

Electronic Supporting Information (ESI)

A Molecular Electron Density Theory Study of the Bimolecular Nucleophilic Substitution Reactions on Monosubstituted Methyl Compounds

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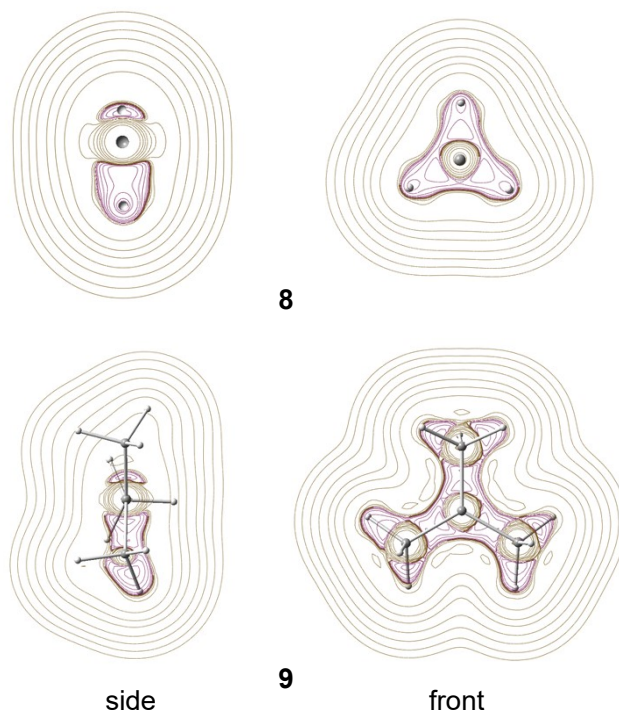


Figure S1. Representations of the contour line maps of the Laplacian $\nabla^2\rho(\mathbf{r})$ of the electron density at the methyl **8** and tert-butyl **9** carbocations.

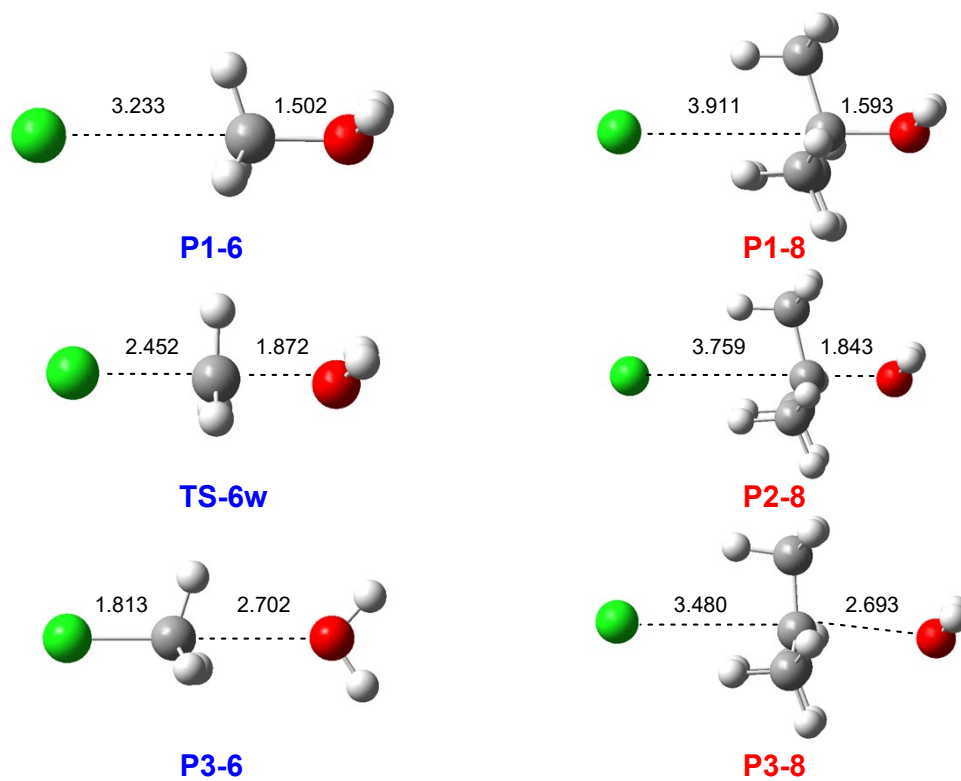


Figure S2. ω B97X-D/6-311+G(d,p) Geometries of the selected points of the scans for the C...OH₂ breaking bond in the reactions of protonated methanol **4** and tert-butanol **14**.

Table S1. ω B97X-D/6-311+G(d,p) total energies, in a.u., in DMSO of the stationary points involved in the S_N2 reactions of methyl-substituted compounds **1** - **4**, and in the S_{Ni} reaction of **6**.

	E
1	-139.749532
2	-500.120692
3	-2614.08799
4	-116.127247
5	-214.237571
F ⁻	-99.9906947
Cl ⁻	-460.393013
Br ⁻	-2574.36375
H ₂ O	-76.4402341
NMe ₃	-174.469667
TS-1	-239.707556
TS-2	-960.479763
TS-3	-3074.45014
TS-4	-600.090922
TS-5	-576.515477
TS-6	-674.573503
6	-791.329495
TS-7	-791.308569
7	-330.976745

ω B97XD/6-311+G(d,p) computed total energies, imaginary frequencies, and Cartesian coordinates, in DMSO, of the stationary points involved in the S_N2 reactions of methyl-substituted compounds **1** - **4**, and in the S_Ni reaction of **6**.

1

E(RwB97XD) = -139.749531605 A.U.

C	0.00000000	0.00000000	-0.64238500
H	0.00000000	1.03520900	-0.98566200
H	0.89651700	-0.51760400	-0.98566200
H	-0.89651700	-0.51760400	-0.98566200
F	0.00000000	0.00000000	0.75681100

2

E(RwB97XD) = -500.120692242 A.U.

C	0.00000000	0.00000000	-1.13867400
H	0.00000000	1.03322900	-1.47526600
H	0.89480200	-0.51661400	-1.47526600
H	-0.89480200	-0.51661400	-1.47526600
Cl	0.00000000	0.00000000	0.66222600

3

E(RwB97XD) = -2614.08799470 A.U.

C	0.00000000	0.00000000	-1.52826200
H	0.00000000	1.03449700	-1.85842000
H	0.89590000	-0.51724800	-1.85842000
H	-0.89590000	-0.51724800	-1.85842000
Br	0.00000000	0.00000000	0.42128100

4

E(RwB97XD) = -116.127247499 A.U.

C	-0.78062100	-0.00179500	0.00000000
H	-1.09678500	-0.50866300	0.90555900
H	-1.06937900	1.04333300	-0.00000100
H	-1.09678600	-0.50866500	-0.90555800
O	0.69302600	-0.00102500	0.00000000
H	1.19779200	-0.82467600	0.00000000
H	1.20468100	0.81764100	0.00000000

5

E(RwB97XD) = -214.237559892 A.U.

C	0.35340100	-0.67953800	0.26234000
H	0.05578800	-0.10167200	1.13515400
H	1.04693000	-0.10612900	-0.34957900
H	-0.52284700	-0.95515300	-0.32114700
N	1.03587900	-1.92782900	0.72230500

C	2.24085900	-1.56926100	1.53133400
C	1.45758200	-2.73258000	-0.46515100
C	0.09250300	-2.72913200	1.56093700
H	1.95288300	-3.63709500	-0.11736600
H	0.57465300	-2.98816600	-1.04752300
H	2.14335500	-2.13693000	-1.06445900
H	-0.20408100	-2.13138300	2.42067300
H	-0.77976700	-2.98259900	0.96145500
H	0.59868400	-3.63436300	1.89000100
H	1.92371600	-0.98578800	2.39328900
H	2.72823300	-2.48602400	1.85755600
H	2.91714100	-0.98489800	0.91056800

TS-1

E(RwB97XD) = -239.707555983 A.U.

1 imaginary frequency -595.2075 cm^{**}-1

C	0.00006600	0.00004100	0.00081000
H	0.00002800	-0.88502700	-0.60873500
H	0.00005900	-0.08540000	1.07211800
H	-0.00003500	0.97055100	-0.46075700
F	-1.85059000	-0.00002200	-0.00041400
F	1.85054000	-0.00001900	-0.00041800

TS-2

E(RwB97XD) = -960.479763313 A.U.

1 imaginary frequency -567.8551 cm^{**}-1

C	-0.00010500	-0.00003100	0.00108400
H	-0.00001400	-0.92487500	-0.54590600
H	-0.00000700	0.93622000	-0.52615500
H	0.00006200	-0.01143300	1.07555300
Cl	-2.34184300	0.00000800	-0.00029300
Cl	2.34187800	0.00000800	-0.00029500

TS-3

E(RwB97XD) = -3074.45013988 A.U.

1 imaginary frequency -538.8185 cm^{**}-1

C	0.76749600	-0.00012200	-0.00078700
H	0.76657500	0.19040800	-1.05849600
H	0.76663600	0.82063900	0.69298400
H	0.76642700	-1.01138600	0.36301100
Br	-1.71230300	0.00001600	0.00010000
Cl	3.11917600	0.00003000	0.00021800

TS-4

E(RwB97XD) = -600.090921991 A.U.

1 imaginary frequency -594.2202 cm^{**}-1

C	-0.55198000	-0.00037200	0.00029000
H	-0.61480400	0.87759800	-0.61534200
H	-0.61499300	-0.97277100	-0.45181100
H	-0.61533500	0.09408200	1.06838300
Cl	1.65132200	0.00009000	-0.00007500
F	-2.54616200	0.00019900	-0.00018800

TS-5

E(RwB97XD) = -576.515490954 A.U.

1 imaginary frequency -504.4729 cm^{**}-1

C	-0.62710800	0.00000700	-0.01440600
H	-0.54886300	-0.92757000	-0.55502100
H	-0.54886300	0.92796900	-0.55436000
H	-0.55520200	-0.00037100	1.05967500
Cl	1.82892300	-0.00000200	0.00718300
O	-2.49391600	-0.00000300	-0.08750900
H	-2.86239900	-0.77291000	0.35704600
H	-2.86239600	0.77290000	0.35705100

TS-6

E(RwB97XD) = -674.573503899 A.U.

1 imaginary frequency -583.8131 cm^{**}-1

C	0.11548900	-0.25091600	0.10139900
H	-0.01138300	-0.00300900	1.14112900
H	1.03492500	0.00019100	-0.39895900
H	-0.59955800	-0.89154000	-0.38553000
N	1.09566200	-2.03648700	0.76296300
Cl	-0.88894400	1.58105700	-0.57723500
C	2.26050500	-1.62931000	1.54399900
C	1.48485600	-2.78453100	-0.42940000
C	0.13950300	-2.78286700	1.57626800
H	1.99662200	-3.72005600	-0.16698900
H	0.59683500	-3.02361500	-1.01771300
H	2.15614900	-2.17705400	-1.03945500
H	-0.17036200	-2.17396000	2.42782400
H	-0.74150600	-3.02285200	0.97788900
H	0.57602900	-3.71791600	1.95189800
H	1.93782700	-1.02878100	2.39670600
H	2.81795400	-2.49924400	1.91604500
H	2.92536600	-1.02659200	0.92231300

6

E(RwB97XD) = -791.329494675 A.U.

N	2.43540700	-0.56610200	0.29453300
C	-1.90480000	-0.31598900	-0.21887100
Cl	-3.52830400	-0.96982500	0.26821000
C	-1.83726100	1.18539600	-0.01753700

C	-0.50820400	1.79749600	-0.47919200
C	0.73606600	1.27323900	0.25664300
C	1.43676600	0.14301800	-0.49624900
H	-2.65682600	1.65472800	-0.56948500
H	-0.38950300	1.64583000	-1.55908900
H	-0.58898600	2.87792100	-0.33516400
H	1.43711300	2.09866100	0.40298500
H	0.45998900	0.91946200	1.25718900
H	0.69864000	-0.59583900	-0.82242200
H	1.88777400	0.55627900	-1.42041500
H	-1.99018300	1.41089400	1.04293800
C	2.92398000	-1.72751300	-0.43172100
H	3.43274200	-1.45159700	-1.37354600
H	3.63381400	-2.28150200	0.18720000
H	2.09164300	-2.39184100	-0.67668000
C	3.54401000	0.29401100	0.67876600
H	4.27890700	-0.28661400	1.24083200
H	4.05219400	0.73576500	-0.19843900
H	3.19960100	1.10671100	1.32012000
H	-1.18344100	-0.85192800	0.39529500
H	-1.77350000	-0.59513900	-1.26364800

TS-7

E(RwB97XD) = -791.308569135 A.U.

1 imaginary frequencies -518.7171 cm^{**}-1

N	1.25839000	-0.76104200	0.00673200
C	-0.92803000	-0.26851300	0.09077400
Cl	-3.17872400	-0.39790900	-0.11907900
C	-0.71710000	1.10604200	0.66922200
C	0.12718400	2.02696900	-0.21813600
C	1.61871200	1.69615200	-0.23858000
C	1.92523800	0.29830300	-0.76017800
H	-1.69365100	1.56325200	0.82573300
H	-0.85168100	-0.42407100	-0.97269700
H	-0.95844700	-1.13800100	0.72494900
H	-0.27176300	2.00400400	-1.23952900
H	0.00242700	3.05220200	0.14005900
H	2.13839700	2.40873100	-0.88530200
H	2.04045400	1.83406000	0.76236100
H	1.56981100	0.21959900	-1.79235400
H	3.01176500	0.12296600	-0.77675800
H	-0.26869600	1.00878200	1.66228000
C	1.29761500	-2.03196400	-0.71015800
H	2.32928600	-2.38205900	-0.85330900
H	0.74871900	-2.78887700	-0.14595400
H	0.82932800	-1.92038000	-1.69018400
C	1.80519400	-0.92110000	1.35102400
H	1.23189700	-1.68085200	1.88622800
H	2.85833800	-1.23442100	1.31784000

H 1.74052400 0.01147100 1.91004900

7

E(RwB97XD) = -330.976744724 A.U.

C	0.09314200	1.23704000	-0.40806700
C	-1.31724000	1.25548000	0.15817800
C	-2.09109400	0.00000800	-0.23874800
C	-1.31725500	-1.25547100	0.15818200
C	0.09310500	-1.23702400	-0.40811600
H	-3.07562500	0.00002300	0.23202900
H	-1.29558300	1.36947400	1.24544500
H	-1.80326500	2.15084700	-0.23509800
H	0.06397200	1.23611400	-1.49941100
H	0.68072100	2.09410500	-0.07826600
H	-1.29555600	-1.36943800	1.24545100
H	-1.80330500	-2.15084400	-0.23504700
H	0.68069000	-2.09412600	-0.07842300
H	0.06386200	-1.23601500	-1.49945900
H	-2.25051300	-0.00000100	-1.32283200
C	1.16683000	-0.00003200	1.44932800
H	1.74310300	-0.89259700	1.68521700
H	1.74356200	0.89225600	1.68514400
H	0.24308100	0.00023400	2.01887100
C	2.16905800	0.00000200	-0.75505200
H	2.72893100	0.89221600	-0.48096900
H	2.72893600	-0.89222300	-0.48101300
H	1.96735400	0.00003100	-1.82429500
N	0.87148000	-0.00001000	-0.01593900