculations based on the PM3 method. The program MOPAC93 was used in this step again.
- 5) The dimerization energies ($E_{\text{dimerization}}$) were calculated from the equation;

$$E_{\text{dimerization}} = E_{\text{dimer}} - 2E_{\text{monomer}}$$

where E_{dimer} is the lowest dimer's energy obtained in the step 4) and E_{monomer} is the monomer's energy obtained in the step 1).

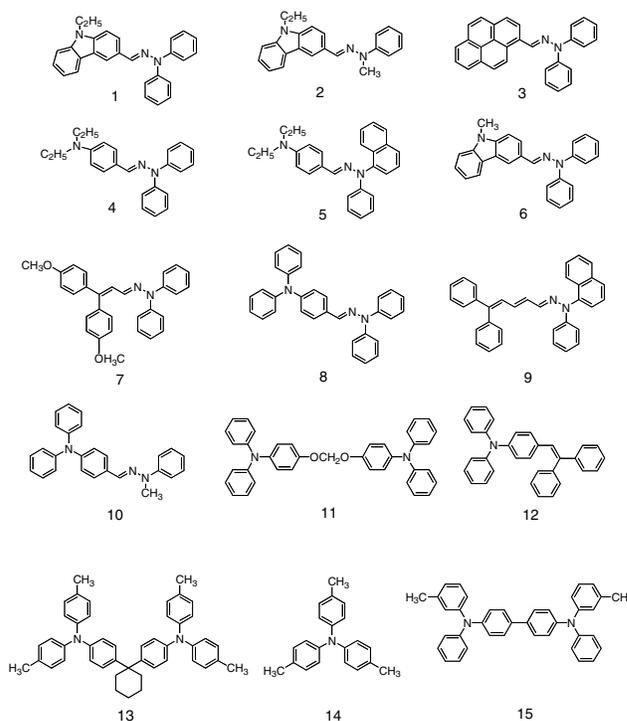


Figure 2. Molecular structures of the existing charge transport molecules

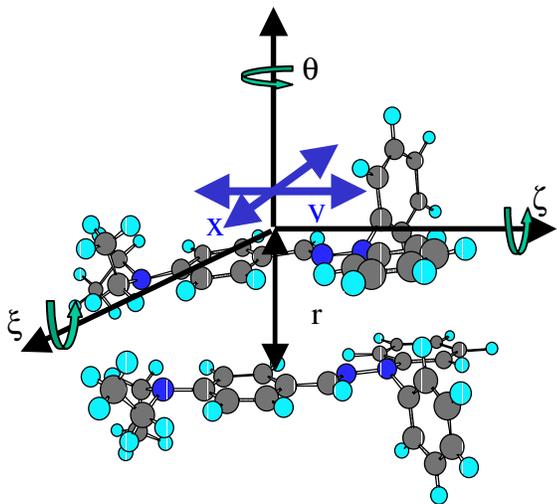


Figure 3. The center of mass of the second CTM is located on one of 18 mesh points which are generated by locating the center of mass of the second CTM 5Å above or below the first CTM molecular plane and sliding the half of molecular size along x or y direction of the plane perpendicular to intermolecular distance line. The second CTM is rotated each angle defined by (ξ, ζ, θ) around the center of mass where ξ and ζ , are $-60^\circ, -30^\circ, 0^\circ, 30^\circ$ or 60° and θ is selected from the angles varied with 30° step starting from 0° .

Results and Discussions

Intramolecular components of reorganization energies ($\lambda_{\text{intramolecular}}$) calculated by PM3 method are shown in Table 1. The $\lambda_{\text{intramolecular}}$ values are compared with zero field hole mobilities obtained in our previous work²⁰⁻²¹ in Figure 4. Sakanoue et al¹⁹ showed that $\lambda_{\text{intramolecular}}$ values obtained by semiempirical molecular orbital calculations based on AM1 approximately agreed with the results of density functional calculations which used usual B3LYP²⁷⁻²⁸ functional with 3-21G* basis set²⁹. Since it is known that the PM3 method is a distinct improvement over the AM1 method without a few cases, the $\lambda_{\text{intramolecular}}$ values obtained in this work would be in better agreement with the DFT results than those obtained by AM1 method. Figure 4 implies that it is difficult to find out good correlation between the intramolecular reorganization energy and hole mobility for several types of hole transport molecules, although Sakanoue et al. showed that hole mobility increased with decreasing the $\lambda_{\text{intramolecular}}$ values for five similar amine compounds¹⁹. This work and our previous work²⁰⁻²¹ suggest that the extension of electronic cloud and the smallness of dipole moment are more important character for hole mobility of CTM than the smallness of $\lambda_{\text{intramolecular}}$ value.

Table 1. Intramolecular component of reorganization energy calculated by PM3 method. (Unit: kcal/mol)

CTM	λ_{neutral}	λ_{cation}	$\lambda_{\text{intramolecular}}$
1	10.3	13.4	23.7
2	10.8	12.7	23.5
3	8.1	10.1	18.2
4	11.9	14.1	26.0
5	14.1	18.1	32.2
6	10.4	13.5	23.9
7	9.4	15.4	24.8
8	13.4	16.9	30.3
9	12.6	15.9	28.5
10	13.3	16.0	29.3
11	8.4	20.3	28.7
12	7.9	11.7	19.5
13	3.5	14.8	18.3
14	2.5	9.3	11.9
15	11.9	20.6	32.5

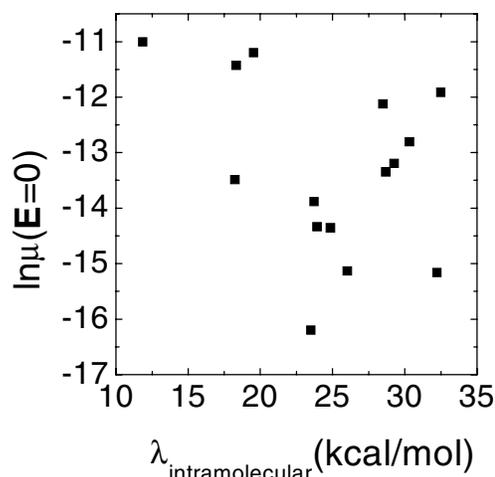


Figure 4 $\ln\mu(E=0)$ vs. $\lambda_{\text{intramolecular}}$

Table 2. Dimerization energies of CTM3, CTM4, and CTM9

CTM	$\mu(E=0)$ ($10^{-6}\text{cm}^2/\text{Vs}$)	$E_{\text{dimerization}}$ (kcal/mol)
3	1.4	-3.7
4	0.27	-8.9
9	5.5	-11.2

The dimerization energies of CTM3, CTM4, and CTM9 are shown with their zero field mobilities in Table 2. Table 2 shows the dimerization energy of homogeneous CTM dimer does not correlate to the zero field mobilities of CTM for the three CTMs. We are studying for other CTMs to make sure how intermolecular interaction among neighboring CTMs contribute to hole mobility. The magnitude of intermolecular interaction's contribution to hole mobility will be compared to those of the extension of electronic cloud and dipole trap depth.

Conclusion

We investigated the effect of intramolecular reorganization and intermolecular interaction of between homogeneous CTM dimer upon hole mobility by using semiempirical molecular orbital theory. The intramolecular reorganization energy was not a good guideline for hole mobility. The intermolecular interaction energies did not correlate to hole mobilities for the investigation of three CTMs. The polarizability and dipole moment calculated by semiempirical molecular orbital method would be more effective guidelines for development of new hole transport molecules for the time being.

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Biography

Takayuki Shoda received his Ph.D degree in chemistry from the University of Hokkaido at Sapporo in 1989. Since 1989 he has worked in Yokohama Research Center at Mitsubishi Chemical Corporation. He studies organic photoconductor and other organic photo-functional materials using both computational chemistry and analytical chemistry.