Supporting Information

Carbanion Translocations via Intramolecular Proton Transfers: A Quantum Chemical Study

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S1. Benchmark Calculations

All quantum chemical calculations involved in our benchmark calculations were performed in Gaussian 09[1] and ORCA 3.0.3.[2] Geometry optimizations of all the minima and transition structures were carried out using the second-order Møller–Plesset perturbation theory (MP2)[3] and the aug-cc-pVTZ basis set[4] with symmetric constraints. The frozen core approximation was applied to speed up the correlation calculations. Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition structure. Single-point energy calculations were performed at the CCSD(T)[5]/aug-cc-pVTZ level (the frozen core approximation was applied) based on the optimized structures computed at the MP2/aug-cc-pVTZ level.

Then, we used these results to assess the performance of other popular computational methods (Table S1), including the spin-component-scaled MP2 (SCS-MP2),[6] BP86,[7,8] PBE,[9] BLYP,[7,10] PBE0,[11] B3LYP,[10,12] mPW1PW91,[13] M06-2X,[14] and ωB97XD[15] by performing single-point energy calculations on the optimized geometries computed at the MP2/aug-cc-pVTZ level. The aug-cc-pVTZ basis set was used for calculations with SCS-MP2 method (the convergence thresholds were set to "TIGHTSCF"), while the 6-311+G(d,p) basis set[16] was used for all density functional theory (DFT) calculations (pruned integration grids with 99 radial shells and 590 angular points per shell were used).

We found that, among the density functionals tested, ωB97XD gave the best results: the root-mean-square deviation (RMSD) is only 1.4 kcal/mol. The SCS-MP2 method may offer even more accurate results (the RMSD is less than 1 kcal/mol). But it suffers from the disadvantage of heavy computational cost. Therefore, in the main text, we used the results calculated at the SCS-MP2/aug-cc-pVTZ//ωB97XD/6-311+G(d,p) level.

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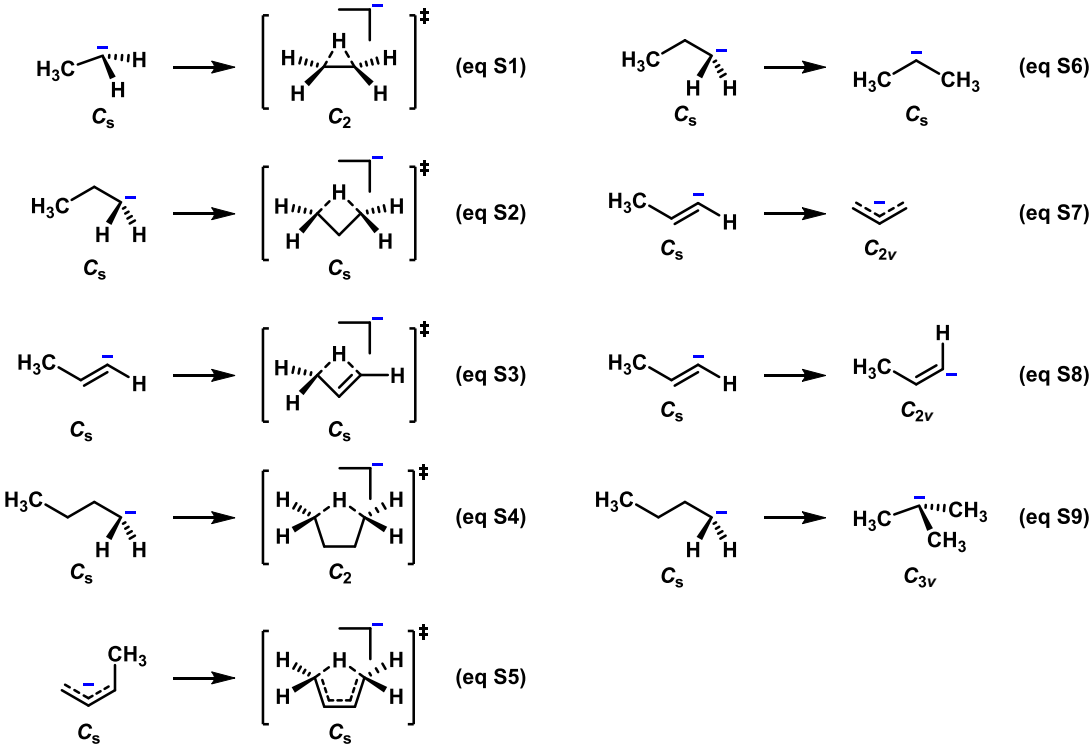
Table S1. Assessment of Several Computational Methods for Kinetics of Intramolecular Proton Transfers and Thermochemistry[a]



computational method	$\Delta E^{\ddagger}$ (kcal/mol)					ΔE_{rxn} (kcal/mol)				RMSD
	eq S1	eq S2	eq S3	eq S4	eq S5	eq S6	eq S7	eq S8	eq S9	
CCSD(T)[b]	50.5	36.7	42.7	19.5	34.2	2.1	−15.4	1.7	−5.8	**0.0**
MP2[b,c]	48.8	35.5	39.9	17.6	31.7	2.4	−18.2	1.8	−7.3	**1.9**
SCS-MP2[b]	51.3	37.8	42.9	20.6	35.0	2.4	−16.6	1.7	−5.6	**0.8**
BP86[d]	44.3	31.4	36.4	13.7	29.7	2.5	−18.9	1.6	−5.6	**4.4**
PBE[d]	43.7	31.4	36.1	13.4	29.5	2.8	−19.1	1.7	−6.1	**4.6**
BLYP[d]	46.1	34.8	39.5	17.0	33.1	3.2	−18.6	1.6	−5.2	**2.4**
PBE0[d]	46.8	33.3	39.9	15.4	32.4	2.1	−18.9	1.7	−4.9	**2.7**
B3LYP[d]	48.4	36.0	42.3	18.2	35.2	2.6	−18.6	1.7	−4.5	**1.5**
mPW1PW91[d]	47.4	33.7	40.5	15.7	32.8	2.0	−18.8	1.7	−4.5	**2.4**
M06-2X[d]	48.0	35.0	42.5	17.9	34.7	2.0	−18.1	1.7	−4.4	**1.5**
ωB97XD[d]	48.7	34.8	43.0	18.2	35.0	1.8	−17.4	1.6	−3.4	**1.4**

[a]Energy differences were based on single-point energy calculations on the optimized geometries computed at the MP2/aug-cc-pVTZ level (without zero-point energy corrections) unless otherwise specified. rxn = reaction. RMSD = root-mean-square deviation.

[b]The aug-cc-pVTZ basis set was used.

[c]Computed at the MP2/aug-cc-pVTZ level.

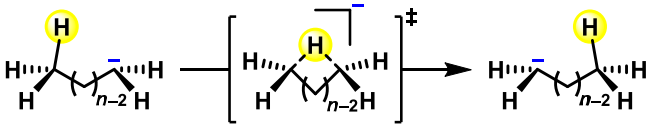
[d]The 6-311+G(d,p) basis set was used.

S2. Tunneling Effect on Intramolecular Proton Transfers

It is well known that quantum tunneling plays an important role in hydrogen transfer reactions.[17] To assess the influence of proton tunneling, we carried out direct dynamics calculations with GAUSSRATE[18] as the interface between Gaussian 09[1] and POLYRATE.[19] Pruned integration grids with 99 radial shells and 590 angular points per shell were used. The ωB97XD functional[15] and the 6-31+G(d,p) basis set[20] were employed. The rate constants starting from the reactive conformers (not the most stable ones) were obtained using canonical variational transition state theory (CVT).[21] The local quadratic approximation (Page–McIver method) was employed to calculate the minimum energy path.[22] Quantum effects of multidimensional tunneling were calculated with small curvature tunneling (SCT) approximation.[17a,23]

As shown in Table S2, quantum tunneling increases the rate constants in a magnitude of 10–7000 at 298.15 K, corresponding to a decrease of 1.4–5.2 kcal/mol in terms of Gibbs energy of activation (according to the conventional transition state theory, in which $\kappa = 1$). These results did not change the fact that the activation barrier for intramolecular proton transfer decreases with n, which is one of our conclusions in the main text. Moreover, these results indicated that our conclusions did not change if we chose different energy starting points because kinetic data shown in Table S2 were computed starting from the reactive conformers, other than the most stable ones, which were discussed in the main text.

Table S2. Theoretical Rate Constants and Gibbs Energies of Activation at 298.15 K



n	CVT		CVT/SCT	
	k (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)	k (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
2	1.78×10^{-21}	45.7	1.31×10^{-17}	40.5
3	7.94×10^{-11}	31.2	1.12×10^{-7}	26.9
4	5.28×10^{1}	15.1	1.29×10^{3}	13.2
5	2.24×10^{4}	11.5	5.46×10^{5}	9.6
6	9.82×10^{6}	7.9	1.01×10^{8}	6.5

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S3. Bond Energy Decomposition Analysis

Table S3. Additional Data for Bond Energy Decomposition Analysis[a]

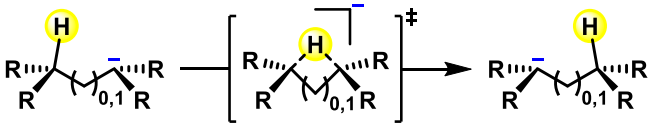
bond angle	180°	170°	160°	150°	140°	130°	120°	110°	100°	90°
ΔE	11.0	11.4	12.5	14.4	17.2	21.5	28.2	38.8	56.1	83.4
$\Delta E_{dis}(CH_4)$	29.5	29.7	30.4	31.5	32.8	34.0	35.3	35.5	35.5	35.7
$\Delta E_{dis}(CH_3^-)$	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.7	1.8
ΔE_{int}	−18.5	−18.3	−17.9	−17.1	−15.6	−12.5	−7.2	3.1	19.9	45.9
ΔE_{Pauli}	116.0	116.4	117.1	118.5	121.4	127.2	137.1	156.4	189.9	245.8
ΔV_{elstat}	−51.5	−51.7	−52.1	−52.8	−54.0	−56.2	−59.7	−66.1	−77.5	−97.0
ΔE_{oi}	−83.0	−83.0	−82.9	−82.8	−83.0	−83.5	−84.6	−87.2	−92.5	−102.9

[a]Energies are reported in kcal/mol. Computed at the ωB97X[24]/ATZ2P[25] level. $\Delta E = \Delta E_{dis}(CH_4) + \Delta E_{dis}(CH_3^-) + \Delta E_{int}$. $\Delta E_{int} = \Delta E_{Pauli} + \Delta V_{elstat} + \Delta E_{oi}$. dis = distortion. int = interaction. Pauli = Pauli repulsion. elstat = electrostatic. oi = orbital interaction.

S4. Substituent Effect on 1,2- and 1,3-Proton Transfers

In the main text, we have discussed the substituent effect on 1,4-proton transfer (Table 3). Herein, we provided some additional results for the substituent effect on 1,2- and 1,3-proton transfers (Table S4). The conclusions are in full accordance with those described in the main text.

Table S4. Substituent Effect on 1,2- and 1,3-Proton Transfers[a]



entry		TS	R	$\Delta E^{\ddagger}$
	1,2-proton shift			
1	**A** → **A**	**TS1**	H	48.2
2	**S** → **S**	**TS16**	CN	43.7
3	**T** → **T**	**TS17**	F	58.8
	1,3-proton transfer			
4	**B** → **B**	**TS2**	H	34.2
5	**U** → **U**	**TS18**	CN	30.4
6	**V** → **V**	**TS19**	F	37.7

[a]Energies are reported in kcal/mol. $\Delta E_{rxn} = 0$ in all cases. rxn = reaction.

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S5. Computed Energies of All Stationary Points

Table S5. Zero-Point Energies (ZPEs) and Single-Point Energies (SPEs)

	ZPE[a] (a.u.)	SPE[a] (a.u.)	SPE[b] (a.u.)
methane	0.044792	−40.515486	−40.422818
methyl anion	0.028626	−39.833263	−39.744735
A	0.057831	−79.136940	−78.961695
B	0.086685	−118.455065	−118.193801
C	0.115646	−157.769191	−157.421263
D	0.144199	−197.082749	−196.648021
E	0.172780	−236.395846	−235.874395
F	0.201322	−275.708752	−275.100573
G	0.074269	−80.354196	−80.171219
H	0.115579	−526.812804	−525.841057
I	0.082514	−1996.272860	−1993.950270
J	0.087333	−554.803924	−553.996453
K	0.114735	−250.020767	−249.515382
L	0.116444	−250.069375	−249.559411
M	0.107647	−617.391436	−616.549407
N	0.108231	−617.411014	−616.565569
O	0.109069	−257.019207	−256.556791
P	0.109075	−257.023968	−256.558222
Q	0.208484	−900.620781	−899.087094
R	0.208631	−900.651698	−899.121500
S	0.058048	−448.186411	−447.388084
T	0.030284	−476.176867	−475.542994
U	0.086738	−487.499626	−486.614686
V	0.058615	−515.489044	−514.768418
TS1	0.053016	−79.059236	−78.880060
TS2	0.081112	−118.398838	−118.133667
TS3	0.110132	−157.739248	−157.386803
TS4	0.138380	−197.054844	−196.614856
TS5	0.167397	−236.372515	−235.844995
TS6	0.196353	−275.684915	−275.070078
TS7	0.069532	−80.335463	−80.148027
TS8	0.111075	−526.793851	−525.822151
TS9	0.077786	−1996.248487	−1993.923443
TS10	0.082320	−554.767894	−553.955037
TS11	0.111497	−250.017453	−249.508720
TS12	0.102944	−617.373324	−616.525956
TS13	0.103695	−256.990593	−256.521788
TS14	0.204178	−900.612229	−899.078251
TS15	0.203908	−900.595557	−899.061709
TS16	0.053284	−448.115624	−447.313660
TS17	0.024784	−476.083577	−475.443725
TS18	0.081244	−487.447505	−486.560725
TS19	0.052777	−515.429584	−514.702558

[a]Computed at the ωB97XD/6-311+G(d,p) level.

[b]Computed at the SCS-MP2/aug-cc-pVTZ//ωB97XD/6-311+G(d,p) level.

S6. Cartesian Coordinates of All Stationary Points

methane

C	0.000290	0.000030	−0.000222
H	1.058815	0.142847	−0.217803
H	−0.581261	0.783951	−0.486910
H	−0.159069	0.047103	1.077740
H	−0.320226	−0.974078	−0.371696

methyl anion

C	0.000157	0.000067	−0.124149
H	−0.610231	0.841454	0.248243
H	−0.424561	−0.948862	0.248119
H	1.033851	0.107008	0.248531

A

C	−0.690397	0.000018	0.015424
C	0.832909	−0.000012	−0.146365
H	−1.141206	−0.875733	−0.478188
H	−1.141025	0.875331	−0.479014
H	−1.113250	0.000296	1.053386
H	1.270068	0.889197	0.344831
H	1.270336	−0.889128	0.344625

B

C	1.224139	−0.275201	0.000018
C	−0.082693	0.563174	−0.000013
C	−1.403928	−0.177249	−0.000025
H	1.251676	−0.926849	0.882076
H	2.138237	0.348954	0.000049
H	1.251671	−0.926788	−0.882083
H	−0.027137	1.232976	0.875528
H	−0.027097	1.232960	−0.875588
H	−1.506116	−0.812939	−0.897661
H	−1.506347	−0.812660	0.897801

C

C	−1.504674	−0.565675	0.095225
C	−0.664410	0.654899	−0.271816
C	0.767187	0.563019	0.286396
C	1.565997	−0.612965	−0.252819
H	−1.025385	−1.462402	−0.309214
H	−2.526104	−0.503693	−0.301348
H	−1.569389	−0.675502	1.186146
H	−0.595798	0.724208	−1.364850
H	−1.163163	1.566830	0.099532
H	1.278004	1.500364	0.017060
H	0.649952	0.609965	1.400785
H	2.647758	−0.442243	−0.139010
H	1.319530	−1.553196	0.268979

D

C	2.375904	−0.176994	−0.128991
C	0.922573	−0.355436	0.306341
C	−0.005528	0.740576	−0.206929
C	−1.466970	0.529720	0.225845
C	−2.086836	−0.754537	−0.302390
H	2.451453	−0.175732	−1.222105
H	3.020528	−0.979478	0.249238
H	2.783852	0.776498	0.228907
H	0.535986	−1.312104	−0.060564
H	0.866627	−0.387456	1.404053
H	0.366423	1.719413	0.146636
H	0.025706	0.740665	−1.305128
H	−1.464736	0.655757	1.339788
H	−2.040449	1.389526	−0.152773
H	−1.793978	−1.631192	0.299941
H	−3.186269	−0.695868	−0.291248

E

C	2.897017	0.542038	0.099265
C	1.765031	−0.419813	−0.258790
C	0.393441	0.065349	0.204796
C	−0.750937	−0.878485	−0.147292
C	−2.119376	−0.340490	0.306465
C	−2.509192	0.976637	−0.345980
H	2.722309	1.525878	−0.348213
H	3.871093	0.180570	−0.249262
H	2.959642	0.683022	1.184056
H	1.739609	−0.564840	−1.346053
H	1.972839	−1.406846	0.176721
H	0.411544	0.220178	1.294744
H	0.171513	1.037484	−0.251364
H	−0.781828	−1.001546	−1.238356
H	−0.553437	−1.867216	0.304757
H	−2.866335	−1.106422	0.048039
H	−2.080742	−0.345013	1.426691
H	−3.597570	1.135093	−0.296260

H	−2.024540	1.838243	0.143715

F

C	−3.655359	0.055804	−0.172810
C	−2.270007	0.538849	0.251878
C	−1.146449	−0.414949	−0.150058
C	0.242742	0.065641	0.261131
C	1.370428	−0.876352	−0.145791
C	2.756518	−0.341110	0.254138
C	3.115988	0.983132	−0.401428
H	−3.709314	−0.063414	−1.260149
H	−4.442289	0.755946	0.126721
H	−3.884361	−0.917366	0.275275
H	−2.073010	1.524009	−0.187120
H	−2.248709	0.680708	1.339763
H	−1.341615	−1.404947	0.288100
H	−1.166679	−0.554819	−1.239484
H	0.448185	1.040507	−0.196545
H	0.270448	0.211176	1.351942
H	1.191703	−1.868412	0.306597
H	1.355266	−0.990937	−1.238082
H	2.766164	−0.356538	1.374816
H	3.492479	−1.103262	−0.043855
H	2.653213	1.838973	0.118627
H	4.205351	1.142287	−0.398959

G

C	1.834912	0.000023	0.000097
C	−1.907265	0.000010	0.000269
H	0.731506	0.000990	0.001812
H	2.206595	−0.544765	0.873669
H	2.206707	1.028949	0.033816
H	2.203646	−0.485171	−0.909052
H	−2.302962	0.647645	−0.804802
H	−2.303920	−1.020296	−0.159749
H	−2.307450	0.372447	0.962112

H

N	−3.148894	1.765414	−0.932989
N	−2.352291	−2.288959	0.229188
N	2.605676	2.303798	−0.225342
N	2.454833	−2.116328	−1.107693
C	−2.346127	1.014270	−0.595778
C	−1.894376	−1.250576	0.046149
C	2.216982	1.216693	−0.059419
C	2.121664	−1.164725	−0.521552
C	−1.309713	0.082064	−0.144721
C	−0.590507	0.575817	1.132330
C	0.717462	−0.202031	1.349135
C	1.684093	−0.050027	0.197322
H	−0.532162	0.010366	−0.921594
H	−0.357869	1.633774	0.983154
H	−1.264593	0.492956	1.990425
H	1.148778	0.151120	2.295478
H	0.493700	−1.264604	1.489594

I

Cl	−2.917479	1.132910	−0.246748
Cl	−2.085682	−1.682543	−0.164715
Cl	2.027127	1.710604	−0.148530
Cl	3.005920	−1.108901	−0.254358
C	−1.492044	0.020854	−0.166511
C	−0.632294	0.319347	1.042649
C	0.724018	−0.394416	0.976308
C	1.431033	−0.093033	−0.345324
H	−0.922342	0.142455	−1.084603
H	−0.459784	1.399284	1.047635
H	−1.176827	0.058388	1.955557
H	1.300252	−0.123815	1.876251
H	0.566375	−1.477998	1.006388

J

F	−2.623189	0.868923	−0.327444
F	−2.066696	−1.246034	−0.139782
F	2.023975	1.280053	−0.124941
F	2.704679	−0.841480	−0.339278
C	−1.531493	0.015422	−0.307723
C	−0.608029	0.362760	0.824456
C	0.706494	−0.419751	0.762164
C	1.506806	−0.042980	−0.486379
H	−1.043926	0.047568	−1.281454
H	−0.385746	1.430688	0.742005
H	−1.146376	0.196309	1.764665
H	1.285155	−0.225915	1.682925
H	0.499306	−1.494520	0.719756

K

N	−3.037323	−0.187052	−0.284655

C	−1.934567	−0.180327	0.059876
C	−0.551444	−0.179531	0.497885
C	0.355879	0.818707	−0.227642
C	1.835059	0.505706	0.115454
C	2.225656	−0.923379	−0.217070
H	−0.057750	−1.157791	0.312651
H	−0.532167	−0.002738	1.579403
H	0.213388	0.697341	−1.307806
H	0.086540	1.852654	0.028854
H	2.425585	1.306944	−0.379336
H	1.957092	0.683800	1.196987
H	2.572125	−1.017139	−1.257958
H	3.012953	−1.300760	0.448766

L

N	2.507756	0.809053	−0.178749
C	1.686567	0.003902	0.085638
C	0.722455	−0.940788	0.365262
C	−0.552239	−1.038822	−0.425565
C	−1.749655	−0.211966	0.099395
C	−1.487964	1.290972	0.064005
H	0.820074	−1.517004	1.279977
H	−0.368626	−0.728814	−1.466105
H	−0.883658	−2.088231	−0.484609
H	−2.652270	−0.446524	−0.489368
H	−1.954606	−0.520670	1.133070
H	−0.576529	1.522483	0.621179
H	−1.333224	1.632519	−0.966062
H	−2.320437	1.863079	0.490747

M

Cl	−2.183066	−0.096864	−0.079080
C	−0.403476	−0.329186	0.311340
C	0.464881	0.793030	−0.199115
C	1.929240	0.521688	0.214542
C	2.478618	−0.794107	−0.311398
H	−0.109521	−1.267628	−0.156455
H	−0.363473	−0.413573	1.398437
H	0.409671	0.816337	−1.292540
H	0.107668	1.752149	0.203445
H	2.520211	1.355487	−0.190649
H	1.953555	0.665860	1.324795
H	3.576411	−0.766860	−0.371174
H	2.202025	−1.643631	0.336293

N

Cl	1.973990	−0.513147	−0.076904
C	0.877464	1.040234	0.381209
C	−0.463908	0.777836	−0.284990
C	−1.355567	−0.216516	0.461188
C	−2.728760	−0.409977	−0.181981
H	1.397163	1.781107	−0.248302
H	−0.974664	1.756924	−0.294761
H	−0.404505	0.448560	−1.344962
H	−0.831455	−1.177371	0.511912
H	−1.463344	0.132236	1.494574
H	−2.632225	−0.781093	−1.208875
H	−3.346428	−1.125129	0.374180
H	−3.277743	0.538806	−0.228952

O

F	−2.292097	−0.171014	−0.114416
C	−0.930267	−0.376552	0.236704
C	−0.060067	0.760407	−0.226728
C	1.393758	0.538711	0.242249
C	2.019296	−0.741871	−0.288028
H	−0.612718	−1.310393	−0.230653
H	−0.909304	−0.475374	1.328325
H	−0.074526	0.792950	−1.321774
H	−0.465518	1.703931	0.169790
H	1.971924	1.402297	−0.115850
H	1.364985	0.657965	1.356195
H	3.117521	−0.691460	−0.234327
H	1.700194	−1.624956	0.292854

P

F	1.529825	−0.941502	0.126170
C	1.280216	0.411446	−0.489916
C	0.139204	0.998916	0.317068
C	−1.268323	0.587264	−0.140401
C	−1.526603	−0.912119	−0.007342
H	2.192157	0.948797	−0.167213
H	0.217638	0.778459	1.407259
H	0.218036	2.093694	0.212279
H	−2.028781	1.142581	0.433522
H	−1.374280	0.876114	−1.193308
H	−1.417115	−1.232974	1.035515
H	−2.535024	−1.182798	−0.346751
H	−0.788021	−1.463394	−0.593286

Q

S	−0.027595	−1.448218	−0.269403
C	−0.008275	−2.201893	1.363864
C	1.479906	−0.330129	−0.129430
C	2.110112	−0.100633	−1.352366
C	3.218707	0.729988	−1.315671
C	3.622462	1.268216	−0.089781
C	2.926347	0.980464	1.080790
C	1.790823	0.141921	1.110486
C	−1.414275	−0.322020	−0.125413
C	−2.423976	−0.417144	−1.075497
C	−3.506945	0.451096	−0.996699
C	−3.566362	1.395578	0.020808
C	−2.543638	1.480685	0.961117
C	−1.455184	0.621632	0.895663
H	0.478744	−1.450240	2.008289
H	−1.030984	−2.435210	1.653499
H	0.597803	−3.104754	1.297507
H	1.767773	−0.542790	−2.283812
H	3.765189	0.951885	−2.225417
H	4.493630	1.917120	−0.058274
H	3.285064	1.430116	2.005543
H	−2.366239	−1.157193	−1.865670
H	−4.301062	0.388066	−1.731346
H	−4.411855	2.071479	0.080217
H	−2.588896	2.224663	1.747879
H	−0.625870	0.691785	1.594809

R

S	−0.001158	1.474239	−0.499799
C	−0.170620	2.697263	0.603403
C	−1.367898	0.289415	−0.261384
C	−1.345894	−0.939559	−0.913169
C	−2.424123	−1.801831	−0.771061
C	−3.512719	−1.437105	0.017126
C	−3.523362	−0.204781	0.657481
C	−2.449500	0.669197	0.513201
C	1.361773	0.311138	−0.126451
C	2.458826	0.314315	−0.977236
C	3.559657	−0.484348	−0.681623
C	3.559869	−1.271041	0.463174
C	2.458500	−1.262974	1.315450
C	1.355806	−0.473128	1.022196
H	−0.049873	2.479391	1.657630
H	0.128787	3.659006	0.213763
H	−0.490450	−1.228953	−1.514276
H	−2.414496	−2.761387	−1.275531
H	−4.351983	−2.114439	0.127471
H	−4.370617	0.083078	1.269710
H	−2.433674	1.648661	0.981966
H	2.454815	0.937847	−1.865145
H	4.415604	−0.490135	−1.346936
H	4.418235	−1.891512	0.694296
H	2.459140	−1.876067	2.209649
H	0.491160	−0.472687	1.677555

S

N	1.982991	−0.186390	2.161125
N	1.983732	−0.170675	−2.161895
N	−0.907272	2.605981	0.009109
N	−2.856765	−1.464177	−0.005236
C	0.555188	−0.634604	−0.002294
C	−0.791599	0.048121	−0.000061
C	1.370612	−0.369796	1.204856
C	1.371016	−0.361042	−1.207206
C	−0.871485	1.443615	0.004956
C	−1.931900	−0.756133	−0.002835
H	0.370205	−1.714143	−0.006221

T

F	1.372211	1.099660	−0.067770
F	1.373260	−1.098833	−0.067337
F	−1.371786	−1.114956	0.087013
F	−1.372642	1.114573	0.087203
C	0.607104	0.000124	0.254029
C	−0.690992	−0.000829	−0.537601
H	0.493941	0.000239	1.349458

U

N	1.242267	2.078583	1.466055
N	3.529500	−0.690631	−0.887143
N	−2.933495	1.664449	−0.818497
N	−1.865079	−2.292226	1.123137
C	1.203527	1.077040	0.903581
C	2.515731	−0.457360	−0.396249
C	−2.205160	0.788757	−0.574103
C	−1.665209	−1.347966	0.468118
C	1.188382	−0.194461	0.174057

C	0.064042	−0.245906	−0.919876
C	−1.308518	−0.251951	−0.320228
H	0.970863	−0.991601	0.894696
H	0.186891	0.611191	−1.584982
H	0.273142	−1.149736	−1.506383

V

F	−1.779601	−0.908096	0.777856
F	−2.135354	0.644780	−0.725251
F	2.351894	−0.648901	−0.484254
F	1.539479	1.138833	0.594634
C	−1.175492	0.157960	0.156507
C	0.079822	−0.238253	−0.564417
C	1.269139	−0.293383	0.408372
H	−1.015433	0.930197	0.910007
H	−0.068155	−1.225006	−1.012472
H	0.255022	0.497326	−1.367172

TS1

C	−0.793147	0.049353	0.027663
C	0.793141	−0.049347	0.027651
H	0.000033	−0.000010	1.050617
H	−1.244953	−0.946466	−0.007202
H	−1.277985	0.738235	−0.684053
H	1.277974	−0.738252	−0.684042
H	1.244969	0.946460	−0.007200

TS2

C	−1.177359	−0.334915	−0.074187
C	0.000032	0.646952	0.089590
C	1.177353	−0.334968	−0.074315
H	0.000028	−1.030995	−0.575994
H	−2.086225	0.074229	−0.551329
H	−1.460104	−0.794076	0.887730
H	−0.000016	1.350557	−0.755411
H	0.000088	1.258097	1.011314
H	2.086677	0.074442	−0.550414
H	1.459391	−0.794668	0.887576

TS3

C	1.333470	−0.686802	−0.117181
C	0.760070	0.685486	0.208818
C	−0.760070	0.685490	−0.208820
C	−1.333468	−0.686797	0.117185
H	−0.000027	−1.227769	0.000013
H	2.100088	−1.029388	0.590088
H	1.730507	−0.745926	−1.143091
H	0.803665	0.847854	1.297302
H	1.265303	1.549227	−0.251678
H	−1.265307	1.549227	0.251677
H	−0.803666	0.847854	−1.297304
H	−1.730524	−0.745925	1.143085
H	−2.100049	−1.029420	−0.590104

TS4

C	−1.399815	1.015970	0.047822
C	−1.284916	−0.487037	−0.239392
C	−0.000016	−1.084699	0.361619
C	1.285039	−0.487045	−0.239087
C	1.399684	1.016089	0.047599
H	−0.000108	1.353884	−0.043400
H	−1.717856	1.182440	1.092820
H	−2.142179	1.497052	−0.611736
H	−2.146205	−1.097780	0.097746
H	−1.234138	−0.638363	−1.330711
H	−0.000152	−0.902318	1.447464
H	0.000014	−2.178362	0.228212
H	2.146262	−1.097546	0.098663
H	1.234741	−0.638820	−1.330361
H	1.718146	1.183006	1.092393
H	2.141616	1.497141	−0.612456

TS5

C	1.377929	1.255019	0.339224
C	1.608009	−0.070507	−0.381071
C	0.746946	−1.216789	0.179778
C	−0.747347	−1.216657	−0.179719
C	−1.608185	−0.070131	0.380942
C	−1.377368	1.255402	−0.339082
H	0.000156	1.475577	0.000161
H	2.009590	2.052710	−0.087137
H	1.629284	1.158212	1.410464
H	1.342740	0.053174	−1.445309
H	2.657585	−0.419582	−0.377809
H	1.165766	−2.176251	−0.163052
H	0.845701	−1.216180	1.275998
H	−0.846087	−1.216203	−1.275944
H	−1.166385	−2.175973	0.163249

H	−2.657888	−0.418809	0.377225
H	−1.343267	0.053331	1.445292
H	−1.627984	1.158779	−1.410505
H	−2.009115	2.053196	0.086939

TS6

C	−1.435350	1.421251	−0.431866
C	−1.715091	0.324208	0.590477
C	−1.433890	−1.082911	0.041363
C	−0.050327	−1.262406	−0.594199
C	1.148215	−1.073956	0.360821
C	2.079888	0.078806	−0.052939
C	1.404416	1.446455	0.065407
H	0.012304	1.485832	−0.349392
H	−1.846629	2.386351	−0.092391
H	−1.898965	1.180422	−1.406135
H	−1.055349	0.490599	1.460460
H	−2.740513	0.309949	1.003223
H	−1.563552	−1.830191	0.840259
H	−2.193122	−1.309439	−0.722206
H	−0.005104	−2.261707	−1.048919
H	0.041013	−0.541061	−1.411523
H	0.783339	−0.871717	1.376628
H	1.722487	−2.010420	0.424701
H	3.015630	−0.021063	0.533186
H	2.376259	−0.096986	−1.099636
H	1.405943	1.770408	1.121807
H	1.959099	2.210344	−0.504434

TS7

C	1.447834	−0.000003	−0.000004
C	−1.447836	0.000004	0.000000
H	0.000042	0.000005	−0.000017
H	1.840722	0.495708	−0.905195
H	1.840657	−1.031800	0.023351
H	1.840591	0.536108	0.881921
H	−1.840686	−0.497039	0.904479
H	−1.840680	1.031829	−0.021823
H	−1.840630	−0.534818	−0.882693

TS8

N	2.728700	−1.901604	−1.025247
N	2.231062	2.392453	−0.184717
N	−2.230942	−2.392513	−0.184774
N	−2.728611	1.901659	−1.025312
C	2.116683	−1.045966	−0.544338
C	1.856605	1.301842	−0.095227
C	−1.856631	−1.301849	−0.095221
C	−2.116710	1.045973	−0.544325
C	1.316555	−0.017857	0.043334
C	0.707883	−0.312780	1.418798
C	−0.707926	0.312790	1.418808
C	−1.316709	0.017854	0.043420
H	0.000046	−0.000040	−0.483489
H	0.627288	−1.397871	1.527738
H	1.309469	0.066556	2.248403
H	−1.309452	−0.066521	2.248471
H	−0.627314	1.397881	1.527733

TS9

Cl	2.620738	−1.200194	−0.488105
Cl	1.975786	1.663091	−0.117776
Cl	−1.975719	−1.663097	−0.117748
Cl	−2.620794	1.200151	−0.488119
C	1.275098	−0.035980	−0.097771
C	0.709701	−0.311902	1.287239
C	−0.709714	0.311969	1.287222
C	−1.275112	0.036005	−0.097775
H	−0.000023	0.000055	−0.684017
H	0.621714	−1.397746	1.390950
H	1.322148	0.063858	2.114202
H	−1.322174	−0.063723	2.114206
H	−0.621698	1.397818	1.390871

TS10

F	−2.396491	0.878802	−0.521162
F	−1.873872	−1.263075	−0.256158
F	1.872914	1.263600	−0.254694
F	2.397339	−0.877589	−0.522012
C	−1.286935	0.030046	−0.317591
C	−0.705336	0.313604	1.057363
C	0.705466	−0.315502	1.056752
C	1.286927	−0.029964	−0.317873
H	−0.000217	0.000387	−0.940104
H	−0.617226	1.401290	1.151993
H	−1.336727	−0.055980	1.876398
H	1.337003	0.052891	1.876214
H	0.617430	−1.403338	1.149817

TS11

N	−2.912372	−0.303462	−0.312061
C	−1.835777	−0.125825	0.087644
C	−0.501319	0.030263	0.567580
C	0.414872	0.966345	−0.218314
C	1.869706	0.425999	−0.028611
C	1.860834	−1.090818	−0.114834
H	0.248132	−0.959178	0.396908
H	−0.507777	0.249029	1.640327
H	0.152510	0.900489	−1.281407
H	0.327424	2.019945	0.074830
H	2.517222	0.958543	−0.745931
H	2.208893	0.735702	0.972284
H	1.966650	−1.452160	−1.148187
H	2.623659	−1.563923	0.514816

TS12

Cl	1.806803	−0.321109	−0.214471
C	0.398521	0.313475	0.827462
C	−0.545416	1.135233	−0.015070
C	−1.570066	0.145782	−0.674876
C	−1.879726	−0.951039	0.337965
H	0.890246	0.873070	1.626116
H	−0.541979	−0.662887	0.978437
H	−1.100175	1.777806	0.686812
H	−0.070857	1.793035	−0.755022
H	−2.428050	0.726630	−1.048684
H	−1.085384	−0.293867	−1.557183
H	−2.730215	−0.688894	0.987603
H	−2.069121	−1.926740	−0.124958

TS13

F	1.778189	−0.509752	−0.492599
C	0.940874	−0.110141	0.633733
C	0.068312	1.031569	0.185492
C	−1.196864	0.421455	−0.519853
C	−1.578525	−0.851496	0.230104
H	1.651524	0.180280	1.420366
H	−0.198099	−0.953023	0.702615
H	−0.263265	1.556196	1.095507
H	0.571445	1.770931	−0.455922
H	−1.975378	1.196717	−0.596179
H	−0.911284	0.167814	−1.549840
H	−2.277100	−0.652751	1.059269
H	−2.004327	−1.626715	−0.419288

TS14

S	0.067957	1.421140	−0.591263
C	−0.203583	2.410125	0.843411
C	−1.429408	0.283495	−0.345738
C	−1.664467	−0.752026	−1.239164
C	−2.778934	−1.537167	−0.976521
C	−3.582214	−1.253975	0.133475
C	−3.280135	−0.192434	0.982082
C	−2.165139	0.623345	0.738895
C	1.409743	0.314507	−0.158937
C	2.581594	0.391883	−0.901958
C	3.645458	−0.443523	−0.580967
C	3.530996	−1.342331	0.472424
C	2.351316	−1.411659	1.207306
C	1.280698	−0.585952	0.893328
H	−1.333639	1.780463	1.176037
H	0.586869	2.248305	1.572954
H	−0.287460	3.453648	0.546589
H	−1.019439	−0.955499	−2.089239
H	−3.025376	−2.365948	−1.630970
H	−4.453404	−1.872684	0.327632
H	−3.927865	−0.004528	1.835178
H	2.662493	1.097078	−1.721343
H	4.562124	−0.390773	−1.156648
H	4.361360	−1.993449	0.720356
H	2.260383	−2.116510	2.025518
H	0.351084	−0.644071	1.448342

TS15

S	−0.000014	−1.459752	−0.008389
C	−0.000110	−1.827726	1.762406
C	1.430313	−0.338027	−0.109068
C	2.497112	−0.747945	−0.903550
C	3.597082	0.096499	−0.964807
C	3.581629	1.296064	−0.252563
C	2.476980	1.657128	0.514895
C	1.351357	0.831056	0.624691
C	−1.430260	−0.337927	−0.109166
C	−2.497220	−0.747980	−0.903362
C	−3.597194	0.096454	−0.964580
C	−3.581613	1.296136	−0.252560
C	−2.476807	1.657356	0.514605

C	−1.351161	0.831322	0.624333
H	−0.000602	−0.877259	2.294779
H	−0.898215	−2.403888	1.982753
H	0.898468	−2.403059	1.982988
H	2.475218	−1.681949	−1.456441
H	4.456196	−0.174232	−1.567735
H	4.443740	1.954314	−0.304384
H	2.498778	2.607237	1.043184
H	−2.475437	−1.682089	−1.456078
H	−4.456417	−0.174385	−1.567304
H	−4.443738	1.954371	−0.304330
H	−2.498504	2.607560	1.042725
H	0.000080	1.054943	0.956410

TS16

N	−2.891636	0.878354	−0.294939
N	−0.631769	−2.834892	0.622789
N	0.631877	2.834859	0.622827
N	2.891595	−0.878318	−0.294933
C	−0.675748	−0.422294	−0.260449
C	0.675690	0.422312	−0.260574
C	−1.891232	0.295799	−0.263373
C	−0.659575	−1.739709	0.248249
C	0.659601	1.739703	0.248207
C	1.891181	−0.295778	−0.263403
H	0.000029	−0.000229	−1.282148

TS17

F	−1.585092	−0.834693	0.407844
F	−1.204574	1.009801	−0.731880
F	1.204605	−1.009813	−0.731864
F	1.585060	0.834714	0.407849
C	−0.684353	0.233789	0.359372
C	0.684355	−0.233803	0.359392
H	−0.000002	0.000004	1.519862

TS18

N	2.514789	−2.207540	−0.211125
N	2.514831	2.207517	−0.211109
N	−2.514819	−2.207524	−0.211101
N	−2.514814	2.207535	−0.211122
C	1.947334	−1.205026	−0.104761
C	1.947357	1.205012	−0.104754
C	−1.947344	−1.205022	−0.104752
C	−1.947342	1.205032	−0.104763
C	1.188504	0.000000	−0.001909
C	0.000021	0.000008	0.997547
C	−1.188508	0.000005	−0.001899
H	−0.000072	0.000000	−0.802610
H	0.000012	−0.886405	1.632783
H	0.000018	0.886431	1.632769

TS19

F	2.206988	−0.968950	−0.110289
F	1.732849	1.186303	0.004070
F	−2.206988	−0.968949	−0.110289
F	−1.732849	1.186303	0.004070
C	1.141972	−0.057833	−0.297626
C	0.000000	−0.337662	0.688464
C	−1.141972	−0.057833	−0.297626
H	0.000000	−0.057586	−1.186755
H	0.000000	−1.402159	0.940073
H	0.000000	0.267351	1.599351