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Theoretical study of ethylbenzenium ions:

The mechanism for splitting off ethene, and the formation of a pi complex of ethene and the benzenium ion.

A short discussion of the failure of MP2 to find a stable benzenium ion/ethene complex is given at the end of this Supporting Information.

Computational Results

e4hb =ethyl-4H-benzene

Calculation Method = RB3LYP Basis Set = CC-pVTZ
E(RB+HF-LYP) = -311.30867636 a.u.

C	-0.23167000	-1.52403200	1.24541200
C	-0.23167000	-0.16665200	1.23053000
C	-0.23687500	0.54242600	0.00000000
C	-0.23167000	-0.16665200	-1.23053000
C	-0.23167000	-1.52403200	-1.24541200
C	-0.23174600	-2.30097900	0.00000000
H	-0.23567900	-2.06555800	2.18269000
H	-0.23855800	0.39308700	2.15576000
H	-0.23855800	0.39308700	-2.15576000
H	-0.23567900	-2.06555800	-2.18269000
C	-0.20500200	2.02566400	0.00000000
C	1.26356700	2.53426800	0.00000000
H	-0.71210700	2.40996900	0.88500500
H	-0.71210700	2.40996900	-0.88500500
H	1.25146800	3.62229500	0.00000000
H	1.80002700	2.19563300	0.88488900
H	1.80002700	2.19563300	-0.88488900
H	-1.07972600	-3.00707400	0.00000000
H	0.62130300	-3.00153700	0.00000000

elhb = ethyl-1H-benzene

Calculation Method = RB3LYP Basis Set = CC-pVTZ
E(RB+HF-LYP) = -311.29381965 a.u.

C	0.49920200	1.41839800	1.23177700
C	0.49920200	0.05244700	1.24014100
C	0.49920200	0.05244700	-1.24014100
C	0.49920200	1.41839800	-1.23177700
C	0.49203800	2.09365200	0.00000000
H	0.50162700	1.98175800	2.15383800
H	0.50802200	-0.49155900	2.17671600
H	0.50802200	-0.49155900	-2.17671600
H	0.50162700	1.98175800	-2.15383800
H	0.48660300	3.17700100	0.00000000

C	0.50884200	-0.72868900	0.00000000
H	1.50550700	-1.22540600	0.00000000
C	-0.47465300	-1.96274200	0.00000000
C	-1.94816800	-1.56951500	0.00000000
H	-0.23339700	-2.56489300	0.87553200
H	-0.23339700	-2.56489300	-0.87553200
H	-2.56239200	-2.46911400	0.00000000
H	-2.21571300	-0.98973100	0.88369800
H	-2.21571300	-0.98973100	-0.88369800

elhb-endo =ethyl-1H-benzene-endo

Calculation Method = RB3LYP Basis Set = CC-pVTZ

E(RB+HF-LYP) = -311.28937220 a.u.

C	0.52286000	1.39302100	1.23232300
C	0.52286000	0.02723400	1.24054300
C	0.52286000	0.02723400	-1.24054300
C	0.52286000	1.39302100	-1.23232300
C	0.51465000	2.06794800	0.00000000
H	0.52724600	1.95693700	2.15404400
H	0.53222900	-0.51715600	2.17678100
H	0.53222900	-0.51715600	-2.17678100
H	0.52724600	1.95693700	-2.15404400
H	0.50820000	3.15133700	0.00000000
C	0.51995900	-0.75341900	0.00000000
H	1.48953700	-1.29667600	0.00000000
C	-0.52640500	-1.93887700	0.00000000
C	-1.99529400	-1.47486700	0.00000000
H	-0.30350700	-2.55050800	0.87232900
H	-0.30350700	-2.55050800	-0.87232900
H	-2.09350500	-0.38935400	0.00000000
H	-2.52113200	-1.84581400	-0.87746800
H	-2.52113200	-1.84581400	0.87746800

TS-proton transfer

Calculation Method = RB3LYP Basis Set = CC-pVTZ

E(RB+HF-LYP) = -311.25255566 a.u.

C	-0.89612700	0.91002500	1.22051100
C	-0.86521200	1.59407300	0.00000000
C	-0.89612700	0.91002500	-1.22051100
C	-0.89612700	-0.46896100	-1.22684800
C	-0.78690800	-1.17529100	0.00000000
C	-0.89612700	-0.46896100	1.22684800
H	-0.93460300	1.46302000	2.14825500
H	-0.85461200	2.67614800	0.00000000
H	-0.93460300	1.46302000	-2.14825500
H	-0.91213900	-1.01964900	-2.15744800
H	-0.88949200	-2.25340800	0.00000000

H	-0.91213900	-1.01964900	2.15744800
H	2.17461500	-1.73687600	-0.92199600
C	2.10207900	-1.17023600	0.00000000
C	2.37790300	0.16010500	0.00000000
H	2.17461500	-1.73687600	0.92199600
H	0.67189000	-1.01577500	0.00000000
H	2.47817600	0.71769100	0.92219000
H	2.47817600	0.71769100	-0.92219000

E-B complex = Ethene/benzenium ion complex

Calculation Method = RB3LYP Basis Set = CC-pVTZ

E(RB+HF-LYP) = -311.26475186 a.u.

C	-0.80537700	-0.30384900	1.24433300
C	-0.80537700	-1.67076300	1.23273800
C	-0.80317500	-2.34438800	0.00000000
C	-0.80537700	-1.67076300	-1.23273800
C	-0.80537700	-0.30384900	-1.24433300
C	-0.76321700	0.45406500	0.00000000
H	-0.81082200	0.24287300	2.17830300
H	-0.81563000	-2.23565200	2.15366300
H	-0.80455700	-3.42763400	0.00000000
H	-0.81563000	-2.23565200	-2.15366300
H	-0.81082200	0.24287300	-2.17830300
H	-1.46675200	1.29887800	0.00000000
H	0.20209200	1.04435400	0.00000000
H	2.88904100	1.53522500	-0.92116600
C	2.52499700	1.97289600	0.00000000
C	1.72123900	3.03286800	0.00000000
H	2.88904100	1.53522500	0.92116600
H	1.39701300	3.50111000	-0.92100900
H	1.39701300	3.50111000	0.92100900

e2hb = ethyl-2H-benzene (orthoprotonated)

Calculation Method = RB3LYP Basis Set = CC-pVTZ

E(RB+HF-LYP) = -311.30621059 a.u.

C	-2.33403000	0.06193900	0.26052500
C	-1.71643600	-1.13967400	0.13011100
C	0.46923800	0.04016000	-0.34249600
C	-0.21197200	1.23374500	-0.21014500
C	-1.57443400	1.24065500	0.08331000
H	-3.38732400	0.13140700	0.48974700
H	-2.26297600	-2.06647000	0.24667300
H	0.30997500	2.17287700	-0.33306900
H	-2.07645600	2.19603000	0.17932100
C	-0.28412800	-1.22141600	-0.19276600
H	0.22815700	-1.87861300	0.52820200

H	-0.16857100	-1.80572900	-1.12297200
C	1.93465200	-0.01125800	-0.59443700
C	2.73506300	0.00880200	0.73245500
H	2.22877900	0.84855900	-1.19715500
H	2.18997100	-0.91432500	-1.15004700
H	3.79799300	-0.02620200	0.50195800
H	2.53756600	0.91605800	1.30105100
H	2.49517000	-0.85131800	1.35695500

e3hb = ethyl-3H-benzene

Calculation Method = RB3LYP Basis Set = CC-pVTZ

E(RB+HF-LYP) = -311.29998219 a.u.

C	-1.52570900	1.31655000	0.02045700
C	-0.15447700	1.14250400	-0.23497800
C	0.48952700	-0.11371700	-0.31084100
C	-0.29685300	-1.22093900	-0.12014400
C	-1.73244900	-1.12188400	0.15250600
C	-2.31238800	0.21916200	0.21300300
H	-1.93974200	2.31397500	0.05769200
H	0.44811800	2.03066400	-0.39111400
H	0.13475500	-2.21311300	-0.17225600
H	-2.29366400	-1.73513500	-0.57596700
C	1.97117600	-0.19636200	-0.57081000
C	2.80704600	0.13985400	0.67321000
H	2.22598600	0.49000600	-1.38087100
H	2.21636600	-1.19856500	-0.92256200
H	3.86754600	0.08703900	0.43385200
H	2.59895000	1.14702000	1.03769100
H	2.60809000	-0.56013600	1.48487500
H	-3.37205900	0.31527300	0.41001700
H	-1.96958600	-1.66804000	1.08422000

dm-e4hb = 2,6-dimethylethyl-4H-benzene

Calculation Method = RB3LYP Basis set 6-311++g(d,p)

E(RB+HF-LYP) = -389.93705195 Hartree

C	1.67538500	-1.24363800	0.14342500
C	0.33536000	-1.25793300	-0.12878600
C	-0.35171100	0.00007200	-0.25333100
C	0.33572700	1.25787400	-0.12874600
C	1.67574200	1.24319200	0.14348000
C	2.43353400	-0.00033600	0.30426400
H	2.21686600	-2.17841300	0.24682200

H	2.21748900	2.17780800	0.24692200
C	-1.82814200	0.00031000	-0.47697900
C	-2.59625400	0.00023200	0.87804500
H	-2.12555400	-0.87986500	-1.04706900
H	-2.12530800	0.88072400	-1.04682300
H	-3.66728500	0.00044300	0.67141000
H	-2.36272200	-0.88373900	1.47300400
H	-2.36242400	0.88395200	1.47326400
H	3.29620200	-0.00044400	-0.38787400
H	2.94730400	-0.00043400	1.28371200
C	-0.38854900	2.57048400	-0.30582800
H	-0.76694100	2.67921700	-1.32600700
H	-1.23891200	2.66301800	0.37239800
H	0.28433000	3.40561000	-0.11211800
C	-0.38927100	-2.57035200	-0.30585600
H	-1.23938900	-2.66282400	0.37268600
H	-0.76808700	-2.67882900	-1.32590000
H	0.28350000	-3.40566000	-0.11255100

dm-elhb = 2,6-dimethylethyl-1H-benzene

Calculation method = RB3LYP Basis set = 6-311++g(d,p)

E(RB+HF-LYP) = -389.93748741 Hartree

1 1

C	1.23326800	1.55166400	0.30199100
C	1.27322100	0.33100200	-0.33024800
C	-1.27322100	0.33100200	-0.33024800
C	-1.23326800	1.55166400	0.30199100
C	0.00000000	2.13845300	0.62282500
H	2.15063600	2.07665600	0.54037000
H	-2.15063600	2.07665600	0.54037000
H	0.00000000	3.10366500	1.12051200
C	0.00000000	-0.38133500	-0.64414900
H	0.00000000	-0.53831000	-1.73680400
C	0.00000000	-1.85907900	-0.05709900
C	0.00000000	-1.92614700	1.46966200
H	0.87319200	-2.36873500	-0.46619500
H	-0.87319200	-2.36873500	-0.46619500
H	0.00000000	-2.97104400	1.78687800
H	0.88359200	-1.45246700	1.90454600
H	-0.88359200	-1.45246800	1.90454600
C	-2.57214400	-0.30331600	-0.70210700
H	-2.84436900	-1.06529200	0.03963600
H	-3.37826500	0.42999700	-0.72617700
H	-2.51822100	-0.80908600	-1.66900600
C	2.57214400	-0.30331600	-0.70210700
H	3.37826500	0.42999600	-0.72617600
H	2.84436900	-1.06529200	0.03963600
H	2.51822100	-0.80908600	-1.66900600

dm-elhb-endo = 2,6-dimethylethyl-1H-benzene-endo

Calculation Method = RB3LYP Basis Set = 6-311++g(d,p)

E(RB+HF-LYP) = -389.93311740 Hartree

C	1.23368900	1.53736900	0.30603300
C	1.27339600	0.32554100	-0.34316600
C	-1.27339600	0.32554100	-0.34316600
C	-1.23368900	1.53736900	0.30603300
C	0.00000000	2.11930300	0.63486100
H	2.15079400	2.06007500	0.55045900
H	-2.15079300	2.06007500	0.55045900
H	0.00000000	3.07768400	1.14563900
C	0.00000000	-0.38539800	-0.65774600
H	0.00000000	-0.56261600	-1.74628200
C	0.00000000	-1.85038000	-0.03716100
C	0.00000000	-1.88713800	1.50573400
H	0.87032500	-2.36384400	-0.44485500
H	-0.87032500	-2.36384400	-0.44485500
H	-0.87759300	-2.41128600	1.88683400
H	0.87759200	-2.41128600	1.88683400
H	0.00000000	-0.89100900	1.95424200
C	-2.57163700	-0.30402400	-0.72556800
H	-2.86010500	-1.05208100	0.02409000
H	-3.37158100	0.43535900	-0.76939400
H	-2.50914300	-0.82273100	-1.68479700
C	2.57163700	-0.30402400	-0.72556800
H	3.37158100	0.43535900	-0.76939300
H	2.86010400	-1.05208200	0.02409000
H	2.50914300	-0.82273100	-1.68479800

dm-TS = dm-TS proton transfer

Calculation Method = RB3LYP Basis Set = 6-311++g(d,p)

E(RB+HF-LYP) = -389.88435775 Hartree

1 1			
C	-1.23177400	0.04480300	1.12808200
C	-1.24478100	-0.82870500	0.05068600
C	1.24479600	-0.82868400	0.05068200
C	1.23177700	0.04482400	1.12807900
C	-0.00000300	0.58248000	1.59343900
H	-2.15983700	0.39033200	1.56990500
H	2.15983400	0.39037000	1.56990000
H	-0.00000700	1.19804400	2.48767700
C	0.00001000	-1.20276400	-0.49657400
H	0.00001500	-1.86192900	-1.36107100
C	-0.00002000	1.96271100	-1.53372400
C	-0.00002600	2.68327400	-0.37557800
H	-0.92380200	1.65752300	-2.01274300

H	0.92376700	1.65754100	-2.01274500
H	0.92353000	3.13669100	-0.02454100
H	-0.92358900	3.13667200	-0.02453800
H	-0.00001300	1.56957400	0.52720500
C	2.52599400	-1.39308600	-0.50687000
H	2.54477900	-1.33911500	-1.59806100
H	3.39863900	-0.86546700	-0.12081700
H	2.62689500	-2.44793000	-0.23471600
C	-2.52597000	-1.39312700	-0.50686700
H	-2.62681600	-2.44799500	-0.23478400
H	-3.39862600	-0.86557200	-0.12075400
H	-2.54478900	-1.33908200	-1.59805400

dm-E-B complex = Ethene/1,3-dimethyl-5H-benzene complex

Calculation Method = RB3LYP Basis set = 6-311++g(d,p)

E(RB+HF-LYP) = -389.89886211 Hartree

C	0.10836500	-1.24865400	-0.65497300
C	1.31745400	-1.25770900	0.00105400
C	1.88665800	0.00000100	0.31199500
C	1.31745100	1.25771300	0.00106700
C	0.10836100	1.24866100	-0.65496000
C	-0.57285700	0.00000400	-0.98557600
H	-0.37879600	-2.18043400	-0.92342000
H	2.84337300	0.00000000	0.83054300
H	-0.37880200	2.18044200	-0.92339800
H	-0.93682400	0.00000900	-2.02679000
H	-1.56455800	0.00000000	-0.45236600
H	-3.43755000	0.92299700	1.64757700
C	-3.63373600	-0.00007600	1.11139200
C	-4.14647900	0.00005900	-0.11929500
H	-3.43761200	-0.92326200	1.64740400
H	-4.38801400	0.92302800	-0.63678300
H	-4.38807500	-0.92279700	-0.63695500
C	2.03402400	2.52786500	0.37806600
H	2.16063500	2.59486000	1.46195100
H	3.02977900	2.56048300	-0.07159400
H	1.48318700	3.40794700	0.04634900
C	2.03403200	-2.52786300	0.37804000
H	3.02978500	-2.56047400	-0.07162300
H	2.16064600	-2.59486700	1.46192400
H	1.48319600	-3.40794300	0.04631600

Discussion of MP2 failure on next page.

Why does MP2 fail to find a stable benzenium ion/ethene complex?

Whereas B3LYP finds that there is a (quantum mechanically) stable benzenium ion/ethene complex and a transition state for its formation from an ethylbenzenium ion, MP2 finds no such complex, and consequently no transition state. This issue was treated in our previous paper (ref. 23) where it was concluded on basis of geometry optimization runs at the CCSD and QCISD levels that there is a minimum on the PES with a structure that is virtually identical to the one found by B3LYP. We have been somewhat intrigued by this discrepancy and the possible reasons for it.

To this end we have performed single point CCSD(T) energy computations with the basis sets 6-311++G(d,p) and cc-pVTZ on the B3LYP structures of the transition state “TS proton transfer” and “E-B complex”. The advantage about these computations is that they give energies for a wide range of approximations, from HF via MP2, MP3, all the way to CCSD(T).

Energies of TS and E-B complex at various levels of theory with the basis sets 6-311++G(d,p) and cc-pVTZ.			
Basis set 6-311++G(d,p)			
	TS (E_h)	E-B complex (E_h)	E(TS)- E(comp)(kJ/mol)
HF	-309.0897604	-309.1207789	81.4
MP2	-310.2292651	-310.2280072	-3.3
MP3	-310.2771386	-310.2884500	29.7
MP4D	-310.3069434	-310.3166138	25.4
MP4DQ	-310.2728876	-310.2862198	35.0
MP4DSQ	-310.2832963	-310.2979707	38.5
CCSD	-310.2842401	-310.2988370	38.3
CCSD(T)	-310.3422764	-310.3527306	27.4
Basis set cc-pVTZ			
H	-309.1234999	-309.1550870	82.9
MP2	-310.4270780	-310.4239985	-8.1
MP3	-310.4704826	-310.4808565	27.2
MP4D	-310.5016087	-310.5099023	21.8
MP4DQ	-310.4583798	-310.4710394	33.2
MP4SDQ	-310.4689651	-310.4829744	36.8
CCSD	-310.4691203	-310.4825915	35.4
CCSD(T)	-310.5399863	-310.5485618	22.5
Gaussian-3, after calculating non-ZPE corrected energies,			20.9

It is seen from the Table that all approximations except MP2 give a higher energy for TS than for the E-B complex. So MP2 is the only computational methodology that does not give a stable complex relative to the TS. It is furthermore observed that the energy difference found by HF computations are far higher than found by the higher level methods, and evidently far too high. When a MP2 computation is carried out this overshoot is corrected, but as is well known MP2

has a tendency for over-correcting. Such an over-correction has evidently taken place here. At the highest levels of theory the computed results are in good agreement. In particular the two computations at the highest level of theory CCSD(T)/cc-pVTZ and Gaussian-3 give almost identical results.

It is worth noting that in this case the MP2 difference in energy between TS and E-B complex does not get better with a larger basis set. This result is in accordance with the result reported earlier (ref. 23) where MP2 gave a stable complex when the basis set 6-31+G(d,p) or smaller basis sets were used.

The failure of the MP2 methodology therefore appears to be because MP2 computed the transition state energy too low, and the energy of a structure corresponding to E-B complex too high.

We have also carried out MP2 calculations (basis set 6-311++G(d,p)) in a situation where we started with the ethene being far away from the benzenium ion. The H⁹-C⁸ distance was made to be 9 Å in the H⁹-C⁸ direction and an optimization run was started. No geometrical constraints were imposed (C₁ symmetry). During the optimization where the H⁹-C⁸ slowly decreased (very small forces), a superficial similarity to the B3LYP complex structure developed, but at the same time C¹-C⁷ decreased even more, so that the ethene moiety came relatively closer to C¹. At a certain stage the C⁴-H⁹ bond was broken and a C⁸-H⁹ bond was formed, giving a formal ethyl cation. The structure of the atomic assembly when this hydrogen transfer took place was visually similar to the TS proton transfer. In a few more optimization steps formation of the C¹-C⁷ bond took place. This again shows that MP2 fails because the TS energy is calculated too low relative to the complex energy.