Electronic Supplementary Material for PCCP

Electronic supplementary information for:

Energetic and electron density analysis of hydrogen dissociation of protonated benzene

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1 Nuclear Coordinates, molecular energies and summary of imaginary vibrational frequencies

Nuclear coordinates of the benzenium cation, transition state of 1-2 proton migration, two-fold saddle point, and dissociation products constrained to C_s symmetry: $[C_6H_6]^+$+ H and $[C_6H_5]^+$+ H_2. Geometry optimizations performed at the MCSCF(6,6)/6-311++G(d,p) level with the GAMESS quantum chemistry program. The geometry optimization criterion was OPTTOL=1.0D-6 except for the partial optimizations during the dissociations which were carried out with OPTTOL=1.0D-5.

In the case of $[C_6H_6]^+$+ H as dissociation products, one significant and one small imaginary frequencies was obtained for a C1-Ha distance of ca. 10 Å. From this geometry, the system

was further optimized without any symmetry constraint and with explicit Hessian calculation (option HESS=CALC) to yield a true minimum. In the case of $[C_6H_5]^+ + H_2$ at the same C1-Ha separation, unconstrained geometry optimization plus Hessian calculation does not change the molecular geometry.

Table 1: Benzenium cation

atom	x	y	z
C	-1.2389977479	2.1229687044	-0.0000689141
C	1.2390093242	2.1229508467	-0.0000652984
C	-1.2500708245	0.7570756452	0.0000418852
C	1.2500630450	0.7570575339	0.0000459073
C	-0.0000096722	-0.0217378769	0.0001060692
C	0.0000106932	2.7942725928	-0.0001215181
H	-2.1508552001	2.6893243222	-0.0001156048
H	2.1508743772	2.6892943899	-0.0001091593
H	-0.0000124408	-0.7068271379	-0.8551297819
H	-2.1803778243	0.2174444422	0.0000846788
H	2.1803632687	0.2174147462	0.0000914883
H	-0.0000148689	-0.7066933412	0.8554484680
H	0.0000178714	3.8711751325	-0.0002082200

Table 2: Transition state of 1-2 proton migration

atom	x	y	z
C	-0.7142053861	0.0522454765	0.0060582971
C	0.7142060824	0.0522454641	0.0060576687
C	-1.4203392479	1.2917835318	0.0031250984
C	1.4203396651	1.2917831874	0.0031255695
C	-0.7117080536	2.4665207328	-0.0025378041
C	0.7117083844	2.4665205047	-0.0025372610
H	-0.0000025435	-0.0124757368	1.0920708089
H	-1.2340685472	-0.8881089796	-0.0384772122
H	1.2340687018	-0.8881094543	-0.0384768275
H	-2.4932226625	1.2793569655	-0.0068154219
H	2.4932230818	1.2793568421	-0.0068135034
H	-1.2351616072	3.4044408875	-0.0073903098
H	1.2351621325	3.4044405783	-0.0073891026

Table 3: Two-fold saddle point

atom	x	y	z
C	-1.4012471289	0.0000006104	-0.0960944193
C	1.4012471296	0.0000006119	-0.0960944251
C	-0.7006361957	-1.2135503875	-0.0958910763
C	0.7006362031	-1.2135503725	-0.0958910781
C	-0.7006361435	1.2135515195	-0.0958903315
C	0.7006361697	1.2135515139	-0.0958903420
H	-2.4675362071	0.0000000855	-0.2235092789
H	2.4675362126	0.0000000823	-0.2235092509
H	-0.0000000783	-0.0000048125	-1.1012755562
H	-1.2338126905	-2.1370258220	-0.2228705398
H	1.2338127070	-2.1370257988	-0.2228705323
H	-1.2338129227	2.1370263830	-0.2228698898
H	1.2338129447	2.1370263870	-0.2228698788

Table 4: $[C_6H_6]^+$+ H (dissociation constrained to C_s symmetry)

atom	x	y	z
C	-1.2416840142	1.6896263357	-1.0621324073
C	1.2416840142	1.6896263357	-1.0621324073
C	-1.2427831136	0.5269009151	-0.3422838702
C	1.2427831136	0.5269009151	-0.3422838702
C	0.0000000000	-0.0606761497	0.0214727805
C	0.0000000000	2.2846923910	-1.4304707809
H	-2.1619288916	2.1597254346	-1.3531921172
H	2.1619288916	2.1597254346	-1.3531921172
H	0.0000000000	-7.7541567843	-7.8269720491
H	-2.1567200793	0.0477954876	-0.0457375813
H	2.1567200793	0.0477954876	-0.0457375813
H	0.0000000000	-0.9760643215	0.5880671347
H	0.0000000000	3.1982269410	-1.9959660781

Table 5: $[C_6H_6]^+$+ H (unconstrained optimization using coordinates of Table 4 as initial geometry)

atom	x	y	z
C	-1.2407619955	1.6889026901	-1.0873135371
C	1.2378659093	1.6637550904	-1.0653269266
C	-1.2271566172	0.5140447015	-0.3624959315
C	1.2510122625	0.5022284272	-0.3487342456
C	0.0113355665	-0.0822730718	0.0086124160
C	-0.0228974066	2.2712544412	-1.4433935321
H	-2.1688381217	2.1463904993	-1.3719662320
H	2.1528696067	2.1432823938	-1.3587637695
H	-0.0049140492	-7.5574223599	-7.6644977055
H	-2.1425940187	0.0335672253	-0.0684753982
H	2.1676880838	0.0287803279	-0.0542656528
H	-0.0045418615	-0.9980513928	0.5735221277
H	-0.0090673584	3.1856594500	-2.0074625577

Table 6: $[C_6H_5]^+ + H_2$

atom	x	y	z
C	-1.2219189945	1.7342175324	0.0428557658
C	1.2219189945	1.7342175324	0.0428557658
C	-1.2783445363	0.3095345544	0.0258818358
C	1.2783445363	0.3095345544	0.0258818358
C	0.0000000000	-0.0606761497	0.0214727805
C	0.0000000000	2.4139420237	0.0509542076
H	-2.1592317915	2.2592773863	0.0491109889
H	2.1592317915	2.2592773863	0.0491109889
H	0.0000000000	-10.6841567843	-0.2754062473
H	-2.1661953586	-0.2901638524	0.0187359356
H	2.1661953586	-0.2901638524	0.0187359356
H	0.0000000000	-10.6671702003	0.4598359972
H	0.0000000000	3.4868410319	0.0637369721

Table 7: MCSCF and MRMP2 molecular energies (in a.u.) and imaginary vibrational frequency magnitudes (in cm^{-1}).

Molecule	MCSCF energy	MCSCF Imaginary frequency	MRMP2 energy
$[C_6H_7]^+$	-231.1200862920	—	-231.8689858764
TS 1-2 mig	-231.1013074788	568.54	-231.8538407563
two-fold saddle	-231.0125220925	2082.72, 2081.53	-231.7891051390
C_s constrained $[C_6H_6]^+$+ H	-231.0053514045	378.03 , 13.10	-231.7409779789
unconstrained $[C_6H_6]^+$+ H	-231.0054146686	—	-231.7406383582
$[C_6H_5]^+$+ H_2	-231.0133268418	—	-231.7536547583

2 Topological properties of the electron density

This section contains:

1. Atomic charge, energy and localization index defined as λ(A)= δ(A,A). For pairs of atoms: delocalization index δ(A,B)

2. Electron density and its Laplacian at bond critical points of $\rho(r)$.

Values for non equivalent atoms or pairs of atoms are reported. The atomic labels are the same as in Scheme 1 of the paper.

In addition:

3. Electron density profiles along the C_6 axis of the molecular graphs of Figure 2(b) of the paper.

Table 8: Atomic properties for benzenium

Atom	Charge	Energy	Localization index
C1	0.056	-37.816	3.903
C2	0.003	-37.878	4.106
C3	0.123	-37.802	3.974
C4	-0.025	-37.897	4.127
Ha	0.113	-0.562	0.364
H2	0.099	-0.584	0.373
H3	0.089	-0.587	0. 379
H4	0.113	-0.580	0.365

Table 9: Delocalization index and properties at bcp for benzenium

A-B	ρ_b	δ(A,B)	$\nabla^2\rho_b$
C1-C2	0.282	1.052	-0.836
C2-C3	0.337	1.395	-1.103
C3-C4	0.315	1.242	-1.007
C1-Ha	0.273	0.891	-0.962
C2-H2	0.300	0.954	-1.155
C3-H3	0.298	0.952	-1.133
C4-H4	0.303	0.949	-1.185

Table 10: Atomic properties for 1-2 proton migration TS

Atom	Charge	Energy	Localization index
C1	-0.049	-37.905	4.094
C3	0.087	-37.814	4.027
C4	0.062	-37.834	4.041
H2	0.133	-0.568	0.347
H3	0.093	-0.585	0.375
H4	0.086	-0.589	0.382
Ha	0.174	-0.508	0.290

Table 11: Delocalization index and properties at bcp for 1-2 proton migration TS

A-B	ρ_b	δ(A,B)	$\nabla^2\rho_b$
C1-C2	0.292	1.066	-0.824 7
C2-C3	0.302	1.167	-0.942
C3-C4	0.332	1.370	-1.069
C4-C5	0.306	1.197	-0.946
C1-Hb	0.300	0.934	-1.160
C3-H3	0.298	0.955	-1.134
C4-H4	0.299	0.957	-1.143
C1-Ha	—	0.478	—
(C1-C2)-Ha	0.189	—	-0.257

Table 12: Atomic properties for $[C_6H_6]^+$+ H (dissociation constrained to C_s symmetry)

Atom	Charge	Energy	Localization index
C1	-0.015	-37.888	4.136
C2	0.082	-37.821	3.992
C3	0.090	-37.821	4.020
C4	0.018	-37.855	4.175
Hb	0.134	-0.570	0.349
H2	0.106	-0.580	0.367
H3	0.099	-0.583	3.725
H4	0.110	-0.580	0.364
Ha	0.000	-0.500	1.000

Table 13: Delocalization index and properties at bcp for $[C_6H_6]^+$+ H (dissociation constrained to C_s symmetry)

A-B	ρ_b	δ(A,B)	$\nabla^2\rho_b$
C1-C2	0.309	1.270	-0.985
C2-C3	0.337	1.386	-1.098
C3-C4	0.306	1.202	-0.953
C1-Ha	0.304	0.943	-1.195
C2-H2	0.299	0.949	-1.149
C3-H3	0.299	0.953	-1.145
C4-H4	0.301	0.958	-1.164
C1-Hb	0.000	0.000	0.000

Table 14: Atomic properties for the asymmetric $[C_6H_6]^+$+ H (unconstrained optimization using coordinates of Table 4 as initial geometry)

Atom	Charge	Energy	Localization index
C1	-0.005	-37.879	4.125
C2	0.118	-37.801	3.976
C3	0.056	-37.841	4.073
C4	0.020	-37.857	4.159
C5	0.122	-37.800	3.974
C6	0.037	-37.851	4.034
Hb	0.130	-0.572	0.351
H2	0.097	-0.583	0.373
H3	0.101	-0.583	0.371
H4	0.109	-0.580	0.365
H5	0.097	-0.583	0.373
H6	0.117	-0.576	0.359
Ha	0.000	-0.500	1.000

Table 15: Delocalization index and properties at bcp for the asymmetric $[C_6H_6]^+$ H (unconstrained optimization using coordinates of Table 4 as initial geometry)

A-B	ρ_b	δ(A,B)	$\nabla^2\rho_b$
C1-C2	0.310	1.243	-0.990
C2-C3	0.337	1.390	-1.100
C3-C4	0.294	1.145	-0.897
C4-C5	0.321	1.284	-1.024
C5-C6	0.330	1.350	-1.075
C6-C1	0.311	1.301	-0.984
C1-Hb	0.303	0.945	-1.189
C2-H2	0.298	0.952	-1.136
C3-H3	0.300	0.955	-1.151
C4-H4	0.301	0.957	-1.164
C5-H5	0.298	0.951	-1.139
C6-H6	0.301	0.946	-1.169
C1-Ha	0.000	0.000	0.000

Table 16: Atomic properties for $[C_6H_5]^+ + H_2$

Atom	Charge	Energy	Localization index
C1	-0.563	-38.396	4.979
C2	0.282	-37.674	3.933
C3	0.081	-37.780	4.050
C4	0.112	-37.789	4.001
Ha	0.000	-0.564	0.500
H2	0.198	-0.529	0.298
H3	0.117	-0.574	0.357
H4	0.094	-0.585	0.375

Table 17: Delocalization index and properties at bcp for $[C_6H_5]^+ + H_2$

A-B	ρ_b	δ(A,B)	$\nabla^2\rho_b$
C1-C2	0.333	1.306	-0.807
C2-C3	0.287	1.160	-0.821
C3-C4	0.317	1.285	-0.984
C1-Ha	—	0.000	—
C2-H2	0.293	0.902	-1.125
C3-H3	0.297	0.941	-1.127
C4-H4	0.298	0.953	-1.134
Ha-Hb	0.266	1.000	-1.120
(Ha-Hb)-C1	0.000	—	0.000

Table 18: Atomic properties for the two-fold saddle point

Atom	Charge	Energy	Localization index
C	-0.020	-37.870	4.055
H	0.109	-0.578	0.364
Ha	0.463	-0.321	0.169

Table 19: Delocalization index and properties at bcp for the two-fold saddle point

A-B	ρ_b	δ(A,B)	$\nabla^2\rho_b$
C–C	0.316	1.277	-0.9813
C–H	0.299	0.947	-1.149
C–Ha	0.066	0.121	0.064

Table 20: Atomic properties for benzene

Atom	Charge	Energy	Localization index
C	0.016	-37.840	4.068
H	-0.016	-0.631	0.462

Table 21: Delocalization index and properties at bcp for benzene

A-B	ρ_b	δ(A,B)	$\nabla^2\rho_b$
C-C	0.318	1.287	-0.991
C-H	0.292	0.987	-1.085

The electron density profiles along the C_6 axis of each of the molecular graphs of Figure 2(b) of the manuscript are shown below. It can be seen that for the structurally stable molecule **1-2S** the electron density decreases monotonically from the H atom towards the aromatic ring and to infinity. It also shows how the bifuraction mechanism operates as the H atom is removed along the C_6 axis: in (b) a degenerate critical point appears to suddenly bifurcate into a ring and a cage critical points in (c).

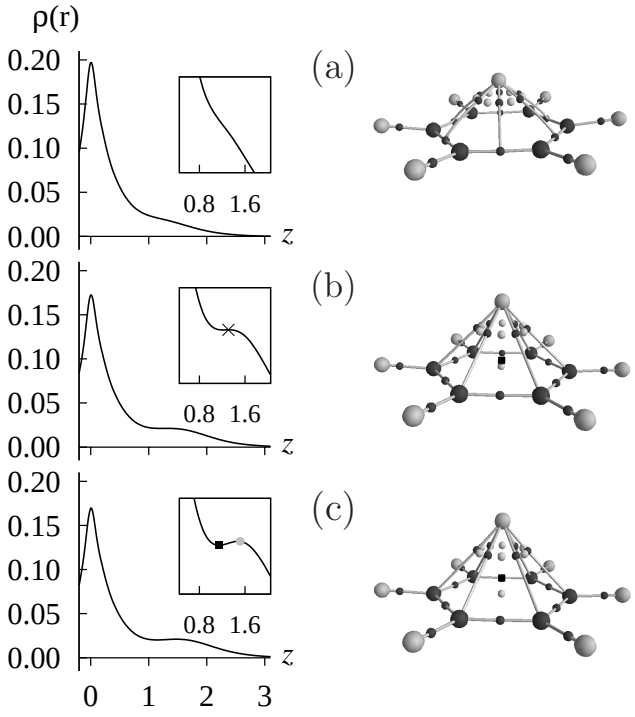

Figure 1: Electron density profiles along the C_6 axis of selected molecular graphs showing the bifurcation mechanism of **1-2S**. In each case the origin is located at the position of the migrating H atom and the z axis is oriented towards the ring of C atoms. The stable critical points are denoted as in Figure 2 and $\times$ refers to the approximate position of the unstable critical point in the inset of (b). Distances are in Å