ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 121 (1999) 1–6

Journal of Photochemistry and Photobiology A:Chemistry

Molecular orbital study on the internal reorganization energy in intramolecular electron transfer reactions[☆]

Xiao-dong Zhang, Yan-ni Wang, Jian-xin Guo, Qi-yuan Zhang*

State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 21 September 1998; received in revised form 5 October 1998; accepted 18 November 1998

Abstract

Nelsen's method was extended for the study of the internal reorganization energy, λ_v, of intramolecular electron transfer (ET) for two donor (D)–spacer (S)–acceptor (A) systems. The semiempirical molecular orbital method AM1 was used in the calculation. The sparkle method was also used to simulate the solvent polarization effect. The meanings of S, A and D are S = cyclohexane, A = 2-naphthalene. For the two donors, D = 4-biphenyl (B) and D = 2-(9,9′ dimethyl) fluorene (2F) are for systems BSN and 2FSN, respectively. For the system BSN, the calculated λ_v (1.12 eV) is consistent with the experimental result (1.13 eV) very well. The replacement of B by 2F caused a change of λ_v ($\Delta\lambda_v = 0.095$ eV). This value, originating from the difference of the low-frequency torsional movement between two donors B and 2F, is consistent with the experimental results. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electron transfer; Reorganization energy; AM1; Sparkle method

---

1. Introduction

The reorganization energy λ, is one of the crucial quantities controlling the rate of the electron transfer (ET) reactions [1–3]. There are two contributions to the total reorganization energy: the solvent reorganization energy, λ_s, and the internal reorganization energy, λ_v. The former is from the polarization changes of solvent molecules and the latter is from the structure change of the reacting species during the ET process. The λ_s can be treated classically from the two-sphere model [1–3] or ellipsoidal cavity model [4–6], but it is difficult to be treated with quantum mechanics due to the complexity of the polarization of solvent molecules. In principle, λ_v can be obtained by vibrational analysis based on the molecular orbital calculations [7–13], but it is not easy for multiatomic molecular systems.

Nelsen [12] and Clark [13] obtained the λ_v for self-exchange ET reactions using the AM1 semiempirical molecular orbital method. We have extended this method to the calculation of the λ_v in back ET within geminate radical ion pairs at both AM1 and ab initio level successfully [14]. In the present paper, Nelsen's method was extended to treat λ_v in the intramolecular ET reactions and the sparkle method was used to simulate the polarization of solvent molecules. In the calculation, the AM1 semiempirical molecular orbital theory was used. In order to compare with the corresponding experimental results, the calculated systems were chosen as $D^-SA \rightleftharpoons DSA^-$, where S = cyclohexane spacer, A = 2-naphthalene acceptor. For the two donors, D denotes 4-biphenyl (B) and 2-(9,9′-dimethyl) fluorene (2F) for systems BSN and 2FSN, respectively. The systems had been studied extensively in experimental methods [15–20]. The corresponding frame sketches and atomic numbering are shown in Fig. 1.

2. Models and calculation methods

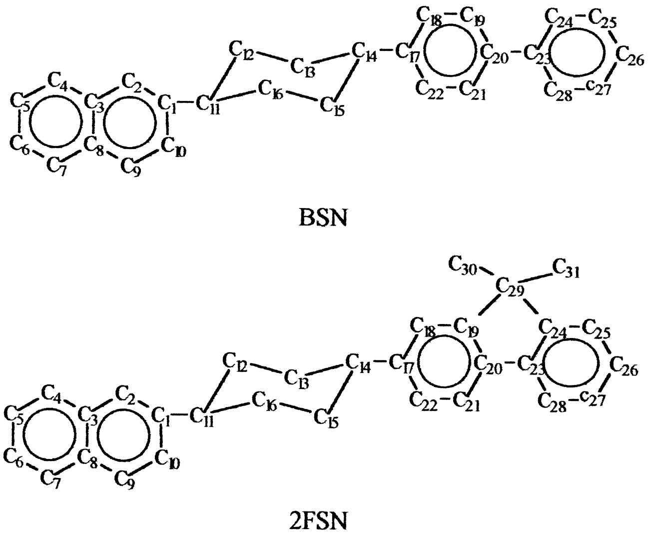
For an intramolecular ET system, the electron being transferred is localized at the donor in the '*Initial State*', and then transfers to the acceptor forming the '*Final State*'. According to the Franck–Condon principle, the nuclear conformation and the momentum are kept the same as in the *Initial State* during the actual ET process. We defined this state as '*ET State 1*' (shown in Scheme 1). After the relaxation, the system takes the geometry of the *Final State*. It is the same case for the back ET. During the factual back ET process, an electron transfers from the acceptor (*Final*

---

*Corresponding author. Fax: +86-10-62569454; e-mail: zhangqy@infoc3.icas.ac.cn

[☆] Project supported by the National Natural Science Foundation of China (29733100, 39890390).

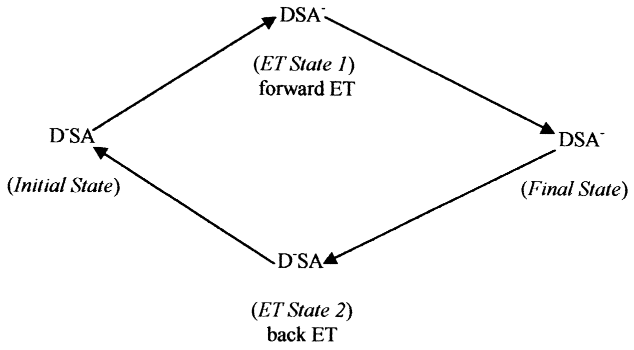
PII: S1010-6030(98)00449-3



BSN

2FSN

Fig. 1. The frame sketches of BSN and 2FSN.



Scheme 1. The definitions of states in ET reactions

State) to the donor, but the structure of the molecule is still in the *Final State*. We defined this state as '*ET State 2*'. After the relaxation, the system takes the geometry of the *Initial State*. The corresponding states are also shown in Scheme 1. The difficulty of the quantum chemical treatment for an intramolecular ET reaction lies in obtaining the *Initial* and *Final States*.

To simulate the *Initial State* and *Final State* mentioned above, we took the sparkle method as the simplest method to simulate the solvent effect for the ET system $D^-SA \Leftrightarrow DSA^-$. We put two point charges (sparkle) around systems D^-SA and DSA^-, and then performed the energy optimization calculation to obtain the positions of these two point charges respectively to imitate the fluctuations of the solvent polarization.

In the intramolecular ET, the reorganization energy is the sum of the reaction free energy ΔE (taken as positive for exothermic process) and the optical excitation energy $E^{\mathrm{e}}_{\mathrm{IT}}$ [21]. In other words, the reorganization energy of an ET reaction can be obtained as the energy difference between the *Final State* with the geometry of *Initial State* and the *Final State* with relaxed geometry.

According to Nelsen's model [12], the internal reorganization energy in self-exchange ET $A + A^+ \leftrightarrow A^+ + A$ can be expressed as Eq. (1) if the changes of the entropy can be neglected [12,13].

$$\lambda_v = [\Delta H_f^0(c^0) - \Delta H_f^0(n^0)] + [\Delta H_f^0(n^+) - \Delta H_f^0(c^+)] \qquad (1)$$

where ΔH_f^0 stands for the enthalpy of formation, (c) and (n) indicate the geometry of the cationic and neutral species, respectively, and the superscripts (0) and (+) indicate the net charge of 0 and +1, respectively.

We can extend the Nelsen's theory to the calculation of λ_v in intramolecular ET reactions. For the forward intramolecular ET, the reorganization energy can be expressed as

$$\lambda_v(\mathit{Forward}) = \Delta H_f^A(\mathit{ET\ State}\ 1) - \Delta H_f^A(\mathit{Final\ State}) \qquad (2)$$

and for the back intramolecular ET, we have

$$\lambda_v(\mathit{Back}) = \Delta H_f^D(\mathit{ET\ State}\ 2) - \Delta H_f^D(\mathit{Initial\ State}) \qquad (3)$$

In Eq. (2) and Eq. (3), the superscript (D) and (A) indicate the electron being transferred is localized on donor and acceptor, respectively.

Since the results of molecular structure and energy obtained by AM1 method were consistent with those by ab initio and experimental determination for these systems [14], the AM1 semiempirical program in MOPAC program package [22,23] (version 6.0) at the unrestricted Hartree–Fock (UHF) levels was used throughout the calculation. The geometry was obtained by the Baker's eigenvector following [24] (EF) geometry optimization. A pair of positive and negative point charges were laid properly near the edge of the donor and acceptor to simulate the polarization of the THF solvent. All molecular geometrical parameters were optimized until the gradient norm was less than $0.01\ \mathrm{kcal}\ \text{Å}^{-1}$. The largest number of the geometrical parameters is 181, and the standard AM1 parameters were used.

3. Results and discussions

3.1. The conformation of molecules

3.1.1. The Initial and Final States in system BSN

Table 1 shows some calculated geometrical parameters of both *Initial* and *Final States* in the intramolecular ET of system BSN.

The electron being transferred is localized on the biphenyl donor in the *Initial State*. It can be seen that atoms on the phenyl rings of the donor are slightly deviated from the ring plane as $C_{21\text{-}20\text{-}19\text{-}18} = -7.018^\circ$, $C_{27\text{-}26\text{-}25\text{-}24} = -2.420^\circ$. The twist angle between the two phenyl rings of the donor is $C_{24\text{-}23\text{-}20\text{-}19} = 0.403^\circ$, which is similar to the coplanarity of the anion radical of biphenyl [14,25,26]. The atoms on naphthalene acceptor are almost in the same plane. The

Table 1
The geometric parameters of BSN in *Initial State* and *Final State*

Parameter	*Initial State*	*Final State*	Parameter	*Initial State*	*Final State*	Parameter	*Initial State*	*Final State*
Bond length								
C_{1-2}	1.391	1.396	C_{1-11}	1.495	1.496	C_{19-20}	1.430	1.407
C_{2-3}	1.418	1.419	C_{11-12}	1.525	1.525	C_{20-21}	1.430	1.407
C_{3-4}	1.419	1.405	C_{12-13}	1.513	1.515	C_{21-22}	1.383	1.394
C_{4-5}	1.385	1.410	C_{13-14}	1.526	1.524	C_{20-23}	1.415	1.456
C_{5-6}	1.412	1.385	C_{14-15}	1.525	1.525	C_{23-24}	1.429	1.406
C_{6-7}	1.386	1.396	C_{15-16}	1.515	1.513	C_{24-25}	1.386	1.395
C_{7-8}	1.419	1.429	C_{14-17}	1.490	1.494	C_{25-26}	1.402	1.398
C_{8-9}	1.419	1.397	C_{17-18}	1.409	1.403	C_{26-27}	1.402	1.399
C_{9-10}	1.384	1.397	C_{18-19}	1.384	1.394	C_{27-28}	1.386	1.394
Bond angle								
C_{3-2-1}	121.041	121.177	$C_{12-11-1}$	110.537	111.533	$C_{21-20-19}$	115.533	118.474
C_{4-3-2}	121.736	121.888	$C_{13-12-11}$	111.201	111.347	$C_{22-21-20}$	121.863	120.693
C_{5-4-3}	120.522	120.421	$C_{14-13-12}$	111.440	111.153	$C_{23-20-19}$	122.233	120.723
C_{6-5-4}	120.576	120.187	$C_{15-14-13}$	109.860	110.010	$C_{24-23-20}$	122.059	120.686
C_{7-6-5}	119.999	121.103	$C_{16-15-14}$	111.301	111.086	$C_{25-24-23}$	121.783	120.422
C_{8-7-6}	120.684	120.125	$C_{17-14-13}$	110.943	111.701	$C_{26-25-24}$	120.915	120.470
C_{9-8-7}	121.987	122.294	$C_{18-17-14}$	120.572	120.038	$C_{27-26-25}$	118.591	119.399
C_{10-9-8}	120.815	121.156	$C_{19-18-17}$	121.257	120.697	$C_{28-27-26}$	120.913	120.424
$C_{11-1-10}$	119.393	119.628	$C_{20-19-18}$	121.848	120.687			
Dihedral angle								
$C_{4-3-2-1}$	−179.072	176.761	$C_{13-12-11-1}$	179.822	179.370	$C_{21-20-19-18}$	−7.018	0.743
$C_{5-4-3-2}$	178.858	−179.954	$C_{14-13-12-11}$	−56.805	−56.836	$C_{22-21-20-19}$	6.994	−0.690
$C_{6-5-4-3}$	0.203	1.041	$C_{15-14-13-12}$	56.316	56.478	$C_{23-20-19-18}$	172.090	−178.739
$C_{7-6-5-4}$	0.301	2.155	$C_{16-15-14-13}$	−56.296	−56.445	$C_{24-23-20-19}$	0.403	−35.462
$C_{8-7-6-5}$	−0.443	−3.798	$C_{17-14-13-12}$	−179.568	179.831	$C_{25-24-23-20}$	−174.795	179.314
$C_{9-8-7-6}$	−179.541	−179.088	$C_{18-17-14-13}$	120.999	120.281	$C_{26-25-24-23}$	−0.646	−0.124
$C_{10-9-8-7}$	178.753	−177.538	$C_{19-18-17-14}$	−176.189	178.425	$C_{27-26-25-24}$	−2.420	0.298
$C_{11-1-10-9}$	−178.123	179.378	$C_{20-19-18-17}$	1.132	−0.064	$C_{28-27-26-25}$	2.434	−0.130
$C_{12-11-1-10}$	117.780	119.402						

corresponding dihedral angles are in the range of 179 ± 1.4°.

In the *Final State*, atoms of the biphenyl donor are located in the plane of corresponding phenyl ring, and the corresponding dihedral angles are in the range of 0 ± 1.0°. But the twist angle between the two phenyl rings is $C_{24-23-20-19} = -35.46°$, which is similar to the twist angle 45° in the ground state of the biphenyl in gas phase [27–29], and in agreement with that of biphenyl in the intermolecular ET systems (ion pairs) of our previous results [14]. Atoms of the naphthalene are located in the same molecular plane just like that in the *Initial States*. The corresponding dihedral angles are in the range of 179 ± 1.13°.

3.1.2. The Initial and Final States in system 2FSN

Table 2 shows some calculated geometrical parameters of both *Initial* and *Final States* for the intramolecular ET of system 2FSN.

In the *Initial State*, it can also be seen that atoms on the naphthalene acceptor and those on two phenyl rings of the donor 2F are located in the common plane. For naphthalene acceptor, the corresponding dihedral angles are in the range of 179 ± 0.8°. The twist angle of the two phenyl rings in 2F donor is $C_{24-23-20-19} = -0.288°$, which shows that the two phenyl rings are in the same plane. It is similar to that for BSN system.

In the *Final State*, atoms in the 2F donor are almost in the same plane because of the existence of C_{29} atom. The corresponding dihedral angles are in the range of 180 ± 0.50°, which is similar to those in the *Initial State*. Atoms in naphthalene acceptor are deviated slightly from the ring plane due to the transferring electron localized on the acceptor. The largest deviation of the dihedral angle is about 4.23° ($C_{10-9-8-7} = -175.76°$), which differs slightly from that in the *Initial State*.

3.2. Enthalpy of formation

The enthalpies of formation of the *Initial* and *Final State* in the processes of intramolecular ET are listed in Table 3.

For the system BSN, the enthalpy of the formation for the *Initial State*, -153.4896 kJ mol^{-1}, is 12.5400 kJ mol^{-1} less than that for the *Final State*, -140.9496 kJ mol^{-1}. This implies that for the molecule BSN, the *Initial State* is more stable than the *Final State*. For the system 2FSN, the enthalpy of formation for the *Initial State*, -149.8948 kJ mol^{-1}, is 9.7812 kJ mol^{-1} less than that for

Table 2
The geometrical parameters of 2FSN in *Initial State* and *Final State*

Parameter	*Initial State*	*Final State*	parameter	*Initial State*	*Final State*	parameter	*Initial State*	*Final State*
Bond length								
C_{1-2}	1.391	1.405	C_{1-11}	1.495	1.493	C_{19-20}	1.452	1.433
C_{2-3}	1.418	1.395	C_{11-12}	1.525	1.525	C_{20-21}	1.409	1.391
C_{3-4}	1.420	1.433	C_{12-13}	1.513	1.515	C_{21-22}	1.390	1.401
C_{4-5}	1.385	1.393	C_{13-14}	1.526	1.524	C_{20-23}	1.412	1.452
C_{5-6}	1.412	1.387	C_{14-15}	1.525	1.525	C_{23-24}	1.452	1.432
C_{6-7}	1.386	1.409	C_{15-16}	1.515	1.513	C_{24-25}	1.376	1.385
C_{7-8}	1.419	1.400	C_{14-17}	1.491	1.495	C_{25-26}	1.410	1.406
C_{8-9}	1.419	1.423	C_{17-18}	1.417	1.411	C_{26-27}	1.401	1.398
C_{9-10}	1.384	1.387	C_{18-19}	1.375	1.383	C_{27-28}	1.393	1.402
C_{19-29}	1.518	1.518	C_{29-30}	1.518	1.518	C_{29-31}	1.522	1.518
Bond Angle								
C_{3-2-1}	121.039	121.384	$C_{12-11-1}$	110.640	111.707	$C_{21-20-19}$	118.434	119.981
C_{4-3-2}	121.747	122.122	$C_{13-12-11}$	111.134	111.407	$C_{22-21-20}$	119.471	118.940
C_{5-4-3}	120.527	120.217	$C_{14-13-12}$	111.500	111.149	$C_{23-20-19}$	109.223	108.659
C_{6-5-4}	120.583	121.135	$C_{15-14-13}$	110.000	110.094	$C_{24-23-20}$	108.067	108.560
C_{7-6-5}	119.984	120.000	$C_{16-15-14}$	111.364	111.075	$C_{25-24-23}$	120.889	120.476
C_{8-7-6}	120.693	120.541	$C_{17-14-13}$	110.844	111.812	$C_{26-25-24}$	119.183	118.933
C_{9-8-7}	121.977	122.255	$C_{18-17-14}$	119.613	119.299	$C_{27-26-25}$	120.445	120.570
C_{10-9-8}	120.831	120.898	$C_{19-18-17}$	119.607	119.280	$C_{28-27-26}$	121.182	121.048
$C_{11-1-10}$	120.809	119.986	$C_{20-19-18}$	121.145	120.626	$C_{31-29-19}$	110.209	111.050
$C_{29-19-20}$	109.327	110.150	$C_{30-29-19}$	112.411	111.987			
Dihedral Angle								
$C_{4-3-2-1}$	−179.075	178.624	$C_{13-12-11-1}$	−179.745	179.403	$C_{21-20-19-18}$	−4.113	0.474
$C_{5-4-3-2}$	178.906	−179.470	$C_{14-13-12-11}$	−56.778	−56.865	$C_{22-21-20-19}$	4.110	−0.585
$C_{6-5-4-3}$	0.207	3.706	$C_{15-14-13-12}$	55.931	56.460	$C_{23-20-19-18}$	176.205	−179.114
$C_{7-6-5-4}$	0.296	−2.863	$C_{16-15-14-13}$	−55.927	−56.433	$C_{24-23-20-19}$	−0.288	−0.080
$C_{8-7-6-5}$	−0.445	−0.918	$C_{17-14-13-12}$	−179.947	179.835	$C_{25-24-23-20}$	−175.756	179.357
$C_{9-8-7-6}$	−179.531	−178.108	$C_{18-17-14-13}$	119.413	121.167	$C_{26-25-24-23}$	−0.657	−0.068
$C_{10-9-8-7}$	178.805	−175.761	$C_{19-18-17-14}$	−176.621	178.275	$C_{27-26-25-24}$	−2.875	0.201
$C_{11-1-10-9}$	−178.201	178.108	$C_{20-19-18-17}$	−0.135	0.158	$C_{28-27-26-25}$	3.238	−0.098
$C_{12-11-1-10}$	117.925	119.700	$C_{30-29-19-18}$	−52.974	−62.637	$C_{31-29-19-18}$	69.087	60.400
$C_{29-19-20-23}$	−4.681	0.469						

Final State, -140.1136 kJ mol^{-1}. Also, for the molecule 2FSN, the *Initial State* is more stable than the *Final State*.

For the Franck–Condon state, the values of the enthalpy of formation for forward and back ET are 110.6028 and 104.5000 kJ mol^{-1}, respectively, for the molecule BSN; and 103.9984 and 98.9406 kJ mol^{-1}, respectively, for the molecule 2FSN. Those states are less stable reasonably.

3.3. *The reorganization energy for intramolecular ET in BSN*

In the process of forward intramolecular ET for molecule BSN, the electron is transferred from the biphenyl anion to the naphthalene. The calculated enthalpy values of formation are -140.9496 and 110.6028 kJ mol^{-1} for the *Final State* and the *ET State 1* (Scheme 1), respectively. The energy of the dipole formed by the two point charges was included in our calculated results. In the calculation for the reorganization energy, the change of the dipole should be excluded. From Eq. (2), we have

$$\lambda_{\mathrm{v}}(Forward) = \Delta H_{\mathrm{f}}^{\mathrm{A}}(ET\ State\ 1) - \Delta H_{\mathrm{f}}^{\mathrm{A}}(Final\ State) + 2E(E) \tag{4}$$

where $E(E)$ is the energy of the dipole moment formed by the two point charges (sparkle), which is -0.76 eV for the two-point charge near the edge of donor and acceptor with

Table 3
The enthalpy of formation (kJ mol^{-1})

System	Forward ET		Back ET	
	$\Delta H_{\mathrm{f}}^{\mathrm{A}}$ (*Final State*)	$\Delta H_{\mathrm{f}}^{\mathrm{A}}$ (*ET State 1*)	$\Delta H_{\mathrm{f}}^{\mathrm{D}}$ (*Initial State 1*)	$\Delta H_{\mathrm{f}}^{\mathrm{D}}$ (*ET State 2*)
BSN	−140.9496	110.6028	−153.4896	104.5000
2FSN	−140.1136	103.9984	−149.8948	98.9406

the distance of 1.89 nm. In this way, the reorganization energy in the forward ET was obtained as $\lambda_v(\mathit{Forward}) = 1.09$ eV.

In the process of back ET of BSN, the electron is transferred from the naphthalene anion to biphenyl. The calculated values of the enthalpy of formation are -153.4896 and $104.5000\ \mathrm{kJ\ mol^{-1}}$ for the *Initial State* and the *ET State 2*, respectively. To exclude the change of the point charge electronic field, we have the following equation:

$$\lambda_v(\mathit{Back}) = \Delta H_f^D(\mathit{ET\ State\ 2}) - \Delta H_f^D(\mathit{Initial\ State}) + 2E(E) \quad (5)$$

and the result of $\lambda_v(\mathit{Back}) = 1.15$ eV.

In our systems, the internal reorganization energy is a function of the difference of the geometrical structure between the *Initial* and *Final States*, and the geometrical structure of the *Initial/Final State* for forward ET process is the same as that of *Final/Initial State* for back ET process. From the molecular structure point of view, absolute values of the internal reorganization energy for forward ET and back ET should be the same for a given system. Therefore, we should take the average value of $\lambda_v(\mathit{Forward})$ and $\lambda_v(\mathit{Back})$ as the internal reorganization energy λ_v of the system,

$$\lambda_v = \frac{[\lambda_v(\mathit{Forward}) + \lambda_v(\mathit{Back})]}{2} \quad (6)$$

For BSN system, we have $\lambda_v = 1.12$ eV, which is in good consistent with the experimental results $\lambda_v = 1.13$ eV by Closs et al. for BSN in solvent tetrahydrofuran (THF) [15].

3.4. The reorganization energy for 2FSN intramolecular ET

The reorganization energy of intramolecular ET in the system 2FSN can be obtained as $\lambda_v(\mathit{Forward}) = 1.00$ eV from Eq. (4) for the forward ET, and as $\lambda_v(\mathit{Back}) = 1.05$ eV from Eq. (5) for back ET, respectively. According to the above analysis, the value of the reorganization energy should be the average of them as Eq. (6), and we have $\lambda_v = 1.025$ eV (Table 4).

The difference of the reorganization energy between systems BSN and 2FSN is 0.095 eV, which is from the contribution of the low-frequency torsional vibration of two phenyl rings in biphenyl of BSN. This is consistent with the experimental results, 0.15 eV [11]. Our previous paper [14] also probed the contribution of the twist movement of two phenyl rings in biphenyl to the reorganization energy, 0.05 eV. It is understandable that this contribution in an intermolecular ET reaction of geminate radical ion pairs is smaller than that in intramolecular ET reactions.

Table 4
The calculated reorganization energy (eV) for systems BSN and 2FSN

System	$\lambda_v(\mathit{Forward})$	$\lambda_v(\mathit{Back})$	$\lambda_v(\mathit{Average})$	λ_v
BSN	1.09	1.15	1.12	1.13[a]
2FSN	1.00	1.05	1.025	
$\Delta\lambda_v$	0.09	0.10	0.095	0.15[b]

[a] [15].
[b] [11].

4. Conclusions

Nelsen's method was extended to the study of the internal reorganization energy for intramolecular ET. The sparkle method was also used to simulate the solvent of THF. The semiempirical quantum chemical method AM1 was used in the calculation.

The calculated internal reorganization energy for the intramolecular ET reaction of system BSN, 1.12 eV, is consistent with the experimental value, 1.13 eV, rather well. The difference of the internal reorganization energy between systems BSN and 2FSN, 0.095 eV, is also comparable with that of experimental results, 0.15 eV.

In the *Final State* of system BSN, the twisted angle of the two phenyl rings in biphenyl donor is about 35°, which is similar to those in the ground state of the biphenyl in gas phase and our previous paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China.

References

[1] R.A. Marcus, J. Chem. Phys. 24 (1956) 966.
[2] R.A. Marcus, Discuss. Faraday Soc. 29 (1960) 21.
[3] R.A. Marcus, N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.
[4] R.A. Marcus, J. Chem. Phys. 43 (1965) 1261.
[5] R.D. Cannon, Chem. Phys. Lett. 49 (1977) 299.
[6] B.S. Brunschwig, S. Ehrensen, N. Sutin, J. Phys. Chem. 90 (1986) 3659.
[7] N.R. Kestner, J. Logan, J. Jortner, J. Phys. Chem. 78 (1974) 2148.
[8] P. Siders, R.A. Marcus, J. Am. Chem. Soc. 103 (1981) 748.
[9] P. Siders, R.A. Marcus, J. Am. Chem. Soc. 103 (1981) 741.
[10] B.S. Brunschwig, J. Logan, M.D. Newton, N. Sutin, J. Am. Chem. Soc. 102 (1980) 5798.
[11] J.R. Miller, B.P. Paulso, R. Bal, G.J. Closs, J. Phys. Chem. 99 (1995) 6923.
[12] S.F. Nelsen, S.C. Balckstock, Y. Kim, J. Am. Chem. Soc. 109 (1987) 677.
[13] G. Rauhut, T. Clark, J. Am. Chem. Soc. 115 (1993) 9127.
[14] Jian-xin Guo, Qi-yuan Zhang, J. Photochem. Photobiol. A Chem. 110 (1997) 247.
[15] G.L. Closs, L.T. Calcaterra, N.J. Green, K.W. Penfield, J.R. Miller, J. Phys. Chem. 90 (1986) 2673.
[16] J.R. Miller, T.V. Beitz, R.K. Huddleston, J. Am. Chem. Soc. 106 (1984) 5057.
[17] J.R. Miller, L.T. Calcaterra, G.L. Closs, J. Am. Chem. Soc. 106 (1984) 3047.

[18] N. Liang, J.R. Miller, G.L. Closs, J. Am. Chem. Soc. 111 (1989) 8741.
[19] N. Liang, J.R. Miller, G.L. Closs, J. Am. Chem. Soc. 112 (1990) 5353.
[20] G.L. Closs, J.R. Miller, Science 240 (1988) 440.
[21] M.D. Newton, Chem. Rev. 91 (1991) 767.
[22] MOPAC program, QCPE 455, 1990..
[23] J.J.P. Stewart, J. Comput.-Aided Mol. Des. 4 (1994) 1.
[24] J. Baker, J. Comput. Chem. 7 (1986) 385.
[25] Y. Takei, T. Yamaguchi, Y. Osamura, K. Fuke, K. Kaya, J. Phys. Chem. 92 (1988) 57.
[26] G. Buntinx, O. Poizat, J. Chem. Phys. 91 (1989) 2153.
[27] O. Bastiansen, Acta Chem. Scand. 3 (1994) 408.
[28] O. Bastiansen, S. Samdal, J. Mol. Struct. 128 (1985) 115.
[29] S. Tsuzuki, K. Tanabe, J. Phys. Chem. 95 (1991) 139.