

Internal Reorganization Energy Contributed by Torsional Motion in Electron Transfer Reaction between Biphenyl and Biphenyl Anion Radical

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Concerning the theoretical estimation of internal reorganization energy contributed by the torsional motion between biphenyl and biphenyl anion radical, direct calculation of self-exchange electron transfer reaction was investigated. With the introduction of a proper average bond length and angle parameters < bond Bp >, a multiple step relaxation Nelson method was developed to deal with the torsional reorganization energy. Based on the above model, an estimation of pure torsional reorganization energy $\lambda_{t,p}$ with an approximation of $\lambda_{t,1}$ was achieved. The results of 0.140 and 0.125 eV of torsional reorganization energy for a cross-reaction at the levels of 4-31G and HP/DZP, respectively, are in good agreement with the value of 0.13 eV obtained by Miller *et al.* from the rate measurements. This implies the efficiency and validity of our method to estimate the reorganization energy contributed by pure torsional motion of Bp.

Keywords multiple step relaxation Nelson method, internal reorganization energy, torsional motion, biphenyl molecule, electron transfer

Introduction

Electron transfer (ET) reactions are found to be an elemental step in many biological processes indeed.¹⁻⁶ It has been believed that the experimental measurement of ET reactions between biphenyl (Bp) and a series of organic systems, designed by Miller *et al.*, is the first successful experimental observation of ET reactions in Marcus' inverted region.^{7,8} In the process of intramolecular

ET, the torsional movement of Bp has been expected to have a substantial effect on ET rates and affect the structure of the spacer and acceptor more strongly than in an intermolecular ET process.

Neutral Bp is a very interesting molecule because of the existence of an approximately 45° torsional angle between the two phenyl rings. Slightly different results have been found to vary in the range of 38°—47°, depending upon the basis sets used in calculations.⁹ Rubio *et al.* applied the geometry optimization using the complete active space self-consistent field method, and obtained a value of 44.3° for the torsional angle which is in agreement with the gas-phase electron diffraction ($44.4 \pm 1.2^\circ$).^{10,11} More recently, the torsional angle ϕ calculated at the MP2/6-311 + G(2d,2p) level was 42.1°, while ϕ calculated using various density functionals with different basis sets was very close to 40°.¹² On the other hand, geometry optimization indicates that all the carbon atoms in biphenyl anion radical (Bp⁻) lie on the same plane with an inter-ring torsional angle of 0°.^{13,14}

Experiments have been performed using both biphenyl and fluorine as the electron donors (BSN and 2FSN systems, Fig. 1) to examine the effect of the inter-ring torsional motion of Bp, because the former will undergo torsion of about 45°, whereas the latter remains planar in the ET process due to the existence of the tetrahedral carbon. Miller *et al.* found an eightfold change in the ET rate between biphenyl and fluorine systems. This

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difference can be attributed to the additional reorganization energy of 0.13 eV due to the torsional vibration of biphenyl.¹⁵ Such results lead to a conclusion that the torsion motion in these ET reactions which involve the biphenyl fragment will make the internal reorganization energy much higher than that of planar π -systems.

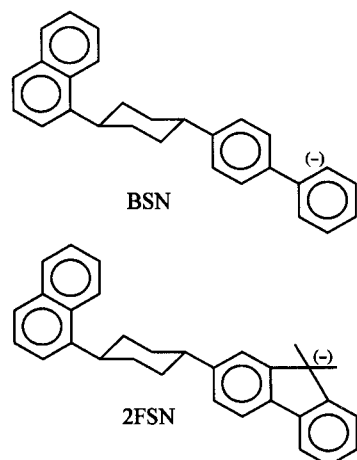


Fig. 1 Frame sketches of BSN and 2FSN.

In theoretical researches, in order to compare with the corresponding experimental results, models that are similar to BSN and 2FSN systems were chosen as the calculated molecules. However, results calculated by Li *et al.* revealed that the difference between Mf^- (9,9'-dimethylfluorene)/A and Bp^- /A that the torsional motion in biphenyl contributes an extra 0.32 eV to the internal reorganization energy, when compared with the rigid coplanar case, which is larger by 0.19 eV than the value of 0.13 eV obtained by Miller *et al.* from the rate measurements.¹⁶

However, beside comparing the difference of the internal reorganization energies of two relating intramolecular ET processes, few theoretical papers exist that directly calculating the internal reorganization energy contributed by torsional movement of Bp through one electron self-exchange reaction. Nelsen ever obtained the internal reorganization energy for self-exchange ET reactions using the AM1 semiempirical molecular orbital method.^{17,18} In the present paper, with some consideration of detailed dynamic process, a multiple step relaxation Nelson method was applied to deal with the torsional reorganization energy directly.

Calculation method

Marcus relation

Chemists have made attempts to gain insight into the reaction mechanism and to predict the rate constant by calculating the necessary dynamic parameters. In the development of electron transfer theory, it was emphasized that the solvent contributions come from modes of such low frequencies that they can be treated with classically, but the internal reorganization energies usually come from skeletal vibrations having high frequencies which often require a quantum mechanical treatment.^{19,20}

Marcus ever presented a method where λ_i is based on the reorganization of the intramolecular degrees of freedom, assuming harmonic approximation.^{21,22}

$$\lambda_i = \sum_j \frac{f_j^R f_j^P}{f_j^R + f_j^P} \Delta q_j^2 \quad (1)$$

According to this, the internal reorganization energy λ_i is the sum over all 3N-6 vibrational modes. f_j^R and f_j^P are the force constants of the reactants and the products, respectively. Δq_j is the change in bond lengths $\Delta q_j = |q_j^P - q_j^R|$. The drawback of this method is the unambiguous assignment of the vibrational modes and the force constants to the bond length changes.²³ Another reason might be that the time scale of electron self-exchange does not allow complete normal mode vibrational motions of the neutral Bp and Bp^- anion radical during the electron transfer.²⁴ Therefore the Marcus relation seems to be not valid for molecules like Bp, where torsional angle changes, as well as bond length and bond angle changes, are the main contribution to the geometrical reorganization.

Nelson method

A different approach, called Nelson method, is to describe the internal reorganization energy by thermodynamic consideration.^{17,18} For a self-exchange reaction, we can optimize the equilibrium geometries for B^- and B, and thus, obtain the corresponding equilibrium energies $E_{eq}(B^-)$ and $E_{eq}(B)$. On the other hand, it can be

calculated the energy $E_{n\text{-eq}}(\text{B})$ for neutral molecule B at the equilibrium configuration of B^- , but $E_{n\text{-eq}}(\text{B}^-)$ for anion radical B^- at the equilibrium configuration of B.¹⁶ Thus the internal reorganization energy λ_i can be obtained from Eq. (2).

$$\lambda_i(\text{B}^-/\text{B}) = E_{n\text{-eq}}(\text{B}) + E_{n\text{-eq}}(\text{B}^-) - E_{\text{eq}}(\text{B}) - E_{\text{eq}}(\text{B}^-) \quad (2)$$

The internal reorganization energy of a cross-reaction $\text{D}^- + \text{A} \rightarrow \text{D} + \text{A}^-$ can be approximated as an average value,

$$\lambda_i(\text{D}^-/\text{A}) = [\lambda_i(\text{D}^-/\text{D}) + \lambda_i(\text{A}^-/\text{A})]/2 \quad (3)$$

Multiple step relaxation Nelson method

Nelsen method has been proved to be applicable and efficient in the internal reorganization energy evaluation.²⁴ However, when the torsional reorganization energy needs to be separated from the whole internal reorganization energy, such as in this paper, the concrete dynamic relation of the torsional motion, and bond length and bond angle changes should be taken into account, which can not be achieved in single step relaxation Nelson model. It is also difficult in treating with internal reorganization energy of Bp-contained systems theoretically.

For instance, if we assume that the torsional motion takes place first and then the bond length and bond angles change for Bp and Bp^- in a self-exchange reaction, the torsional reorganization energy can be described as:

$$\lambda_{i,1} = \lambda_i(\text{bond Bp}, \phi, \text{anion} \rightarrow \text{bond Bp}, \text{co-plane}, \text{anion}) + \lambda_i(\text{bond Bp}^-, \text{co-plane}, \text{neutral} \rightarrow \text{bond Bp}^-, \phi, \text{neutral}) \quad (4)$$

where $\lambda_i(\text{bond Bp}, \phi, \text{anion} \rightarrow \text{bond Bp}, \text{co-plane}, \text{anion})$ is obtained by varying the torsion angle of Bp to the co-plane structure and keeping its other bond length and angle unchanged, similarly $\lambda_i(\text{bond Bp}^-, \text{co-plane}, \text{neutral} \rightarrow \text{bond Bp}^-, \phi, \text{neutral})$ is the torsion barrier from the Bp^- to the torsion conformation without variation of other bond lengths and angles.

Here $\lambda_i(\text{bond Bp}, \phi, \text{anion} \rightarrow \text{bond Bp}, \text{co-plane}, \text{anion})$ and $\lambda_i(\text{bond Bp}^-, \text{co-plane}, \text{neutral} \rightarrow \text{bond Bp}^-, \phi, \text{neutral})$ can be expressed as following, respectively.

$$\lambda_i(\text{bond Bp}, \phi, \text{anion} \rightarrow \text{bond Bp}, \text{co-plane}, \text{anion}) = E_{(\text{bond Bp}, \phi, \text{anion})} - E_{(\text{bond Bp}, \text{co-plane}, \text{anion})} \quad (5)$$

$$\lambda_i(\text{bond Bp}^-, \text{co-plane}, \text{neutral} \rightarrow \text{bond Bp}^-, \phi, \text{neutral}) = E_{(\text{bond Bp}^-, \text{co-plane}, \text{neutral})} - E_{(\text{bond Bp}^-, \phi, \text{neutral})} \quad (6)$$

It is found that the potential value of equilibrium $E_{(\text{bond Bp}, \phi, \text{anion})}$ is very high. This is because that the negative charge of anion is quite repulsed not only by the ϕ angle, but also by the equilibrant bond lengths and angles of neutral Bp. So $E_{(\text{bond Bp}, \phi, \text{anion})}$ can be evaluated approximately.

$$E_{(\text{bond Bp}, \phi, \text{anion})} = \Delta E(\phi \leftarrow \rightarrow \text{anion}) + \Delta E(\text{bond Bp} \leftarrow \rightarrow \text{anion}) \quad (7)$$

where $\Delta E(\phi \leftarrow \rightarrow \text{anion})$ stands for the potential rise due to the interaction of ϕ angle and negative charge of anion, while $\Delta E(\text{bond Bp} \leftarrow \rightarrow \text{anion})$ is the potential rise due to the incompatibility of negative charge of anion and equilibrant bond lengths and angles of Bp. Analogous analysis can also be applied to $E_{(\text{bond Bp}, \text{co-plane}, \text{anion})}$, $E_{(\text{bond Bp}^-, \text{co-plane}, \text{neutral})}$ and $E_{(\text{bond Bp}^-, \phi, \text{neutral})}$, respectively.

Here, we approximately regard $\Delta E(\text{bond Bp} \leftarrow \rightarrow \text{neutral})$, $\Delta E(\phi \leftarrow \rightarrow \text{neutral})$, $\Delta E(\text{bond Bp} \leftarrow \rightarrow \phi)$, $\Delta E(\text{bond Bp}^- \leftarrow \rightarrow \text{anion})$, $\Delta E(\text{anion} \leftarrow \rightarrow \text{co-plane})$ and $\Delta E(\text{co-plane} \leftarrow \rightarrow \text{Bp}^-)$ as 0. Obviously, λ_i in this case can be expressed as:

$$\lambda_{i,1} = \Delta E(\phi \leftarrow \rightarrow \text{anion}) - \Delta E(\text{bond Bp} \leftarrow \rightarrow \text{co-plane}) + \Delta E(\text{co-plane} \leftarrow \rightarrow \text{neutral}) - \Delta E(\text{bond Bp}^- \leftarrow \rightarrow \phi) \quad (8)$$

On the contrary, if we assume that the bond lengths and bond angles changes strictly take place earlier than the torsional movement for Bp and Bp^- in a self-exchange reaction, the torsional reorganization energy would be described as:

$$\lambda_{i,2} = \lambda_i(\text{bond Bp}^-, \phi, \text{anion} \rightarrow \text{bond Bp}^-, \text{co-plane}, \text{anion}) + \lambda_i(\text{bond Bp}, \text{co-plane}, \text{neutral} \rightarrow \text{bond Bp}, \phi, \text{neutral}) \quad (9)$$

Following the same treatment above, λ_i can be obtained

under this assumption:

$$\lambda_{t,2} = \Delta E(\phi \leftarrow \rightarrow \text{anion}) + \Delta E(\text{bond Bp}^- \leftarrow \rightarrow \phi) + \Delta E(\text{co-plane} \leftarrow \rightarrow \text{neutral}) + \Delta E(\text{bond Bp} \leftarrow \rightarrow \text{co-plane}) \quad (10)$$

However, in Eqs. (8) and (10), $\Delta E(\text{bond Bp} \leftarrow \rightarrow \text{co-plane})$ and $\Delta E(\text{bond Bp}^- \leftarrow \rightarrow \phi)$ both come from the interaction of torsional movement and bond length and angle changes, and should not be included in the pure contribution of torsional motion to internal reorganization energy. This implies that considering the low-frequency torsional movement and high-frequency bond length and angle changes to be separated strictly is not convincing.

In principle, in order to reduce the interaction of torsional movement and bond length and angle changes to 0, proper average bond length and angle parameters $\langle \text{bond Bp} \rangle$ which meets the following equation can be introduced:

$$\frac{\Delta E(\phi \leftarrow \rightarrow \langle \text{bond Bp} \rangle)}{\Delta E(\text{co-plane} \leftarrow \rightarrow \langle \text{bond Bp} \rangle)} = \quad (11)$$

An imagined and detailed ET model in order to calculate torsional reorganization energy (Fig. 2) is shown considering the following steps.

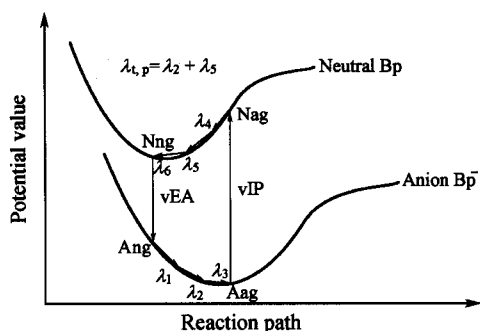


Fig. 2 Potential energy curves of the ET reaction $\text{Bp}^-/\cdot\text{Bp}$.

To the relaxed neutral molecule (Nng) one electron is added. The energy difference in the neutral geometry (Ang) is equal to the vertical electron affinity (vEA). Then, the anion changes its bond lengths and angles to $\langle \text{bond Bp} \rangle$, yielding the relaxation energy λ_1 ; then its torsional angle changes from ϕ to co-plane without any other variations, and this step yields λ_2 ; at last, its bond

lengths and angles change from $\langle \text{bond Bp} \rangle$ to (bond Bp^-) and yield λ_3 . Removing the electron without geometry relaxation results in the neutral molecule in the anion geometry (Nag) corresponding to the vertical ionization potential (vIP). Similarly the relaxation of the molecule to the neutral geometry (Nng) results in energy $\lambda_4 + \lambda_5 + \lambda_6$. Therefore, once through the geometry optimization the $\langle \text{bond Bp} \rangle$ which suits for Eq. (11) can be obtained, $\lambda_2 + \lambda_5$, the sum of both pure torsional reorganization energies in the neutral molecule and in the anion radical, can be regarded as the calculation result of internal reorganization energy contributed by torsional motion of Bp in a self-exchange reaction.

Estimation of torsional reorganization energy

Another simple approach to estimate the contribution of torsional motion may exist. Comparing Eqs. (11) and (13), the pure torsional reorganization energy $\lambda_{t,p}$ can be obtained by averaging the two $\lambda_{t,1}$, $\lambda_{t,2}$ in Eqs. (8) and (10)

$$\lambda_{t,p} = \frac{\lambda_{t,1} + \lambda_{t,2}}{2} \quad (12)$$

Torsional potential barriers of $17.64 \text{ kJ} \cdot \text{mol}^{-1}$ at the 4-31G level and $14.86 \text{ kJ} \cdot \text{mol}^{-1}$ at the DZP level (dunning's 9s6p/5s3p basis sets with polarization functions on all the atoms) have been obtained by varying the torsion angle of Bp to the co-plane structure and keeping the other bond parameters unchanged. Similarly the torsion barrier from the Bp^- to the torsion conformation has been found to be 36.11 and $32.16 \text{ kJ} \cdot \text{mol}^{-1}$ at the levels of 4-31G and HP/DZP, respectively.^{23,25} As defined above, the value of $\lambda_{t,2}$ is the sum of these two torsional potential barriers, and it is 53.75 and $47.02 \text{ kJ} \cdot \text{mol}^{-1}$ at the levels of 4-31G and HP/DZP, respectively. In the case of $\lambda_{t,1}$, in fact, the difference between $\Delta E(\phi \leftarrow \rightarrow \text{anion})$ and $\Delta E(\text{bond Bp} \leftarrow \rightarrow \text{co-plane})$ is small, which is also true between $\Delta E(\text{co-plane} \leftarrow \rightarrow \text{neutral})$ and $\Delta E(\text{bond Bp}^- \leftarrow \rightarrow \phi)$. As a result, $\lambda_{t,1}$ can be simply regarded as 0, and therefore torsional reorganization energy of self-exchange reaction of $\lambda_{t,p}$ is about $27 \text{ kJ} \cdot \text{mol}^{-1}$ at the 4-31G level and $24 \text{ kJ} \cdot \text{mol}^{-1}$ at the HP/DZP level. According to Eq. (3), the internal reorganization energy contributed by torsional motion of Bp is about $13.5 \text{ kJ} \cdot \text{mol}^{-1}$ (or about 0.140 eV) and $12 \text{ kJ} \cdot \text{mol}^{-1}$ (or about

0.125 eV) for a cross-reaction at the levels of 4-31G and HP/DZP, respectively.

Conclusions

The results of 0.140 and 0.125 eV for torsional reorganization energy at the levels of 4-31G and HP/DZP, respectively, are in good agreement with the value of 0.13 eV obtained by Miller *et al.* from the cross-reaction rate measurements,¹⁵ and better than indirectly calculation conclusions by comparing the internal reorganization energy difference between two relating ET reactions.^{16,25-28} This implies the efficiency and validity of our method to estimate the reorganization energy contributed by pure torsional motion of Bp. The data suggest that the low-frequency torsional movement strictly takes place later than high-frequency bond length and angle changes and it may be ill-considered in evaluation of low-frequency torsional reorganization energy. Investigating long-distance intramolecular ET reactions that depend critically on these low-frequency torsional motions will need to address these issues to estimate the effect of torsional motions on solvent reorganization energy, internal reorganization energy and ET rates.²⁹⁻³³

References

- 1 Petrov, E. G.; May, V. *J. Phys. Chem. A* **2001**, *105*, 10176.
- 2 Olofsson, J.; Larsson, S. *J. Phys. Chem. B* **2001**, *105*, 10398.
- 3 Ito, H.; Nakatsuji, H. *J. Comp. Chem.* **2001**, *22*, 265.
- 4 Porath, D.; Bezryadin, A.; de Vries, S.; Dekker, C. *Nature* **2000**, *403*, 635.
- 5 Lower, S. K.; Hochella, M. F.; Beveridge, T. J. *Science* **2001**, *292*, 1360.
- 6 Balabin, I. A.; Onuchic, J. N. *Science* **2000**, *290*, 114.
- 7 Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.
- 8 Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.
- 9 Tsuzuki, S.; Tanabe, K. *J. Phys. Chem.* **1991**, *95*, 139.
- 10 Rubio, M.; Merchan, M.; Ortí, E. *Theor. Chim. Acta* **1995**, *91*, 17.
- 11 Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J. *J. Mol. Struct.* **1985**, *128*, 59.
- 12 Arulmozhiraja, S.; Fujii, T. *J. Chem. Phys.* **2001**, *115*, 10589.
- 13 Takei, Y.; Yamaguchi, T.; Osamura, Y.; Fuke, K.; Kaya, K. *J. Phys. Chem.* **1988**, *92*, 577.
- 14 Buntinx, G.; Poizat, O. *J. Phys. Chem.* **1989**, *91*, 2153.
- 15 Miller, J. R.; Paulson, B. P.; Bal, R.; Closs, G. L. *J. Phys. Chem.* **1995**, *99*, 6923.
- 16 Li, X. Y.; Tong, J.; He, F. C. *Chem. Phys.* **2000**, *260*, 283.
- 17 Nelsen, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677.
- 18 Nelsen, S. F.; Yunta, M. J. R. *J. Phys. Org. Chem.* **1994**, *7*, 55.
- 19 Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748.
- 20 Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741.
- 21 Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
- 22 Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
- 23 Li, X. Y.; Xiao, S. Q.; He, F. C. *Sci. China, Ser. B: Chem.* **1999**, *42*, 441.
- 24 Kelterer, A. M.; Landgraf, S.; Grampp, G. *Spectrochim. Acta, Part A* **2001**, *57*, 1959.
- 25 Li, X. Y.; Tang, X. S.; Xiao, S. Q.; He, F. C. *J. Mol. Struct.* **1995**, *342*, 181.
- 26 Li, X. Y.; He, F. C. *J. Comp. Chem.* **1999**, *20*, 597.
- 27 Zhang, X. D.; Wang, Y. N.; Guo, J. X.; Zhang, Q. Y. *J. Photochem. Photobiol. A* **1999**, *121*, 1.
- 28 Guo, J. X.; Zhang, Q. Y. *J. Photochem. Photobiol. A* **1997**, *110*, 247.
- 29 Kumar, K.; Kurnikov, I. V.; Beratan, D. N.; Waldeck, D. H.; Zimmt, M. B. *J. Phys. Chem. A* **1998**, *102*, 5529.
- 30 Min, W.; Sun, L. *Acta Phys.-Chim. Sin.* **2001**, *17*, 924 (in Chinese).
- 31 Davis, W. B.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 877.
- 32 Skokov, S.; Wheeler, R. A. *J. Phys. Chem. A* **2000**, *104*, 6314.
- 33 Zong, Y. P.; McHale, J. L. *J. Chem. Phys.* **1997**, *106*, 4963.

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