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Supplementary information

for

Inter-molecular electron transfer states of 1-methyl-3-(*N*-(1,8-naphthalimidyl)ethyl)imidazolium iodide obtained by constrained density functional theory

Submitted by

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1. Computational details

In this study, all DFT and CDFT calculations were performed with NWChem program package.[S1] In order to explore potential energy surfaces (PESs) of the ground (charge separated state; S_{CS}) and electron transfer state (S_{ET}) states of MNEI-I complex, we used familiar standard hybrid exchange-correlation functional, Becke-3-parameter-Lee-Yang-Parr (B3LYP) functional[S2-S5] with the basis sets of 6-31G(d) for H, C, N and O atoms,[S6] and of DZVP for iodine atom.[S7]

In CDFT calculations of MNEI-I complex system, we divided the MNEI-I complex to two areas for the charge constrain, that is, MNEI and iodine anion/atom. For the S_{CS} state, we set one positive and negative charge to MNEI and iodine, respectively. This S_{CS} state could be regarded as the ordinary ground state of MNEI-I complex. For the state after the S_{ET} state, we set the charge difference between MNEI and iodine atom to zero. We employed Löwdin weight population scheme for the charge constraint in the CDFT calculations, which provides the stable CDFT single point energy and CDFT geometry optimization calculations in MNEI-I complex system. For the geometry optimization in S_{CS} state by DFT and CDFT calculations, we also evaluated the dispersion effect by using DFT-D method[S8].

2. Structural comparison among conventional DFT, CDFT, DFT-D, and CDFT-D

We have compared the structures that is optimized with conventional DFT, DFT-D2, CDFT, and CDFT-D2 at the B3LYP/6-31G* level. The structures are shown in Figure S1. The conventional DFT shows that MNEI conformation of MNEI-I is anti structure (θ = 100.8°). This structure is improved by including dispersion correction (DFT-D2). The minimum structure in the S_{CS} state at the CDFT level (S_{CS} Min) has the near structure with DFT-D2. Therefore, we think that the S_{CS} state at the CDFT level can be regarded as the ground state of MNEI-I. The inclusion of dispersion with CDFT makes MNEI conformation more syn structure than that at the CDFT-D.

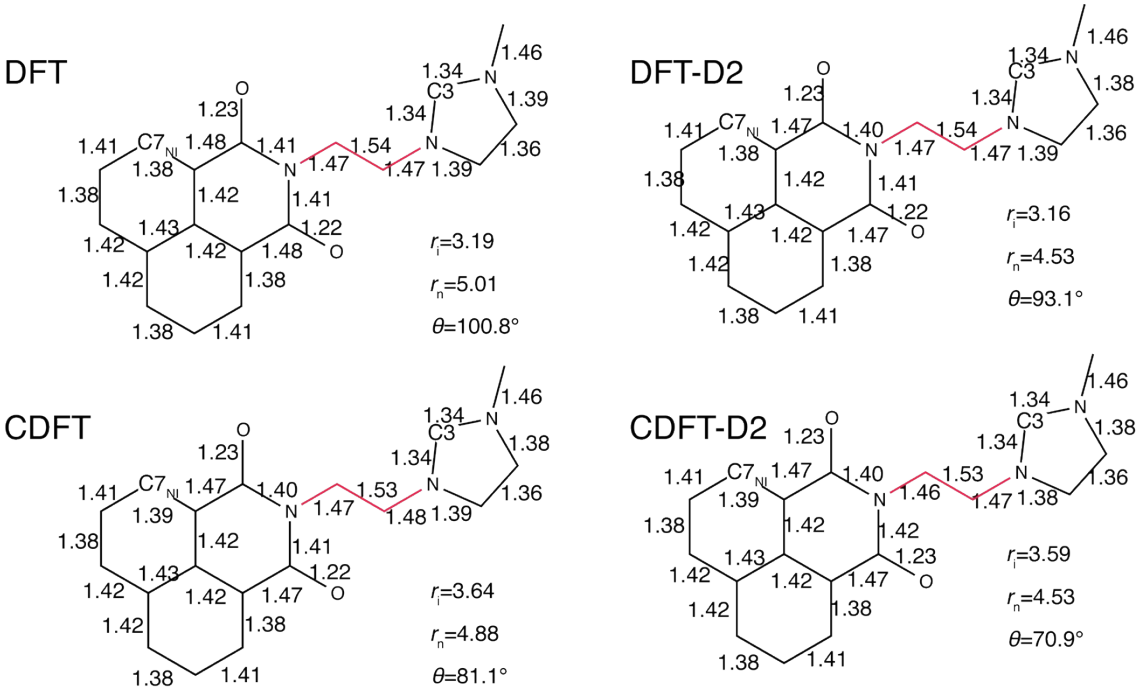

Figure S1. Schematic optimized structures with DFT DFT-D2, CDFT, and CDFT-D2 at the B3LYP/6-31G* level (iodine atoms do not shown). r_i and r_n are the bond lengths of C3—I and $C7_{NI}$—I respectively. q is the dihedral angle shown in red.

3. Potential energy surfaces of ground state (S_{CS}) by DFT and CDFT

Here we describe the potential energy surface (PES) of the ground state of MNEI-I complex by conventional DFT and constrained DFT (CDFT). Figure S1 shows the PESs of the S_{CS} state by DFT and CDFT calculations. Although the energetic difference between DFT and CDFT increases with the shorting of the C3—I (r_i) length, the S_{CS} PES at the CDFT level is qualitatively same with that at the DFT level.

According to the population analyses (Mulliken and Löwdin) of the iodine atom along the PES in Figure S2, there is correlation between the charge of the iodine and the energetic difference. As tabulated in Table S1, the charge of the iodine atom decreases with the shorting of r_i at the DFT level. Since the charge density of the iodine atom is always set to −1.0 at the CDFT level in contrast to the DFT level, the large energetic difference appears in the short region of r. Therefore, we conclude that the length r_i of the optimized structure at the CDFT level is probably determined purely by the electrostatic interaction between iodine anion and MNEI without self-interaction error.

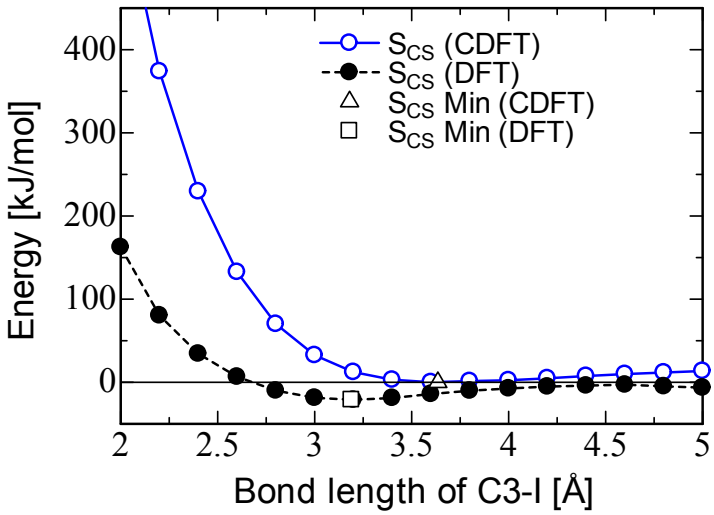

Figure S2. S_{CS} relaxed potential energy surfaces (PESs) as the function of the bond length of C3-I (r_i) by conventional DFT and constrained DFT calculations.

Table S1. Mulliken and Löwdin population analyses of the iodine atom and the total energy differences between DFT and CDFT (*ΔE*).

C3—I (r_i) / Å	Mulliken	Löwdin	ΔE [kJ/mol]
2.60	-0.61	-0.59	-126.00
3.00	-0.79	-0.79	-51.25
3.40	-0.88	-0.89	-21.96
3.80	-0.92	-0.93	-11.57
4.20	-0.93	-0.94	-9.98
4.60	-0.91	-0.92	-12.73
5.00	-0.87	-0.88	-20.06
	S_{CS} Min (DFT)		
3.19	-0.84	-0.84	

4. Cartesian coordinates of S_{CS} Min, S_{ET} Min, and S_{ET} MinL

Cartesian coordinate of S_{CS} Min:

C	1.87740949	−2.05372312	1.74542815
C	0.62113901	−1.79301197	1.22243009
C	0.05289990	−2.66616385	0.26105821
C	0.78435251	−3.81377030	−0.16748221
C	2.06707386	−4.04948608	0.39117604
C	2.60040308	−3.18904502	1.32951256
H	2.29399746	−1.36518097	2.47267338
C	−1.23008245	−2.41386854	−0.28295628
C	0.19864316	−4.67012706	−1.13559338
H	2.62948905	−4.92014834	0.06288941
H	3.58526758	−3.37884894	1.74557660
C	−1.05341716	−4.40466051	−1.65250262
C	−1.77305162	−3.27152327	−1.22509432
H	0.75583901	−5.54219679	−1.46880293
H	−1.48639888	−5.06529084	−2.39747226
H	−2.75490121	−3.04783914	−1.62840487
C	−1.99883352	−1.23610556	0.15439519
C	−0.11101691	−0.59140380	1.65795286
N	−1.37447638	−0.37848796	1.09050453
O	0.33727157	0.20309011	2.48873853
O	−3.13288154	−0.97702716	−0.22894055
C	−2.17962913	0.75825824	1.54762440
H	−3.18127235	0.38088281	1.76433007
H	−1.73554881	1.12642197	2.47268585
C	−2.36645107	1.87190739	0.50967999
H	−2.53717155	1.43055028	−0.47404794
H	−3.24857320	2.45898365	0.78554706
N	−1.24742503	2.82656102	0.37575757
C	−1.27226324	3.90642521	−0.48942687

C	-0.03033323	2.75201717	0.92390143
C	-0.04326039	4.48701746	-0.44302455
H	-2.14653469	4.14958243	-1.07169187
H	0.30498673	1.97980657	1.60756686
H	0.36062018	5.32986404	-0.98056401
N	0.71382128	3.75824432	0.45302335
C	2.15643405	3.89770450	0.66495605
H	2.68168219	3.42700045	-0.17072173
H	2.40780504	4.95816121	0.73484237
H	2.42582970	3.39739213	1.59604011
I	1.11603386	0.95827840	-2.02313911

Cartesian coordinate of S_{ET} Min:

C	1.86028929	-2.32551431	1.68793034
C	0.61894752	-2.03667110	1.14821257
C	-0.01063166	-2.96118542	0.27696557
C	0.64057287	-4.19151469	-0.04166244
C	1.91285535	-4.45293043	0.53123938
C	2.50825735	-3.53900895	1.37687177
H	2.31979874	-1.59980041	2.35059589
C	-1.28031413	-2.67376986	-0.28327970
C	-0.01394672	-5.09765217	-0.91688930
H	2.41380598	-5.38787264	0.29240920
H	3.48248447	-3.75041384	1.80757459
C	-1.25123634	-4.79776791	-1.45017760
C	-1.88859796	-3.58000659	-1.13407726
H	0.47687076	-6.03614924	-1.16288291
H	-1.74046690	-5.49981801	-2.11881483
H	-2.85984314	-3.33142993	-1.54900205
C	-1.96267921	-1.39737695	0.03512734

C	-0.04503741	-0.75532276	1.49118736
N	-1.30203742	-0.52119524	0.91204214
O	0.46449802	0.06474126	2.24685385
O	-3.05409949	-1.09363561	-0.42990521
C	-2.00656824	0.73391238	1.22695897
H	-3.04559455	0.46668796	1.42351161
H	-1.55636497	1.13413167	2.13382796
C	-1.94542826	1.78648783	0.08921417
H	-1.60674903	1.30446596	-0.84039314
H	-2.95302410	2.16948870	-0.09234339
N	-1.10745422	2.92331280	0.40416150
C	-1.43361828	4.23765068	0.01787207
C	0.33217584	2.82881242	0.41035584
C	-0.33621359	5.00416801	0.14427441
H	-2.44595813	4.50865194	-0.24237518
H	0.71196757	2.15365187	1.17587068
H	-0.21295025	6.06905457	0.01440029
N	0.71523766	4.19953168	0.61927428
C	2.09973557	4.60004217	0.54613779
H	2.53293359	4.43775565	-0.45346053
H	2.17704242	5.66014882	0.80546962
H	2.69023549	4.02804906	1.27020936
I	1.16858187	1.94853073	-1.50485983

Cartesian coordinate of S_{ET} MinL:

C	1.76648471	0.39335268	-1.30266897
C	0.34232924	0.76779524	-1.20172426
C	-0.05559883	1.98303066	-0.58390450
C	0.92651605	2.95707797	-0.20602956
C	2.31086585	2.69282803	-0.55516576

C	2.70014304	1.52446435	-1.10694742
H	1.97316102	-0.20398793	-2.18750748
C	-1.42458822	2.28918131	-0.36170548
C	0.51904407	4.13791305	0.40957162
H	3.03801623	3.48396643	-0.38238412
H	3.74225820	1.36854998	-1.37458900
C	-0.83719106	4.40633065	0.66072237
C	-1.80004879	3.49134759	0.26484724
H	1.27349287	4.87185436	0.68735230
H	-1.12673742	5.33524105	1.14384509
H	-2.85851524	3.67831869	0.41570000
C	-2.45703924	1.36699832	-0.81235106
C	-0.62564236	-0.12983239	-1.68893482
N	-1.99964658	0.21477215	-1.47405631
O	-0.37466829	-1.23374685	-2.25404732
O	-3.67776815	1.53572306	-0.66405922
C	-3.02484588	-0.63514219	-2.06540492
H	-3.73374829	-0.00416648	-2.61025050
H	-2.52356496	-1.30447084	-2.76537028
C	-3.87643672	-1.40385088	-1.04832193
H	-4.35363614	-0.68270119	-0.38291587
H	-4.64655779	-1.97719624	-1.57583003
N	-3.11700363	-2.35200556	-0.20049525
C	-3.60303382	-2.93604942	0.95635741
C	-1.85336852	-2.75265762	-0.38749317
C	-2.60151510	-3.70341805	1.46986943
H	-4.60278789	-2.74593854	1.31373475
H	-1.18616698	-2.39205686	-1.19138523
H	-2.56212914	-4.31523174	2.35719613
N	-1.51763552	-3.57093645	0.62022229
C	-0.18889840	-4.17080439	0.78607506
H	0.57163526	-3.42298163	0.52536299

H	-0.06889847	-4.46002262	1.83128475
H	-0.09053664	-5.05251953	0.14770219
I	2.40788719	-1.15099738	0.27310072

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