Supportin Information on
A Theoretical Study on Excited State Double Proton Transfer Reaction of 7-Azaindole Dimer: *Ab Initio* Potential Energy Surface and its Empirical Valence Bond Model

Kohei Ando, Shigehiko Hayashi and Shigeki Kato

Contents

Atom indices of a 7-AI monomer

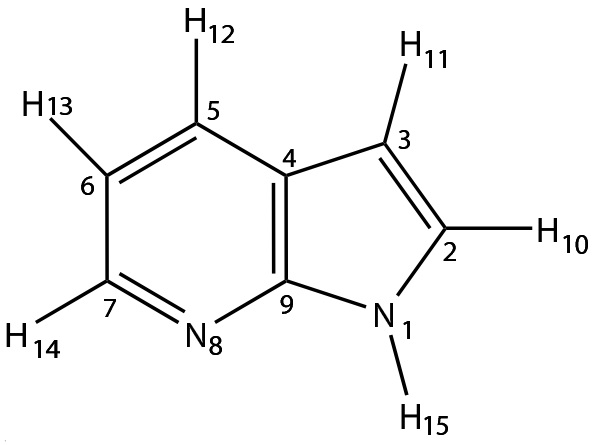

Figure S1: Atom indices of a 7-AI monomer. For a tautomer, the transferring H is labeled as 15.

Definition of internal coordinates

Table S1: Definition of internal coordinates [() for monomers of a tautomer.]

coordinate	type	induces of atoms			
r_1	bond	1	2		
r_2	bond	2	3		
r_3	bond	3	4		
r_4	bond	4	5		
r_5	bond	5	6		
r_6	bond	6	7		
r_7	bond	7	8		
r_8	bond	8	9		
r_9	bond	9	4		
r_{10}	bond	9	1		
r_{11}	bond	2	10		
r_{12}	bond	3	11		
r_{13}	bond	5	12		
r_{14}	bond	6	13		
r_{15}	bond	7	14		
θ_{16}	angle	1	2	10	
θ_{17}	angle	2	3	11	
θ_{18}	angle	4	5	12	
θ_{19}	angle	5	6	13	
θ_{20}	angle	6	7	14	
ϕ_{21}	dihedral	9	1	2	10
ϕ_{22}	dihedral	1	2	3	11
ϕ_{23}	dihedral	9	4	5	12
ϕ_{24}	dihedral	4	5	6	13
ϕ_{25}	dihedral	5	6	7	14
θ_{26}	angle	9	1	2	
θ_{27}	angle	1	2	3	
θ_{28}	angle	2	3	4	
θ_{29}	angle	3	4	9	
θ_{30}	angle	4	9	1	
θ_{31}	angle	7	8	9	
θ_{32}	angle	8	9	4	
θ_{33}	angle	9	4	5	
θ_{34}	angle	4	5	6	
θ_{35}	angle	5	6	7	
θ_{36}	angle	6	7	8	
ϕ_{37}	dihedral	9	1	2	3
ϕ_{38}	dihedral	1	2	3	4
ϕ_{39}	dihedral	2	3	4	9
ϕ_{40}	dihedral	3	4	9	1
ϕ_{41}	dihedral	4	9	1	2
ϕ_{42}	dihedral	7	8	9	4
ϕ_{43}	dihedral	8	9	4	5
ϕ_{44}	dihedral	9	4	5	6
ϕ_{45}	dihedral	4	5	6	7
ϕ_{46}	dihedral	5	6	7	8
ϕ_{47}	dihedral	6	7	8	9
ϕ_{48}	dihedral	1	9	4	5
ϕ_{49}	dihedral	8	9	4	3
r_{50}	bond	1 (8)	15 (15)		
θ_{51}	angle	9 (9)	1 (8)	15 (15)	
ϕ_{52}	dihedral	4 (4)	9 (9)	1 (8)	15 (15)

The internal coordinates using in Eq. (5)

The internal coordinates using in Eq. (5) (natural internal coordinates) is given as follows:

$$q_i = r_i \qquad (\text{for } i = 1,\ldots,15), \tag{S1}$$

$$q_i = \theta_i \qquad (\text{for } i = 16,\ldots,20), \tag{S2}$$

$$q_i = \phi_i \qquad (\text{for } i = 21,\ldots,25), \tag{S3}$$

$$q_{26} = 0.6324\theta_{26} - 0.5117\theta_{27} + 0.1954\theta_{28} + 0.1954\theta_{29} - 0.5116\theta_{30}, \tag{S4}$$

$$q_{27} = 0.3717\theta_{27} - 0.6015\theta_{28} + 0.6015\theta_{29} - 0.3717\theta_{30}, \tag{S5}$$

$$q_{28} = 0.5774\theta_{31} - 0.2887\theta_{32} - 0.2887\theta_{33} + 0.5774\theta_{34} - 0.2887\theta_{35} - 0.2887\theta_{36}, \tag{S6}$$

$$q_{29} = 0.5000\theta_{32} - 0.5000\theta_{33} + 0.5000\theta_{35} - 0.5000\theta_{36}, \tag{S7}$$

$$q_{30} = 0.4082\theta_{31} - 0.4082\theta_{32} + 0.4082\theta_{33} - 0.4082\theta_{34} + 0.4082\theta_{35} - 0.4082\theta_{36}, \tag{S8}$$

$$q_{31} = 0.6324\phi_{37} - 0.5117\phi_{38} + 0.1954\phi_{39} + 0.1954\phi_{40} - 0.5116\phi_{41}, \tag{S9}$$

$$q_{32} = 0.3717\phi_{38} - 0.6015\phi_{39} + 0.6015\phi_{40} - 0.3717\phi_{41}, \tag{S10}$$

$$q_{33} = 0.5774\phi_{42} - 0.2887\phi_{43} - 0.2887\phi_{44} + 0.5774\phi_{45} - 0.2887\phi_{46} - 0.2887\phi_{47}, \tag{S11}$$

$$q_{34} = 0.5000\phi_{43} - 0.5000\phi_{44} + 0.5000\phi_{46} - 0.5000\phi_{47}, \tag{S12}$$

$$q_{35} = 0.4082\phi_{42} - 0.4082\phi_{43} + 0.4082\phi_{44} - 0.4082\phi_{45} + 0.4082\phi_{46} - 0.4082\phi_{47}, \tag{S13}$$

$$q_{36} = 0.7071\phi_{48} - 0.7071\phi_{49}, \tag{S14}$$

where $\{r_i\}$, $\{\theta_i\}$ and $\{\phi_i\}$ are given in Table S1.

The definition of ϑ in Eq. (10)

The definition of ϑ in Eq. (10) is an angle between two planes each of which includes two protons and the averaged position of C and N atoms of each monomer.

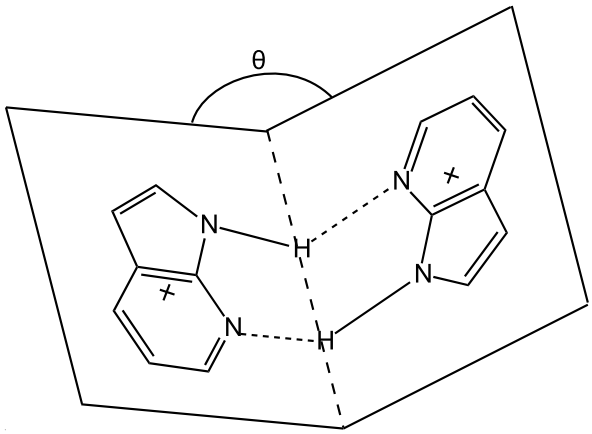

Figure S2: Graphical definition of ϑ (θ in the figure). "H" are the transferring H atoms (H_{29} and H_{30}), and "$\times$" are the averaged positions of C and N atoms of each monomer, respectively.

The internal coordinates at the equilibrium geometries in Eq. (5)

Table S2: The internal coordinates at the equilibrium geometries. [unit: a.u. for length, radian for angle]

coordinates	A	A*	T	T*
q_1^X	2.5925372	2.4518200	2.6275132	2.4308217
q_2^X	2.5667306	2.7180162	2.5654832	2.7399253
q_3^X	2.7218150	2.7696040	2.7353528	2.8063599
q_4^X	2.6708075	2.7061183	2.5859045	2.7161306
q_5^X	2.6135025	2.7064303	2.7208457	2.7266622
q_6^X	2.6841343	2.6052897	2.5779752	2.5511454
q_7^X	2.4917979	2.5687652	2.6002479	2.6132843
q_8^X	2.5383235	2.5426987	2.5467361	2.6155990
q_9^X	2.6263435	2.5862249	2.7650053	2.5638161
q_{10}^X	2.5811553	2.7053270	2.4459721	2.6498177
q_{11}^X	2.0231191	2.0231007	2.0289360	2.0289667
q_{12}^X	2.0249011	2.0243302	2.0238963	2.0252201
q_{13}^X	2.0321786	2.0257161	2.0312925	2.0238338
q_{14}^X	2.0299443	2.0325190	2.0277068	2.0300379
q_{15}^X	2.0336426	2.0341529	2.0252684	2.0284492
q_{16}^X	2.1059131	2.1557256	2.0682843	2.1283642
q_{17}^X	2.1972201	2.1816701	2.2284846	2.2324353
q_{18}^X	2.1227640	2.1615093	2.1240036	2.1524406
q_{19}^X	2.1169384	2.0951695	2.1058832	2.0970655
q_{20}^X	2.0861695	2.0634408	2.1483318	2.1217328
q_{21}^X	3.1415927	3.1415927	3.1415927	3.1415927
q_{22}^X	3.1415927	3.1415927	3.1415927	3.1415927
q_{23}^X	3.1415927	3.1415927	3.1415927	3.1415927
q_{24}^X	3.1415927	3.1415927	3.1415927	3.1415927
q_{25}^X	3.1415927	3.1415927	3.1415927	3.1415927
q_{26}^X	-0.0227403	0.0454976	-0.1901739	-0.1421547
q_{27}^X	0.0119608	0.0027608	-0.0128891	-0.0153030
q_{28}^X	-0.1225686	-0.2819491	0.0009346	-0.1315385
q_{29}^X	0.0461145	0.0560220	-0.0058846	-0.0022476
q_{30}^X	-0.1192271	-0.1390426	0.0154060	0.0098503
q_{31}^X	0.0000000	0.0000000	0.0000000	0.0000000
q_{32}^X	0.0000000	0.0000000	0.0000000	0.0000000
q_{33}^X	0.0000000	0.0000000	0.0000000	0.0000000
q_{34}^X	0.0000000	0.0000000	0.0000000	0.0000000
q_{35}^X	0.0000000	0.0000000	0.0000000	0.0000000
q_{36}^X	0.0000000	0.0000000	0.0000000	0.0000000

Partial charges in Eq. (8)

Table S3: Partial charges [unit:a.u.]

charge	A	A*	T	T*
$Q_1^{0,X}$	-0.169834	-0.082821	-0.581416	-0.490232
$Q_2^{0,X}$	-0.263313	-0.066338	0.074665	0.074726
$Q_3^{0,X}$	-0.327666	-0.020124	-0.407244	-0.066384
$Q_4^{0,X}$	0.095316	0.036474	0.162125	0.081614
$Q_5^{0,X}$	-0.151021	-0.339202	-0.112857	-0.235512
$Q_6^{0,X}$	-0.204233	-0.271592	-0.202760	-0.241682
$Q_7^{0,X}$	0.170251	0.069170	-0.187674	-0.243371
$Q_8^{0,X}$	-0.478876	-0.637976	-0.068190	-0.137908
$Q_9^{0,X}$	0.264236	0.263393	0.275304	0.237133
$Q_{10}^{0,X}$	0.223053	0.180178	0.156244	0.123750
$Q_{11}^{0,X}$	0.193080	0.170111	0.157577	0.123871
$Q_{12}^{0,X}$	0.155419	0.145060	0.148979	0.145596
$Q_{13}^{0,X}$	0.118982	0.134074	0.152760	0.171421
$Q_{14}^{0,X}$	0.086008	0.117481	0.175848	0.193623
$Q_{15}^{0,X}$	0.288597	0.302112	0.256638	0.263355

The dumping function in Eq. (7)

The dumping function used in Eq. (7) is as follows:

$$f(r_{\alpha\beta}) = \begin{cases} \left(\frac{r_{\alpha\beta}}{s_{\alpha\beta}}\right)^4 - 2\left(\frac{r_{\alpha\beta}}{s_{\alpha\beta}}\right)^2 + 2\left(\frac{r_{\alpha\beta}}{s_{\alpha\beta}}\right) & (r_{\alpha\beta} < s_{\alpha\beta}), \\ 1 & (r_{\alpha\beta} \geq s_{\alpha\beta}), \end{cases} \tag{S15}$$

where

$$s_{\alpha\beta} = A(a_\alpha a_\beta)^{1/6}. \tag{S16}$$

Here $\{a_\alpha\}$ denote the "volume" of each atom derived from the atomic polarizability and are given for the atomic species as follows; $a_{\mathrm{C}} = 1.405$ Å^3, $a_{\mathrm{H}} = 0.514$ Å^3, and $a_{\mathrm{N}} = 1.105$ Å^3. A is a scaling factor and given as $A = 2.6$.

Parameters used in the PEF

Table S4: Parameters used in the PEF (unit:a.u.).

term	AA^*	TT^*
V_0^X	-378.693877071	-378.666779221
D_e^X	$2.556996307 \times 10^{-1}$	$2.408089647 \times 10^{-1}$
α^X	1.002760889	1.019491804
r^X	1.927998115	1.934760239
α_θ^X	$2.414311060 \times 10^{-1}$	$2.777469250 \times 10^{-1}$
θ^X	2.176783012	2.057857084
α_ϕ^X	$2.113007700 \times 10^{-2}$	$4.205127250 \times 10^{-2}$
ϕ^X	3.141592654	3.141592654
$V_0^{X^*}$	-378.525263596	-378.568184655
$D_e^{X^*}$	$2.391871087 \times 10^{-1}$	$2.562908779 \times 10^{-1}$
α^{X^*}	1.013914033	1.003143599
r^{X^*}	1.940549747	1.926430678
$\alpha_\theta^{X^*}$	$2.386010320 \times 10^{-1}$	$2.676720880 \times 10^{-1}$
θ^{X^*}	2.130919718	2.108576850
$\alpha_\phi^{X^*}$	$5.529704930 \times 10^{-2}$	$3.437585380 \times 10^{-2}$
ϕ^{X^*}	3.141592654	3.141592654
$V_2^{A^*A}$ ($V_1^{T^*T}$)	2.262166652	2.731388624
$\zeta_2^{A^*A}$ ($\zeta_1^{T^*T}$)	1.461380588	1.491409338
$\tilde{V}_2^{A^*A}$ ($\tilde{V}_1^{T^*T}$)	$1.240963675 \times 10^{-1}$	$1.258089837 \times 10^{-1}$
$\tilde{\zeta}_2^{A^*A}$ ($\tilde{\zeta}_1^{T^*T}$)	$6.322459320 \times 10^{-1}$	$6.869198610 \times 10^{-1}$
$V_4^{A^*A}$ ($V_3^{T^*T}$)	2.282898550	2.734431873
$\zeta_4^{A^*A}$ ($\zeta_3^{T^*T}$)	1.461331602	1.491443718
$\tilde{V}_4^{A^*A}$ ($\tilde{V}_3^{T^*T}$)	$1.248733091 \times 10^{-1}$	$1.258842582 \times 10^{-1}$
$\tilde{\zeta}_4^{A^*A}$ ($\tilde{\zeta}_3^{T^*T}$)	$6.375272414 \times 10^{-1}$	$6.651187377 \times 10^{-1}$
$a_{\varphi_2}^{A^*A}$ ($a_{\varphi_1}^{T^*T}$)	$2.480882688 \times 10^{-1}$	$2.313455213 \times 10^{-1}$
$a_{\varphi_4}^{A^*A}$ ($a_{\varphi_3}^{T^*T}$)	$2.642175920 \times 10^{-1}$	$2.207843240 \times 10^{-1}$
$V_{\text{corr }0}^{X^*X}$	$-1.667780276 \times 10^{-2}$	$-1.621894161 \times 10^{-2}$
$(a_{\text{corr}}^{X^*X})^{1/6}$	4.377336791	4.618272738
a_ϑ	$1.570261956 \times 10^{-1}$	$1.518469875 \times 10^{-1}$
V^{NN}	$7.500000000 \times 10^{-5}$	$7.500000000 \times 10^{-5}$
ζ^{NN}	$1.000000000 \times 10^{+1}$	$1.000000000 \times 10^{+1}$
R^{NN}	5.000000000	5.000000000
a_{mod}	$1.000000000 \times 10^{-1}$	$1.000000000 \times 10^{-1}$

The terms in the off-diagonal element in Eq. (14)

The terms in the off-diagonal element, Eq. (14), is as follows.

$$a_1' = \quad 1.362672513\times10^{-1}, \tag{S17}$$

$$a_2' = \quad 1.047629760\times10^{-3}\xi_1^{\,2} - 2.848680071\times10^{-2}\xi_1 + 4.827950385\times10^{-1}, \tag{S18}$$

$$a_3' = \quad 1.853914153\times10^{-2}, \tag{S19}$$

$$a_1'' = -4.453415570\times10^{-2}\xi_1^{\,2} + 3.721369096\times10^{-3}\xi_1 - 1.335184827\times10^{-1}, \tag{S20}$$

$$a_2'' = -1.194755309\times10^{-1}\xi_1^{\,2} - 1.355779708\times10^{-2}\xi_1 + 5.613355470\times10^{-1}, \tag{S21}$$

$$a_3'' = -1.523253963\times10^{-2}. \tag{S22}$$

If $a_2'' \leq 0$, the second term of Eq. (14) is neglected, *i.e.*, $a_1'' = 0$.

The force constant matrices in Eq. (5)

The force constant matrices in Eq. (5) are in another file. In the file, the parameters are tabulated as follws.

```
#
# ----- force constant matrix for monomer A, a^{A}_{i,j} -----
#
#j\i                 1                 2                 3                 4
   1  0.4768785930D+00  0.5564599340D-01 -0.1796669960D-01  0.7318808400D-02
   2 ................. ................. ................. .................
   .      .                 .                 .                 .
  36 ................. ................. ................. .................

#j\i                 5                 6                 7                 8
   1 ................. ................. ................. .................
   .      .                 .                 .                 .
   .      .                 .                 .                 .

#j\i                33                34                35                36
   1 ................. ................. ................. .................
   .      .                 .                 .                 .
   .      .                 .                 .                 .
  36 ................. ................. ................. .................

# ------------------------------------------------------------------------
#
# ----- force constant matrix for monomer A*, a^{A*}_{i,j} -----
#
#j\i                 1                 2                 3                 4
   1  0.6822566280D+00  0.5550027470D-01  0.2299298890D-01 -0.3148648080D-01
   .      .                 .                 .                 .
   .      .                 .                 .                 .

# ------------------------------------------------------------------------
#
# ----- force constant matrix for monomer T, a^{T}_{i,j} -----
#
#j\i                 1                 2                 3                 4
   1 ................. ................. ................. .................
   .      .                 .                 .                 .
   .      .                 .                 .                 .

# ------------------------------------------------------------------------
#
# ----- force constant matrix for monomer T*, a^{T*}_{i,j} -----
#
#j\i                 1                 2                 3                 4
   1 ................. ................. ................. .................
   .      .                 .                 .                 .
   .      .                 .                 .                 .
```

The CRK matrices in Eqs. (7)-(8)

The CRK matrices in Eqs. (7)-(8) are in another file.
In the file, the parameters are tabulated as follws.

```
#
# ----- charge response kernel for monomer A, K^{A}_{i,j} -----
#
#j\i                 1                 2                 3                 4                 5
   1 -0.4149651000D+01  0.9245640000D+00  0.1956897000D+01 -0.1654392000D+01  0.3792570000D+00
   2 ................. ................. ................. ................. .................
   .      .                 .                 .                 .                 .
  15 ................. ................. ................. ................. .................

#j\i                 6                 7                 8                 9                10
   1 ................. ................. ................. ................. .................
   .      .                 .                 .                 .                 .
   .      .                 .                 .                 .                 .

#j\i                11                12                13                14                15
   1 ................. ................. ................. ................. .................
   .      .                 .                 .                 .                 .
   .      .                 .                 .                 .                 .
  15 ................. ................. ................. ................. .................

#
# ------------------------------------------------------------------------------------------
#
# ----- charge response kernel for monomer A*, K^{A*}_{i,j} -----
#
#j\i                 1                 2                 3                 4                 5
   1 ................. ................. ................. ................. .................
   .      .                 .                 .                 .                 .
   .      .                 .                 .                 .                 .

#
# ------------------------------------------------------------------------------------------
#
# ----- charge response kernel for monomer T, K^{T}_{i,j} -----
#
#j\i                 1                 2                 3                 4                 5
   1 ................. ................. ................. ................. .................
   .      .                 .                 .                 .                 .
   .      .                 .                 .                 .                 .

#
# ------------------------------------------------------------------------------------------
#
# ----- charge response kernel for monomer T*, K^{T*}_{i,j} -----
#
#j\i                 1                 2                 3                 4                 5
   1 ................. ................. ................. ................. .................
   .      .                 .                 .                 .                 .
   .      .                 .                 .                 .                 .
```