Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Effects of Hydrogen Bonding on the Gas-phase Reactivity of Didehydroisoquinolinium Cation Isomers

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X-ray structure (1-iodo-5-nitroisoquinoline)

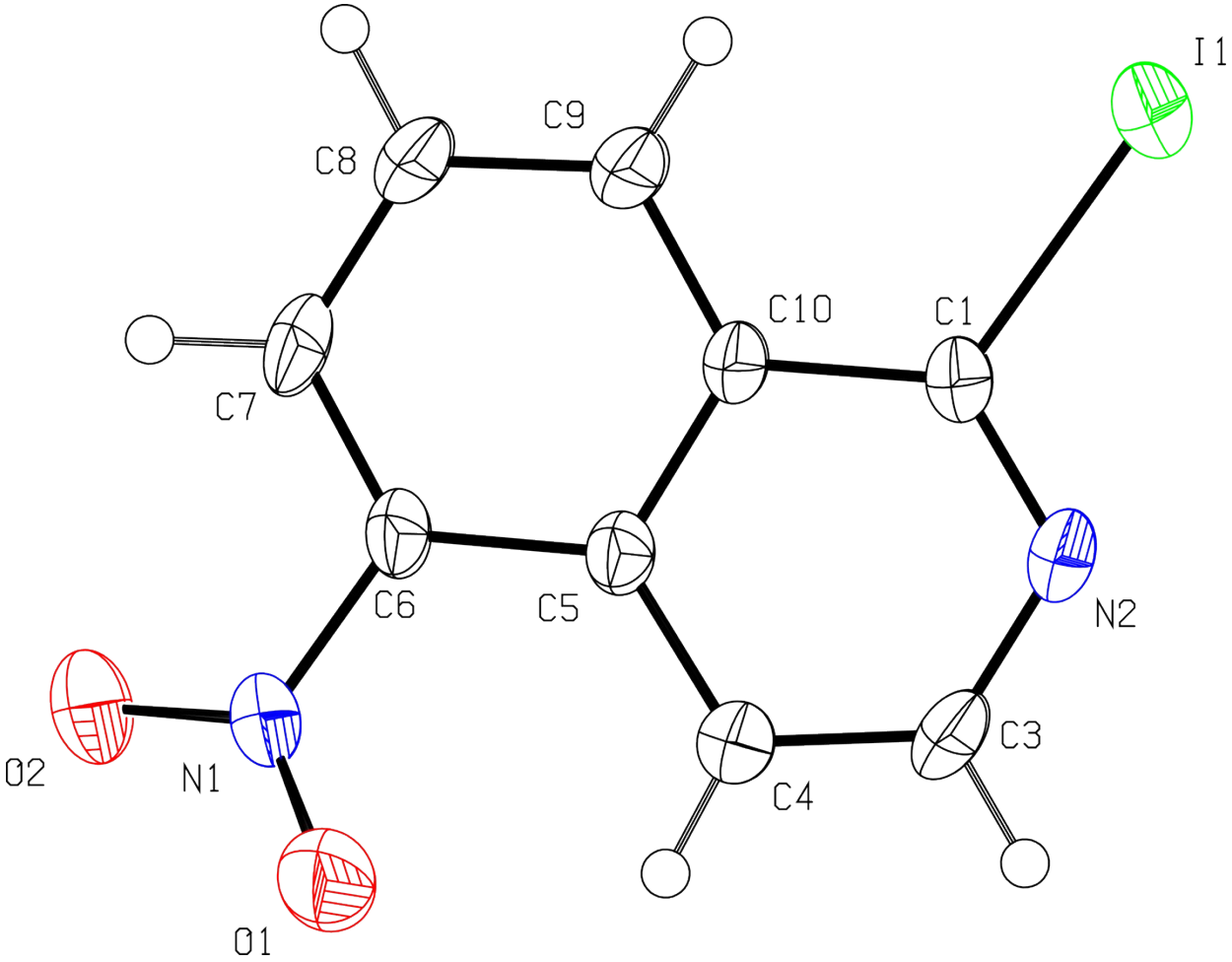

Table 1. Experimental details

Crystal data	
Chemical formula	$C_9H_5IN_2O_2$
M_r	300.05
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, b, c (Å)	7.6101 (13), 8.0298 (7), 8.5371 (9)
α, β, γ (°)	81.120 (6), 65.955 (12), 73.612 (11)
V (Å^3)	456.60 (11)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	27.36
Crystal size (mm)	0.22 × 0.16 × 0.10
Data collection	
Diffractometer	Rigaku Rapid II curved image plate diffractometer
Absorption correction	Multi-scan *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.201, 0.648
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1677, 1677, 1666
R_{int}	0.071
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.097, 1.04
No. of reflections	1677
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.91, -1.45

Computer programs: *CrystalClear* (Rigaku, 2001), *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1996), PATTY (*DIRDIF*, Beurskins, 2008), *SHELXL2017*/1 (Sheldrick, 2017), SHELXLE Rev816 (Hübschle *et al.*, 2011).

Table 2. Table of Bond Distances in Angstroms (Å)

Atoms	Distance	Atoms	Distance
I1—C1	2.114 (5)	C4—H4	0.9500
O1—N1	1.222 (6)	C5—C6	1.424 (6)
O2—N1	1.233 (5)	C5—C10	1.424 (6)
N1—C6	1.463 (6)	C6—C7	1.364 (6)
N2—C1	1.302 (6)	C7—C8	1.395 (7)
N2—C3	1.347 (7)	C7—H7	0.9500
C1—C10	1.431 (6)	C8—C9	1.376 (6)
C3—C4	1.373 (6)	C8—H8	0.9500
C3—H3	0.9500	C9—C10	1.417 (6)
C4—C5	1.416 (6)	C9—H9	0.9500

Numbers in parentheses are standard uncertainties in the least significant digits.

Table 3. Table of Bond Angles in Degrees (º)

Atoms	Angle	Atoms	Angle
O1—N1—O2	122.4 (5)	C7—C6—C5	123.1 (4)
O1—N1—C6	119.9 (4)	C7—C6—N1	116.4 (4)
O2—N1—C6	117.7 (4)	C5—C6—N1	120.5 (4)
C1—N2—C3	117.8 (4)	C6—C7—C8	119.7 (4)
N2—C1—C10	124.6 (4)	C6—C7—H7	120.2
N2—C1—I1	114.1 (3)	C8—C7—H7	120.2
C10—C1—I1	121.3 (3)	C9—C8—C7	120.2 (4)
N2—C3—C4	124.0 (4)	C9—C8—H8	119.9
N2—C3—H3	118.0	C7—C8—H8	119.9
C4—C3—H3	118.0	C8—C9—C10	120.7 (4)
C3—C4—C5	119.3 (4)	C8—C9—H9	119.7
C3—C4—H4	120.3	C10—C9—H9	119.7
C5—C4—H4	120.3	C9—C10—C5	120.1 (4)
C4—C5—C6	126.5 (4)	C9—C10—C1	123.0 (4)
C4—C5—C10	117.3 (4)	C5—C10—C1	116.9 (4)
C6—C5—C10	116.2 (4)		

Numbers in parentheses are standard uncertainties in the least significant digits.

Minimum Energy Geometries

1-dehydroisoquinolinium cation (1)
CASSCF(11,11)/cc-pVTZ
2A' doublet state (Cs)

C	2.440242	-0.713584	0.000000
C	1.275425	-1.429820	0.000000
C	0.043506	-0.728281	0.000000
C	0.002664	0.688458	0.000000
C	1.227503	1.394483	0.000000
C	2.412605	0.704252	0.000000
H	3.383376	-1.221992	0.000000
H	1.276903	-2.501281	0.000000
C	-1.200352	-1.357353	0.000000
C	-1.265916	1.341224	0.000000
H	1.218130	2.466476	0.000000
H	3.339136	1.243424	0.000000
C	-2.419090	0.627818	0.000000
H	-1.318035	2.410914	0.000000
H	-3.401903	1.047131	0.000000
H	-3.186792	-1.288084	0.000000
N	-2.344503	-0.748046	0.000000

E = -399.3189271 au
E (CASPT2)= -400.74336714 au

4-dehydroisoquinolinium cation (2)
CASSCF(11,11)/cc-pVTZ
2A' doublet state (Cs)

C	2.405671	0.732857	0.000000
C	1.209250	1.394560	0.000000
C	0.001967	0.647040	0.000000
C	0.045916	-0.770003	0.000000
C	1.295393	-1.429834	0.000000
C	2.446521	-0.685407	0.000000
H	-1.355169	2.344790	0.000000
H	3.323974	1.285006	0.000000
H	1.171369	2.466382	0.000000
C	-1.254596	1.278178	0.000000
C	-1.203060	-1.419812	0.000000
H	1.326641	-2.500626	0.000000
H	3.397719	-1.179667	0.000000
C	-2.395404	-0.793356	0.000000
H	-3.354166	-1.265107	0.000000
H	-3.237734	1.069067	0.000000
N	-2.367294	0.578632	0.000000

E = -399.3199978 au
E (CASPT2)= -400.74364635 au

5-dehydroisoquinolinium cation (4)
CASSCF(11,11)/cc-pVTZ
2A' doublet state (Cs)

C	2.407843	0.865857	0.000000
C	1.173533	1.456930	0.000000
C	-0.000131	0.652286	0.000000
C	0.097211	-0.760962	0.000000
C	1.394530	-1.295721	0.000000
C	2.531078	-0.552420	0.000000
H	-1.449190	2.275237	0.000000
H	3.292938	1.470028	0.000000
H	1.079811	2.525195	0.000000
C	-1.284237	1.216597	0.000000
C	-1.089964	-1.538135	0.000000
H	3.498340	-1.013992	0.000000
C	-2.298473	-0.919582	0.000000
H	-1.040196	-2.607418	0.000000
H	-3.239350	-1.426408	0.000000
H	-3.248055	0.882037	0.000000
N	-2.349153	0.446808	0.000000

E = -399.3233535 au
E (CASPT2)= -400.74691986 au

8-dehydroisoquinolinium cation (3)
CASSCF(11,11)/cc-pVTZ
2A' doublet state (Cs)

C	2.524792	-0.588033	0.000000

4,5-didehydroisoquinolinium cation (5)
UB3LYP/cc-pVTZ
3A' triplet state (Cs)

6	2.414561	0.755343	0.000000

4,5-didehydroisoquinolinium cation (5)
UB3LYP/cc-pVTZ
1A' singlet state (Cs)

6	2.414481	0.767955	0.000000

C	1.373014	-1.301000	0.000000	6	1.195829	1.383840	0.000000	6	1.188394	1.378094	0.000000
C	0.090089	-0.720151	0.000000	6	0.000000	0.625261	0.000000	6	0.000000	0.606755	0.000000
C	-0.000795	0.693505	0.000000	6	0.077855	-0.823836	0.000000	6	0.079368	-0.846493	0.000000
C	1.194519	1.455132	0.000000	6	1.351457	-1.371223	0.000000	6	1.365858	-1.367490	0.000000
C	2.417112	0.831679	0.000000	6	2.505992	-0.664297	0.000000	6	2.512400	-0.649843	0.000000
H	-1.089968	-2.545430	0.000000	1	-1.407841	2.284420	0.000000	1	-1.387976	2.279519	0.000000
H	3.484078	-1.064814	0.000000	1	3.325424	1.337968	0.000000	1	3.319468	1.359391	0.000000
C	-1.090026	-1.474420	0.000000	1	1.137507	2.463828	0.000000	1	1.113961	2.457070	0.000000
C	-1.295504	1.279097	0.000000	6	-1.269922	1.212515	0.000000	6	-1.264808	1.205967	0.000000
H	1.132245	2.525264	0.000000	6	-1.144212	-1.492348	0.000000	6	-1.155738	-1.495178	0.000000
H	3.312830	1.420912	0.000000	1	3.475268	-1.145851	0.000000	1	3.483428	-1.128415	0.000000
C	-2.401194	0.491119	0.000000	6	-2.355709	-0.912789	0.000000	6	-2.361034	-0.904523	0.000000
H	-1.411483	2.343773	0.000000	1	-3.308545	-1.418974	0.000000	1	-3.314983	-1.408928	0.000000
H	-3.405329	0.857072	0.000000	1	-3.271435	0.933929	0.000000	1	-3.269851	0.948051	0.000000
H	-3.081910	-1.429638	0.000000	7	-2.372212	0.467126	0.000000	7	-2.373939	0.474549	0.000000
N	-2.255628	-0.868697	0.000000								

E = -399.3237112 au
E (CASPT2)= -400.74739722 au

4,5-didehydroisoquinolinium cation (5)
CASSCF(12,12)/cc-pVTZ
3A' triplet state (Cs)

C	2.413948	0.759890	0.000000
C	1.194314	1.384521	0.000000
C	0.001833	0.611360	0.000000
C	0.075895	-0.806769	0.000000
C	1.352355	-1.380167	0.000000
C	2.505447	-0.659642	0.000000
H	-1.408660	2.267556	0.000000
H	3.313322	1.342600	0.000000

E = -401.0542357 au
ZPVE = 0.123501 au
(H298 - E0) = 4.8 kcal/mol

4,5-didehydroisoquinolinium cation (5)
CASSCF(12,12)/cc-pVTZ
1A' singlet state (Cs)

C	2.413189	0.772339	0.000000
C	1.186799	1.379310	0.000000
C	0.002202	0.593026	0.000000
C	0.077952	-0.828136	0.000000
C	1.368447	-1.378052	0.000000
C	2.512328	-0.645651	0.000000
H	-1.389435	2.262771	0.000000
H	3.306946	1.363448	0.000000

E = -401.0550217 au
ZPVE = 0.123347 au
(H298 - E0) = 4.8 kcal/mol

1,5-didehydroisoquinolinium cation (6)
UB3LYP/cc-pVTZ
3A' triplet state (Cs)

6	2.404032	0.875478	0.000000
6	1.180213	1.493323	0.000000
6	0.000000	0.711920	0.000000
6	0.067932	-0.733541	0.000000
6	1.353619	-1.259962	0.000000
6	2.502339	-0.543361	0.000000
1	3.310764	1.464344	0.000000
1	1.100237	2.570635	0.000000

H	1.129742	2.454952	0.000000	H	1.106594	2.448673	0.000000	6	-1.286357	1.218320	0.000000
C	-1.273726	1.204682	0.000000	C	-1.268564	1.198287	0.000000	6	-1.133834	-1.491311	0.000000
C	-1.146117	-1.500459	0.000000	C	-1.158976	-1.502869	0.000000	1	3.474946	-1.018669	0.000000
H	3.462458	-1.141964	0.000000	H	3.471603	-1.123858	0.000000	6	-2.342277	-0.875362	0.000000
C	-2.354457	-0.903729	0.000000	C	-2.360713	-0.896147	0.000000	1	-1.086370	-2.570259	0.000000
H	-3.300785	-1.399986	0.000000	H	-3.308310	-1.390119	0.000000	1	-3.295632	-1.378987	0.000000
H	-3.248316	0.933085	0.000000	H	-3.246293	0.947088	0.000000	1	-3.285701	0.978796	0.000000
N	-2.363236	0.468984	0.000000	N	-2.364740	0.476371	0.000000	7	-2.384607	0.511588	0.000000

E = -398.6635645 au
E (CASPT2)= -400.05237065 au

E = -398.6629585 au
E (CASPT2)= -400.05394182 au

E = -401.0524977 au
ZPVE = 0.123182 au
(H298 - E0) = 4.9 kcal/mol

1,5-didehydroisoquinolinium cation (6)
UB3LYP/cc-pVTZ
1A' singlet state (Cs)

6	2.410179	0.885701	0.000000	C	2.401738	0.877345	0.000000	C	2.407535	0.880673	0.000000
6	1.182084	1.495099	0.000000	C	1.175722	1.489039	0.000000	C	1.180420	1.491240	0.000000
6	0.000000	0.718729	0.000000	C	0.000521	0.693302	0.000000	C	0.004840	0.699328	0.000000
6	0.061463	-0.747536	0.000000	C	0.070030	-0.723172	0.000000	C	0.063550	-0.730033	0.000000
6	1.349998	-1.224783	0.000000	C	1.359422	-1.273975	0.000000	C	1.352809	-1.256508	0.000000
6	2.509343	-0.530542	0.000000	C	2.504784	-0.541215	0.000000	C	2.505464	-0.535595	0.000000
1	3.314655	1.477771	0.000000	H	3.295543	1.468454	0.000000	H	3.301402	1.471468	0.000000
1	1.096351	2.571322	0.000000	H	1.089834	2.557045	0.000000	H	1.093159	2.558581	0.000000
6	-1.286161	1.211145	0.000000	C	-1.293250	1.216870	0.000000	C	-1.288469	1.208962	0.000000
6	-1.139911	-1.505514	0.000000	C	-1.132636	-1.487364	0.000000	C	-1.138545	-1.493176	0.000000
1	3.475903	-1.017272	0.000000	H	3.466307	-1.014764	0.000000	H	3.462077	-1.018577	0.000000
6	-2.344600	-0.887212	0.000000	C	-2.339878	-0.869062	0.000000	C	-2.343679	-0.872622	0.000000
1	-1.090026	-2.583476	0.000000	H	-1.089196	-2.557038	0.000000	H	-1.094204	-2.562283	0.000000
1	-3.297990	-1.390626	0.000000	H	-3.285309	-1.366942	0.000000	H	-3.290122	-1.368457	0.000000
1	-3.281732	0.966659	0.000000	H	-3.265075	0.975142	0.000000	H	-3.259955	0.975413	0.000000

7	-2.381647	0.497870	0.000000	N	-2.379253	0.509288	0.000000	N	-2.376977	0.504537	0.000000

E = -401.0613224 au
ZPVE = 0.122787 au
(H298 - E0) = 4.9 kcal/mol

E = -398.6619538 au
E (CASPT2)= -400.05112253 au

E = -398.6692209 au
E (CASPT2)= -400.06496710 au

4,8-didehydroisoquinolinium cation (7)
UB3LYP/cc-pVTZ
3A' triplet state (Cs)

4,8-didehydroisoquinolinium cation (7)
UB3LYP/cc-pVTZ
1A' singlet state (Cs)

4,8-didehydroisoquinolinium cation (7)
CASSCF(12,12)/cc-pVTZ
3A' triplet state (Cs)

6	2.436621	0.801617	0.000000	6	2.444841	0.776291	0.000000	C	2.436314	0.799301	0.000000
6	1.219198	1.381213	0.000000	6	1.226851	1.353875	0.000000	C	1.217874	1.393844	0.000000
6	0.000000	0.696800	0.000000	6	0.000000	0.705361	0.000000	C	0.002044	0.684076	0.000000
6	0.068442	-0.748746	0.000000	6	0.064717	-0.759006	0.000000	C	0.066356	-0.732916	0.000000
6	1.326910	-1.377929	0.000000	6	1.321549	-1.391460	0.000000	C	1.327141	-1.374114	0.000000
6	2.476456	-0.621263	0.000000	6	2.476670	-0.644873	0.000000	C	2.477407	-0.623282	0.000000
1	-1.352902	2.398173	0.000000	1	-1.339437	2.414718	0.000000	H	-1.357952	2.379252	0.000000
1	3.355233	1.373025	0.000000	1	3.362677	1.348526	0.000000	H	3.341837	1.371757	0.000000
6	-1.250233	1.322924	0.000000	6	-1.245833	1.339316	0.000000	C	-1.254350	1.313172	0.000000
6	-1.177011	-1.383019	0.000000	6	-1.184100	-1.363538	0.000000	C	-1.178685	-1.393477	0.000000
1	1.377266	-2.456915	0.000000	1	1.362595	-2.470288	0.000000	H	1.370669	-2.444470	0.000000
1	3.440858	-1.111764	0.000000	1	3.436995	-1.142990	0.000000	H	3.430128	-1.114935	0.000000
6	-2.375461	-0.778530	0.000000	6	-2.380450	-0.752050	0.000000	C	-2.374100	-0.772403	0.000000
1	-3.337887	-1.266538	0.000000	1	-3.343955	-1.237825	0.000000	H	-3.329703	-1.250690	0.000000
1	-3.257533	1.087292	0.000000	1	-3.253804	1.117252	0.000000	H	-3.234278	1.082633	0.000000
7	-2.367795	0.602619	0.000000	7	-2.367220	0.626730	0.000000	N	-2.358540	0.601211	0.000000

E = -401.0538861 au
ZPVE = 0.123583 au
(H298 - E0) = 4.8 kcal/mol

E = -401.0608073 au
ZPVE = 0.123305 au
(H298 - E0) = 4.8 kcal/mol

E = -398.6634337 au
E (CASPT2)= -400.05213178 au

4,8-didehydroisoquinolinium cation (7)

1,5-didehydroisoquinolinium cation (6)

1,5-didehydroisoquinolinium cation (6)

CASSCF(12,12)/cc-pVTZ

1A' singlet state (Cs)

C	2.436171	0.794784	0.000000
C	1.213215	1.380838	0.000000
C	-0.003727	0.688703	0.000000
C	0.070240	-0.739978	0.000000
C	1.331702	-1.377044	0.000000
C	2.481688	-0.625466	0.000000
H	-1.361891	2.382954	0.000000
H	3.337167	1.374057	0.000000
C	-1.258831	1.317338	0.000000
C	-1.174022	-1.384085	0.000000
H	1.375283	-2.446951	0.000000
H	3.434737	-1.116232	0.000000
C	-2.372768	-0.766960	0.000000
H	-3.325277	-1.251279	0.000000
H	-3.238969	1.084207	0.000000
N	-2.362553	0.604076	0.000000

E = -398.6699660 au

E (CASPT2)= -400.06398478 au

tetrahydrofuran

B3LYP/cc-pVTZ

1A' singlet state (Cs)

6	-0.089144	1.011239	0.775270
6	-0.089144	-0.484988	1.134463
6	-0.089144	1.011239	-0.775270
6	-0.089144	-0.484988	-1.134463
8	0.449942	-1.153223	0.000000
1	0.804088	1.500261	1.160704

UB3LYP/cc-pVTZ

1A' singlet state (Cs)

6	0.000000	0.718810	0.000000
6	0.061471	-0.747559	0.000000
6	-1.140081	-1.505091	0.000000
6	1.349889	-1.225630	0.000000
6	-2.344829	-0.886722	0.000000
6	2.509211	-0.531371	0.000000
7	-2.381787	0.498678	0.000000
6	2.410367	0.885055	0.000000
6	-1.285938	1.211816	0.000000
6	1.182445	1.494810	0.000000
1	-1.090672	-2.583153	0.000000
1	-3.298370	-1.389883	0.000000
1	3.475923	-1.017937	0.000000
1	-3.281926	0.967551	0.000000
1	3.315063	1.476836	0.000000
1	1.097288	2.571134	0.000000

E = -401.0613224 au

ZPVE = 0.122779 au

(H298 - E0) = 4.9 kcal/mol

alpha-dehydrotetrahydrofuran

UB3LYP/cc-pVTZ

2A doublet state (C1)

6	1.255516	0.196966	0.132024
6	0.541837	-1.117583	0.042679
6	0.132592	1.202635	-0.205974
6	-1.126351	0.422419	0.169217
8	-0.810710	-0.951534	-0.115583

H atom abstraction transition state C-1

UB3LYP/cc-pVTZ

1A singlet state (C1)

6	-1.994042	2.101770	0.140348
6	-0.139239	0.091386	-0.235393
1	-0.267154	3.386651	-0.011231
1	-2.707672	2.898146	0.285611
1	1.249730	-0.641304	-0.572875
1	1.214467	1.551730	-0.339468
6	2.417913	-0.632900	-0.911057
8	2.888504	0.655420	-0.615410
6	3.223038	-1.631851	-0.101294
1	2.365442	-0.781553	-1.989978
6	3.865044	0.591530	0.472061
6	3.689032	-0.788109	1.093560
1	4.073123	-1.975326	-0.695377
1	2.646164	-2.508922	0.184637
1	4.849833	0.724483	0.023250
1	3.668511	1.421052	1.147302
1	4.610287	-1.157343	1.537750
1	2.925256	-0.767285	1.871692
6	-1.467153	-0.309269	-0.088362
6	-1.889828	-1.658534	-0.127877
6	-2.436870	0.753125	0.109691
6	-3.743827	0.321334	0.248144
6	-3.215427	-1.978155	0.017815
1	-3.535591	-3.010354	-0.014607
6	-4.183087	-0.958308	0.212780
1	-5.229173	-1.210681	0.327490
7	0.213642	1.358443	-0.204354
6	-0.678111	2.389811	-0.017579

1	-0.953374	1.525793	1.193222	1	2.102307	0.270293	-0.554045	1	-1.151411	-2.432728	-0.277455
1	-1.110991	-0.837799	1.327968	1	1.651106	0.381157	1.137703				
1	0.530232	-0.732867	1.994495	1	0.929092	-2.035995	-0.370860		**E = -633.6205313 au**		
1	0.804088	1.500261	-1.160704	1	0.131147	1.421796	-1.274077		**ZPVE = 0.236940 au**		
1	-0.953374	1.525793	-1.193222	1	0.217324	2.143236	0.335655		**(H298 - E0) = 8.4 kcal/mol**		
1	0.530232	-0.732867	-1.994495	1	-2.008069	0.684521	-0.411640				
1	-1.110991	-0.837799	-1.327968	1	-1.358789	0.520649	1.234242				

E = -232.5379455 au
ZPVE = 0.116556 au
(H298 - E0) = 3.7 kcal/mol

E = -231.8810227 au
ZPVE = 0.102683 au
(H298 - E0) = 3.7 kcal/mol

5-dehydroisoquinolinium cation
UB3LYP/cc-pVTZ
2A' doublet state (Cs)

6	-1.277904	1.225343	0.000000
6	0.000000	0.664202	0.000000
6	0.097859	-0.774121	0.000000
6	-1.090733	-1.543799	0.000000
6	-2.300429	-0.923618	0.000000
1	1.086217	2.535362	0.000000
1	-3.267471	0.884440	0.000000
1	-1.445080	2.293048	0.000000
6	1.174681	1.457722	0.000000
6	1.389560	-1.283423	0.000000
1	-1.039290	-2.622104	0.000000
1	-3.246847	-1.439816	0.000000
6	2.529491	-0.554678	0.000000
6	2.408768	0.862931	0.000000
1	3.507957	-1.017532	0.000000
1	3.305627	1.466847	0.000000

7	-2.355552	0.445200	0.000000

E = -401.7530963 au
ZPVE = 0.136641 au
(H298 - E0) = 4.8 kcal/mol