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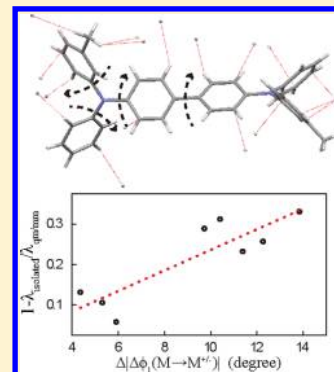
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# Influence of Molecular Packing on Intramolecular Reorganization Energy: A Case Study of Small Molecules

Haoyuan Li, Lian Duan,\* Deqiang Zhang, and Yong Qiu

Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China

**ABSTRACT:** The reorganization energy is one important parameter regarding the charge transfer in organic semiconductors. In the past, the influence of the molecular packing on the intramolecular reorganization energy was commonly neglected in theoretical estimations. Here, the quantum mechanic/molecular mechanic (qm/mm) method is used to study this influence for four small molecules: *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB), 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP), and 4,7-diphenyl-1,10-phenanthroline (Bphen). An approximate linear relationship between the intramolecular reorganization energy and the change of the torsion angle during the molecular relaxation which causes the most steric hindrance is found. Furthermore, reorganization energies from qm/mm calculations are smaller depending on the degree of reduced conformational change.



## INTRODUCTION

Organic electronic devices have come a long way in the past two decades.<sup>1–4</sup> The charge transport process, which is crucial to the performance of devices, has been found to show a hopping behavior. Evaluation of this hopping rate is therefore of great importance to understand the charge transport abilities. The hopping rate is often described using the Marcus equation.<sup>5–8</sup> It has also been shown that the nuclear tunneling effect is also very important.<sup>9</sup> Recently, nonadiabatic molecular dynamics has been used to understand the charge transfer in organic materials.<sup>10–13</sup> Until now, the mechanisms of the charge transport in organic semiconductors are still not fully known.

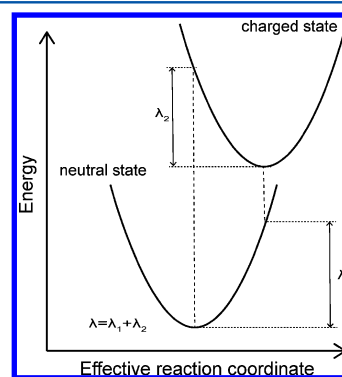
The reorganization energy  $\lambda$  is one important parameter that affects the charge transfer rate, which comprises internal and external parts. The latter is related to the polarization of the surrounding medium and is found to be small.<sup>14,15</sup> However, the molecular packing will also change the conformations of neutral and charged states, which may in turn affect intramolecular reorganization. Nevertheless, this influence has commonly been neglected in the past. Recently, Yang and co-workers showed that the molecular packing indeed has a very small influence on the intramolecular reorganization energies of two bow-shaped thiophene compounds.<sup>16</sup> This seems to validate the previous approximation of estimating  $\lambda$  using calculations on isolated molecules.

Here, the quantum mechanic/molecular mechanic (qm/mm) method is used to study the influence of the molecular packing on the intramolecular reorganization energies of four commonly used small-molecule organic semiconductors: *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB), 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl

(CBP), and 4,7-diphenyl-1,10-phenanthroline (Bphen).<sup>17</sup> Different from Yang and co-workers' conclusions, the influence of the molecular packing on the calculated intramolecular reorganization energies is found to be large. The significance of this influence depends on the degree of reduced conformational change compared with the case of isolated molecules.

## COMPUTATIONAL METHODS

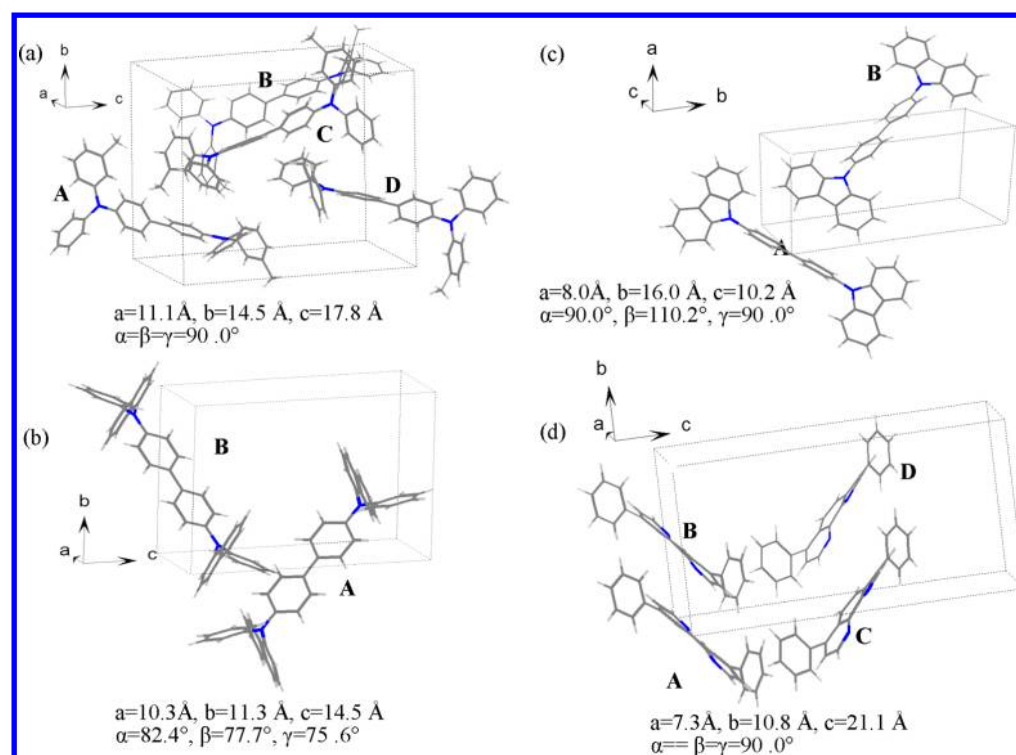
During the charge transfer, both the changes in the geometries of the inner sphere and the surrounding medium contribute to  $\lambda$ . Here, the latter is neglected since it has been considered small.<sup>14,15</sup>  $\lambda$  is calculated using the four-point method (Figure 1).<sup>18</sup>



**Figure 1.** Illustration of the calculation of the reorganization energy using the four-point method.

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**Figure 2.** Crystal structures and labeling of the molecules for (a) TPD, (b) NPB, (c) CBP, and (d) Bphen.

The geometries of neutral, positive, and negative molecules are optimized using the NWChem package.<sup>19</sup> The b3lyp functional<sup>20</sup> and 6-31G(d,p) basis set are used, which are considered to provide enough accuracy.<sup>21</sup> In qm/mm calculations, the molecular packing is taken from the crystal structures<sup>22–25</sup> (Figure 2). The space groups for TPD, NPB, CBP, and Bphen are  $P2_12_12_1$ ,  $P1$ ,  $P2_1/c$ , and  $C2cb$ , respectively. The molecule labeled A is set as the qm molecule, and its structures at different charged states are optimized. The other parts of the system are treated as mm, and their coordinates are fixed during the optimizations. Antechamber from Amber tools 12<sup>26</sup> is used to generate the general AMBER force field (GAFF).<sup>27</sup> Super cells are used to ensure sufficient contact around the qm atoms.

## RESULTS AND DISCUSSION

The calculated intramolecular reorganization energies are shown in Table 1. For TPD,  $\lambda_h$  (for hole transfer) and  $\lambda_e$  (for electron transfer) from calculations on isolated molecules are 250 and 549 meV, respectively, close to the results from other groups.<sup>28–30</sup> For CBP,  $\lambda_h$  and  $\lambda_e$  are close to the results

**Table 1.** Calculated Intramolecular Reorganization Energies for TPD, NPB, CBP, and Bphen

material	method	$\lambda_h$ (meV)	$\lambda_e$ (meV)
TPD	isolated molecule	250	549
	qm/mm	172	408
NPB	isolated molecule	267	161
	qm/mm	205	144
CBP	isolated molecule	137	387
	qm/mm	119	259
Bphen	isolated molecule	346	398
	qm/mm	326	283

from our previous calculations using Gaussian 03<sup>31</sup> at the b3lyp/6-31g(d) level (135 and 375 meV for hole and electron, respectively).<sup>32</sup>

It can be seen from Table 1 that the molecular packing has a great influence on the calculated intramolecular reorganization energies. For TPD, if the molecular packing is taken into account, the intramolecular reorganization energies are 31% and 26% lower for hole and electron, respectively. For NPB, they are 23% and 11%, respectively. For CBP, they are 13% and 33%, respectively. For Bphen, they are 6% and 29%, respectively. From the Marcus theory,  $\lambda$  greatly affects the charge transfer process, and small  $\lambda$  leads to large hopping rates. This means that the estimated charge mobilities might be higher if the molecular packing is taken into account.

Table 2 shows the torsion angles of the molecules at optimized structures, and the angles are defined in Figure 3. The torsion angles for the isolated TPD and CBP molecules are close to the results from other groups.<sup>28,33</sup> It can be seen from Table 2 that the molecules endure large conformational change from neutral to charged states in the case of isolated molecules.

We found an approximate linear relationship between  $\lambda$  and the change of  $\phi_1$  in the molecular relaxation, which is the torsion angle that causes the most steric hindrance, as shown in Figure 4a. The existence of such a relationship suggests that the energy of the molecule during the relaxation could be approximately represented by the change of one torsion angle. As shown in Figure 4c, the relative flat potential energy surface near the optimized structures may be one reason that the energy changes nearly linearly with the difference in torsion angle.

The molecule cannot rotate freely in the surrounding medium. As a result, the torsion angle change during the molecular relaxation is limited. In qm/mm calculations, the reduced torsion angle change is also linked to the degree of decreased reorganization energies, as shown in Figure 4b. It can

Table 2. Torsion Angles at Neutral and Charged States, Calculated at the b3lyp/6-31G(d,p) Level<sup>a,b</sup>

material	method		M	M <sup>+</sup>	M <sup>−</sup>	$\Delta(M \rightarrow M^+)$	$\Delta(M \rightarrow M^-)$
TPD	isolated molecule	$\phi_{1,I}$	−39.423	−26.164	−59.081	13.259	−19.658
		$\phi_{1,II}$	−36.041	−26.120	−58.458	9.922	−22.417
		$\phi_{2,I}$	−41.994	−49.282	−28.712	−7.288	13.282
		$\phi_{2,II}$	−43.342	−48.847	−32.135	−5.506	11.207
		$\phi_{3,I}$	−42.697	−48.780	−35.409	−6.083	7.288
		$\phi_{3,II}$	−43.677	−49.053	−31.919	−5.376	11.758
		$\phi_4$	−32.538	−20.786	12.954	11.752	45.493
		$\phi_{1,I}$	−20.415	−21.955	−29.366	−1.541	−8.951
	qm/mm	$\phi_{1,II}$	−32.582	−33.416	−41.182	−0.834	−8.599
		$\phi_{2,I}$	−46.137	−49.004	−37.245	−2.867	8.891
		$\phi_{2,II}$	−36.630	−39.477	−32.638	−2.846	3.992
		$\phi_{3,I}$	−56.809	−55.559	−52.750	1.251	4.059
		$\phi_{3,II}$	−55.765	−53.382	−49.529	2.383	6.236
		$\phi_4$	−34.516	−31.688	−20.459	2.828	14.057
NPB	isolated molecule	$\phi_{1,I}$	39.725	24.086	46.304	−15.638	6.580
		$\phi_{1,II}$	−39.725	−24.086	−46.304	15.638	−6.580
		$\phi_{2,I}$	33.768	46.365	24.422	12.597	−9.346
		$\phi_{2,II}$	−33.768	−46.365	−24.422	−12.597	9.346
		$\phi_{3,I}$	67.477	65.512	69.134	−1.965	1.657
		$\phi_{3,II}$	−67.477	−65.512	−69.134	1.965	−1.657
		$\phi_4$	−0.102	−0.150	−0.284	−0.047	−0.182
	qm/mm	$\phi_{1,I}$	26.498	22.287	27.703	−4.211	1.205
		$\phi_{1,II}$	−26.505	−22.151	−27.847	4.354	−1.342
		$\phi_{2,I}$	44.488	47.618	41.740	3.131	−2.748
		$\phi_{2,II}$	−44.306	−47.648	−41.401	−3.342	2.905
		$\phi_{3,I}$	63.005	62.899	64.234	−0.106	1.229
		$\phi_{3,II}$	−64.042	−63.797	−65.389	0.245	−1.347
		$\phi_4$	−0.701	−0.686	−0.712	0.014	−0.011
CBP	isolated molecule	$\phi_{1,I}$	−53.864	−44.800	−69.411	9.051	−15.623
		$\phi_{1,II}$	53.814	44.768	69.376	−9.046	15.562
		$\phi_4$	0.005	−0.001	0.007	−0.006	0.002
	qm/mm	$\phi_{1,I}$	−50.403	−43.608	−50.808	6.795	−0.405
		$\phi_{1,II}$	44.065	41.436	47.103	−2.629	3.038
		$\phi_4$	2.283	1.456	1.427	−0.827	−0.856
Bphen	isolated molecule	$\phi_{1,I}$	56.454	44.935	40.578	−11.519	−15.876
		$\phi_{1,II}$	56.454	44.935	40.578	−11.519	−15.876
	qm/mm	$\phi_{1,I}$	51.643	46.005	45.555	−5.638	−6.087
		$\phi_{1,II}$	51.650	46.066	45.432	−5.584	−6.218

<sup>a</sup>I and II indicate different sides of the molecule. <sup>b</sup>Angles are defined in Figure 3. Unit in degrees.

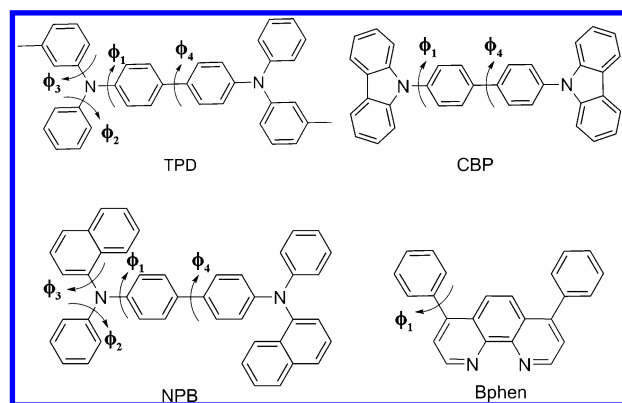
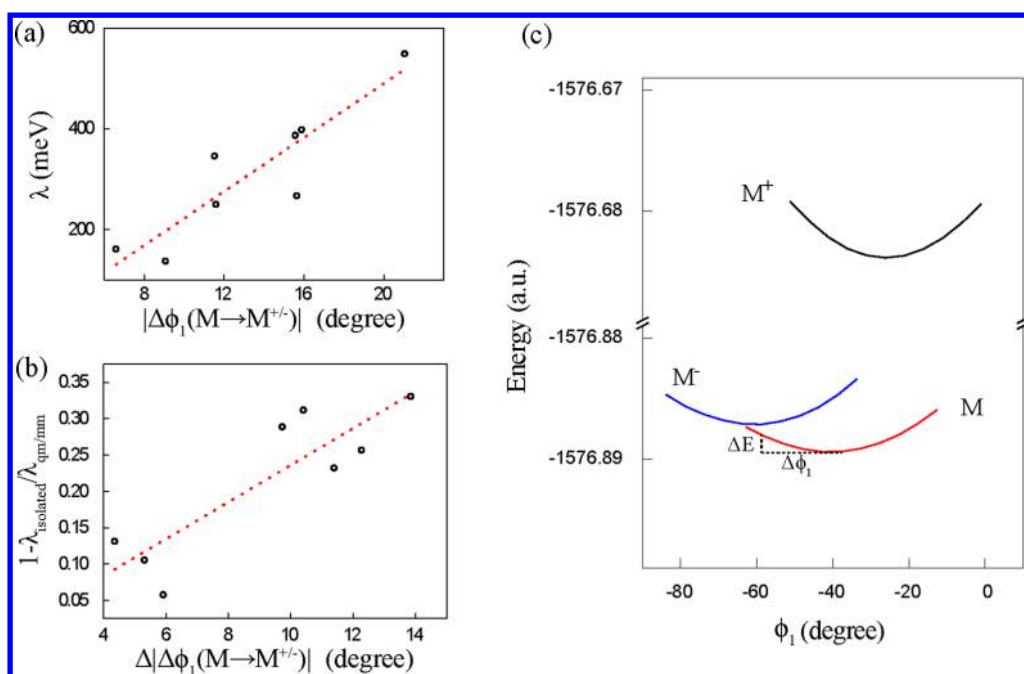


Figure 3. Definition of the torsion angles for TPD, NPB, CBP, and Bphen.

be seen that the more the molecular packing influences the conformational change, the less the calculated reorganization energies are.

We will now discuss why the molecular packing has little influence on the intramolecular reorganization energies of the two bow-shaped thiophene compounds studied by Yang and co-workers.<sup>16</sup> The four molecules we studied endured large conformational change from neutral to charged states in the case of isolated molecules. However, this change is small for the two molecules studied by Yang and co-workers. We carried out calculations at b3lyp/6-31g(d,p) level, and the largest torsion angle changes from neutral to charged states for these two molecules are 0.7° and 3.0°, respectively. In the presence of the surrounding medium, the molecule motion is restricted. Although this influence is significant for TPD, NPB, CBP, and Bphen, for the two molecules Yang and co-workers studied, where the torsion angle change is already small in the case of isolated molecules, the molecular packing has a small influence on the degree of the conformation change. This is why they found that the calculated reorganization energy remains nearly the same when the surrounding medium is considered.



**Figure 4.** (a) Relationship between the intramolecular reorganization energy and the change of  $\phi_1$  in the molecular relaxation ( $|\Delta\phi_1(M \rightarrow M^{+/-})|$ ) from calculations on isolated molecules. (b) Relationship between the degree of reduced intramolecular reorganization energy and the difference of  $|\Delta\phi_1(M \rightarrow M^{+/-})|$  between calculations on isolated molecules and qm/mm systems.  $|\Delta\phi_1(M \rightarrow M^{+/-})|$  is calculated as:  $(|\Delta\phi_{1,I}(M \rightarrow M^{+/-})| + |\Delta\phi_{1,II}(M \rightarrow M^{+/-})|)/2$ . Dotted lines are linear fits. (c) Potential energy surface obtained by optimizing the structure of isolated TPD molecule at fixed  $\phi_1$  of different values.

## CONCLUSIONS

In summary, the intramolecular reorganization energies of TPD, NPB, CBP, and Bphen are calculated both in the cases of isolated molecules and in solids. An approximate linear relationship is found between the reorganization energy and the change of the torsion angle which causes the most steric hindrance during the molecular relaxation. When the molecular packing is taken into account, the torsion angle changes less during the charge transfer process. The degree of decreased reorganization energy is linked to the reduced conformational change. It is suggested that to avoid large deviations in mobility estimations the molecular packing should be taken into consideration when calculating the intramolecular reorganization energy.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: duanl@mail.tsinghua.edu.cn. Phone: (+86)10-6277-9988.

### Notes

The authors declare no competing financial interest.

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