– Supporting Information –

Concerted Proton Electron Transfer or Hydrogen Atom Transfer? An Unequivocal Strategy to Discriminate these Mechanisms in Model Systems

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Table S1. Electronic reaction and activation energies (kcal mol^{-1}) computed for each system at different levels of theory. $\Delta E_1^{\ddagger}$ and $\Delta E_2^{\ddagger}$ refer to the relaxed and the partially constrained transition states, while $\Delta\Delta E^{\ddagger}$ represents the energy difference between the two species. All geometries have been optimized at M06-2X/6-31G(d) level of theory.

reaction		M06-2X/6-311+G(d,p)	ZORA-M06-2X/TZ2P	DLPNO-CCSD(T)/cc-pVTZ-DK	MP2/aug-cc-pVTZ
phenol + $^{\bullet}$OOH	ΔE	3.5	4.5	2.4	24.5
	$\Delta E_1^{\ddagger}$	9.6	10.8	15.4	32.3
	$\Delta E_2^{\ddagger}$	15.5	16.5	23.3	27.2
	$\Delta\Delta E^{\ddagger}$	5.9	5.8	8.0	-5.1
phenoxyl/ phenol	$\Delta E_1^{\ddagger}$	0.8	1.6	-	1.2
	$\Delta E_2^{\ddagger}$	5.1	5.9	-	7.3
	$\Delta\Delta E^{\ddagger}$	4.7	4.3	-	6.2
benzyl/ toluene	$\Delta E_1^{\ddagger}$	13.4	15.0	-	34.5
	$\Delta E_2^{\ddagger}$	17.0	17.6	-	38.4
	$\Delta\Delta E^{\ddagger}$	3.6	2.6	-	3.9
methoxyl/ methanol	$\Delta E_1^{\ddagger}$	7.2	7.7	9.6	10.1
	$\Delta E_2^{\ddagger}$	8.8	9.3	11.5	12.3
	$\Delta\Delta E^{\ddagger}$	1.6	1.6	1.9	2.1

DLPNO-CCSD(T) calculations were not computed for the biggest systems due to the high computational cost.

Table S2. Electronic activation energies (kcal mol^{-1}) computed for methoxyl/methanol self-exchange reaction with different basis set and M06-2X functional. $\Delta E_1^{\ddagger}$ and $\Delta E_2^{\ddagger}$ refer to the relaxed and the partially constrained transition states, while $\Delta\Delta E^{\ddagger}$ represents the energy difference between the two species.

	cc-pVTZ	def2TZVP	6-311+G(d,p)	6-311+G(d,p)// 6-31G(d)
$\boldsymbol{\Delta E_1^{\ddagger}}$	6.23	7.01	7.06	7.19
$\boldsymbol{\Delta E_2^{\ddagger}}$	8.13	8.73	8.68	8.82
$\boldsymbol{\Delta\Delta E^{\ddagger}}$	1.90	1.72	1.62	1.64

No significant geometrical variation is observed using the cc-pVTZ, def2TZVP and 6-311+G(d,p) basis sets, neither in the minima, nor in the transition states. Furthermore, the energies remain consistent with the ones reported in the main text.

Table S3. Electronic activation energies (kcal mol^{-1}) computed for methoxyl/methanol self-exchange reaction with functionals. $\Delta E_1^{\ddagger}$ and $\Delta E_2^{\ddagger}$ refer to the relaxed and the partially constrained transition states, while $\Delta\Delta E^{\ddagger}$ represents the energy difference between the two species. All geometries have been optimized with 6-31G(d) basis set, while energies are obtained by single point calculation with 6-311+G(d,p) basis set.

	BLYP-D3BJ	**BLYP**	**M06L**	**PBE1PBE-D3BJ**	**PBE1PBE**	**M06**	**M05-2X**	**M06-2X**
$\mathbf{\Delta E_1^{\ddagger}}$	-4.48	-2.74	1.22	3.57	4.51	5.25	8.27	7.19
$\mathbf{\Delta E_2^{\ddagger}}$	-4.26	-2.54	1.76	4.51	5.39	6.52	9.97	8.82
$\mathbf{\Delta\Delta E^{\ddagger}}$	0.22	0.20	0.53	0.95	0.87	1.26	1.69	1.64

GGA functional (BLYP and BLYP-D3BJ) does not reproduce the energy barriers which become negative with respect to free reactants. During TS optimization, the C-O-O-C dihedral angle increases, which becomes similar to the one of the partially constrained TS; thus, similar energies are computed. Meta-GGA (M06L) and hybrid functionals (PBE1PBE and PBE1PBE-D3BJ) improve the description of the energy barriers (positive numbers) as well as the energy difference between the two TSs; still, a slight increase of the C-O-O-C dihedral angle is computed. The best agreement with M06-2X functional is found with meta-hybrid functionals of the same family (M06 and M05-2X), which are also suggested by the QM-ORSA protocol.

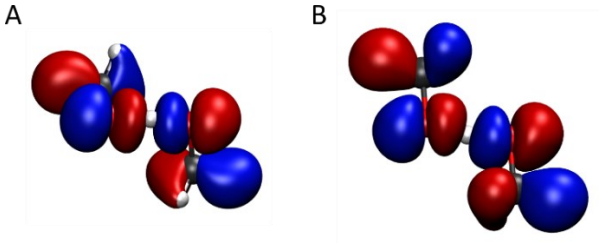

Figure S1. SOMO of the transition state for the methoxyl/methanol self-exchange reaction. (A) Relaxed structure and (B) partially constrained structure with a C-O-O-C dihedral angle of 175°. Level of theory: M06-2X/6-311+G(d,p)//M06-2X/6-31G(d).

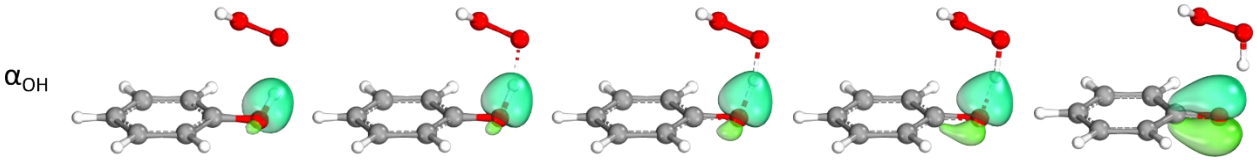

Figure S2. Changes in the α_{OH} spin IBOs involved in the hydrogen abstraction from phenol by $^{\bullet}$OOH along the reaction path: α_{OH} spin IBO of the OH σ bond (green). Level of theory: M06-2X/def2TZVP//M06-2X/6-31G(d).

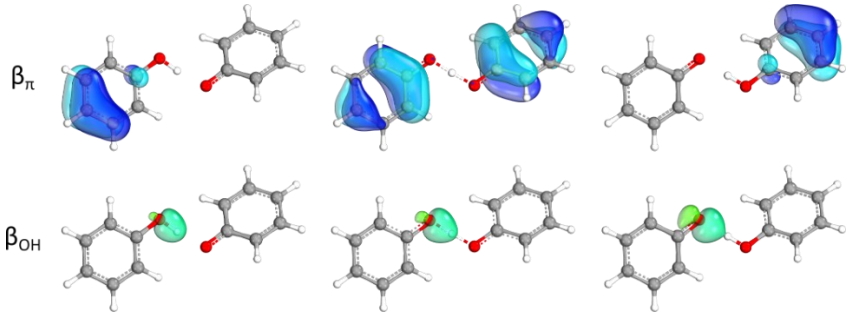

Figure S3. Changes in the main spin IBOs involved in the phenoxyl/phenol self-exchange reaction along the energetically disfavored reaction path via the partially constrained transition state: β_{π} spin IBO (blue) transferred from the π system of the ring, and β_{OH} spin IBO of the OH σ bond (green). Level of theory: M06-2X/def2TZVP//M06-2X/6-31G(d).

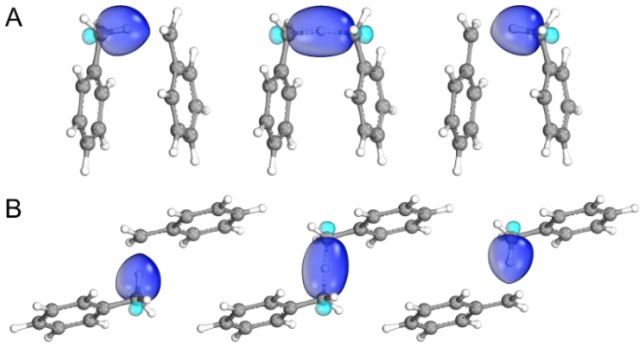

Figure S4. Changes in the main β spin IBO involved in the benzyl/toluene self-exchange reaction along (A) the relaxed and (B) the disfavored reaction path. Level of theory: M06-2X/def2TZVP//M06-2X/6-31G(d).

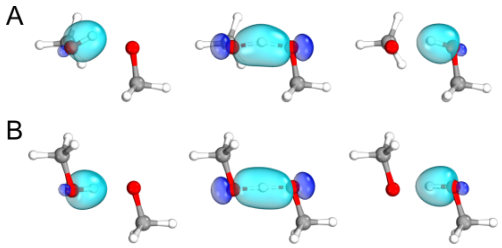

Figure S5. Changes in the main β spin IBO involved in the methoxyl/methanol self-exchange reaction along (A) the relaxed and (B) the disfavored reaction path. Level of theory: M06-2X/def2TZVP//M06-2X/6-31G(d).

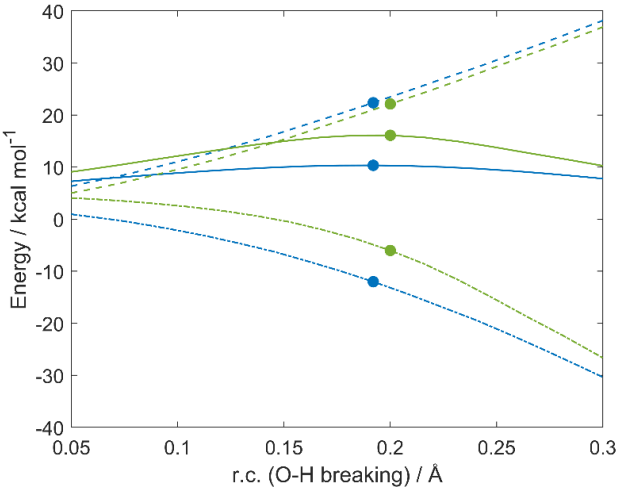

Figure S6. Activation strain analysis of the hydrogen abstraction from phenol by ˙OOH: energy profiles (solid lines), ΔE_{strain} (dashed lines), ΔE_{int} (dash-dotted lines) along the relaxed (blue lines) and the disfavored reaction path (green lines). The filled circles represent the position of the transition states. The reaction coordinate is defined as the degree of O-H bond breaking with respect to the same distance in the reactant complex. Level of theory: ZORA-M06-2X/TZ2P//M06-2X/6-31G(d).

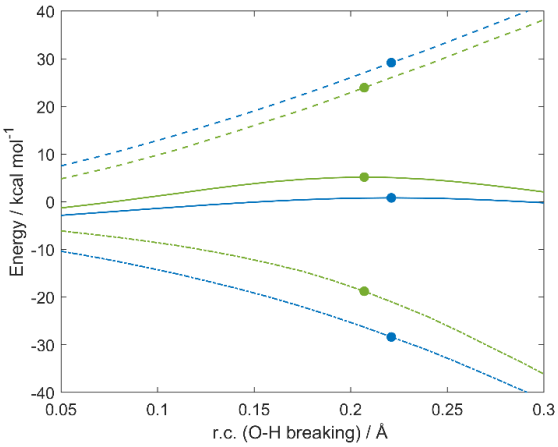

Figure S7. Activation strain analysis of the phenoxyl/phenol self-exchange reaction: energy profiles (solid lines), ΔE_{strain} (dashed lines), ΔE_{int} (dash-dotted lines) along the relaxed (blue lines) and the disfavored reaction path (green lines). The filled circles represent the position of the transition states. The reaction coordinate is defined as the degree of O-H bond breaking with respect to the same distance in the reactant complex. Level of theory: ZORA-M06-2X/TZ2P//M06-2X/6-31G(d).

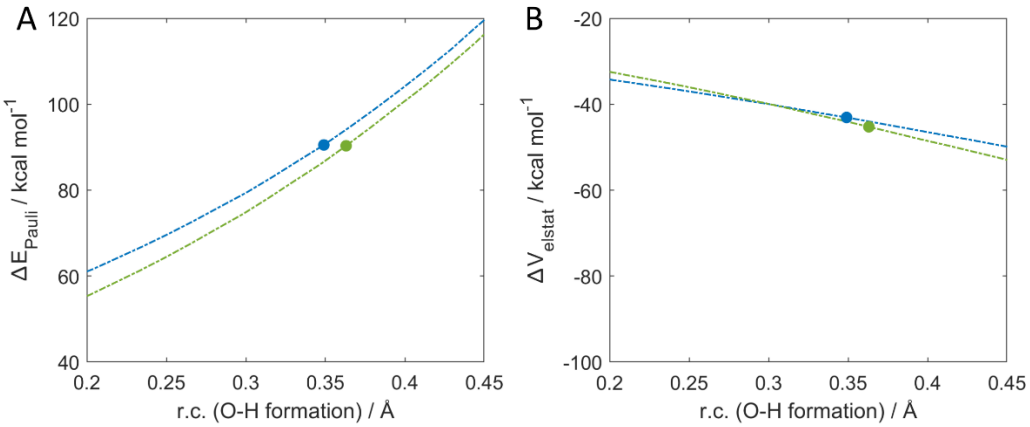

Figure S8. Energy decomposition analysis of the phenoxyl/phenol self-exchange reaction: (A) ΔE_{Pauli}, (B) ΔV_{elstat} along the relaxed (blue lines) and the disfavored reaction path (green lines). The filled circles represent the position of the transition states. The reaction coordinate is defined as the degree of O-H bond formation with respect to the same distance in the reactant complex. Level of theory: ZORA-M06-2X/TZ2P//M06-2X/6-31G(d).

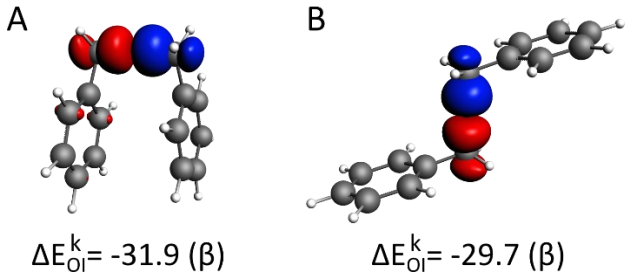

Figure S9. Deformation densities of the dominating contributions to ΔE_{OI} of (A) the relaxed and (B) the partially constrained reaction path at r.c.=0.39 of the benzyl/toluene self-exchange reaction, according to the EDA-NOCV scheme. Blue/red phases correspond to accumulation/depletion of β electron densities, respectively; isosurface value 0.003. Level of theory: ZORA-M06-2X/TZ2P//M06-2X/6-31G(d).

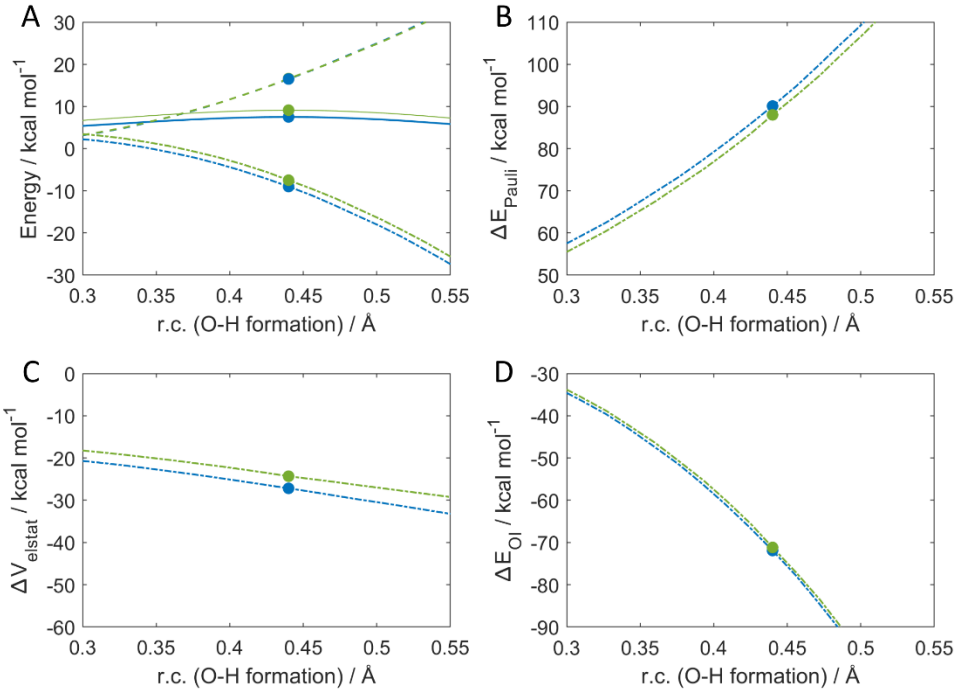

Figure S10. (A) Activation strain analysis of the methoxyl/methanol self-exchange reaction: energy profiles (solid lines), ΔE_{strain} (dashed lines), ΔE_{int} (dash-dotted lines) along the relaxed (blue lines) and the disfavored reaction path (green lines). Energy decomposition analysis: (B) ΔE_{Pauli}, (C) ΔV_{elstat}, (D) ΔE_{OI}. The filled circles represent the position of the transition states. The reaction coordinate is defined as the degree of O-H bond formation with respect to the same distance in the reactant complex. Level of theory: ZORA-M06-2X/TZ2P//M06-2X/6-31G(d).

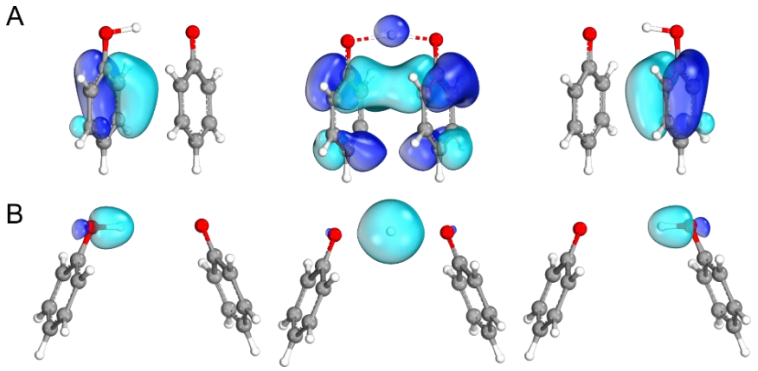

Figure S11. Changes in the main β spin IBO involved in the phenoxyl/phenol self-exchange reaction along a reaction path with an increased O-O distance in the transition state of (A) 1 Å and (B) 2 Å. Level of theory: M06-2X/def2TZVP//M06-2X/6-31G(d).

Table S4. Coordinates (Å) and energies (E, Hartree) of stationary points and number of imaginary frequencies (Nimag, cm^{-1}) of transition states. Level of theory: M06/6-31G(d).

Phenol + ˙OOH

˙OOH E= -150.832724

O	0.055503	0.709875	0.000000
O	0.055503	-0.601901	0.000000
H	-0.888054	-0.863793	0.000000

HOOH E= -151.4681908

O	0.000000	0.713705	-0.055572
O	0.000000	-0.713705	-0.055572
H	-0.812252	-0.891397	0.444578
H	0.812252	0.891397	0.444578

Phenol E= -307.329665839

C	1.459724	-0.002560	-1.590836
C	0.302766	-0.357463	-0.902738
C	2.613494	0.351389	-0.898429
H	-0.598328	-0.633926	-1.445875
H	3.513008	0.627411	-1.438130
C	0.300782	-0.358135	0.491987
C	2.600694	0.347461	0.495887
H	3.494895	0.621866	1.047414
C	1.452993	-0.004672	1.194890
H	1.424902	-0.013201	2.279137
H	1.453956	-0.004310	-2.676608
O	-0.797984	-0.695042	1.222970
H	-1.523307	-0.915719	0.622098

Phenoxyl E= -306.686310713

C	0.799615	0.004475	-2.571996
C	-0.367308	-0.250990	-1.894008
C	1.975755	0.312346	-1.863132
H	-1.293812	-0.491755	-2.404912
H	2.892466	0.513271	-2.408071
C	-0.409810	-0.208942	-0.444793
C	1.978709	0.363475	-0.456758
H	2.898800	0.602945	0.067107
C	0.825003	0.112008	0.244990
H	0.787856	0.142112	1.328994
H	0.822951	-0.029247	-3.656719
O	-1.465645	-0.439057	0.182761

TS E= -458.147730965

Nimag= -2139.66

O	9.260700	12.992977	0.769349
O	8.040723	12.406342	0.957669
H	9.889566	12.258488	0.896182
C	8.977317	13.329684	3.583297
C	9.687323	12.502222	4.488119
C	9.585580	14.523147	3.118156

H	9.203395	11.592486	4.827806
H	9.029277	15.144210	2.424601
C	10.944196	12.872955	4.926149
C	10.854071	14.873702	3.556595
H	11.480267	12.244915	5.630790
H	11.315112	15.788826	3.199207
C	11.533979	14.056553	4.459716
H	12.523470	14.338140	4.805600
O	7.766086	12.990930	3.203845
H	7.737715	12.801439	2.057462

TSconstreined E= -458.138757278

Nimag= -3552.74

O	0.000000	0.000000	0.000000
O	0.000000	0.000000	2.366573
C	1.247505	0.000000	2.735785
C	2.324822	0.375829	1.885192
O	0.745869	-1.138708	-0.200838
H	1.557556	-0.803229	-0.619804
C	1.551899	-0.478666	4.042206
H	0.722209	-0.798679	4.663066
C	2.852111	-0.486222	4.497222
H	2.093729	0.738976	0.890189
C	3.628355	0.331185	2.353375
H	3.068480	-0.819551	5.507292
C	3.902430	-0.091677	3.653375
H	4.441631	0.627327	1.698303
H	4.926456	-0.124302	4.010267
H	-0.110103	0.029625	1.202148

TSdistance E= -458.062551204

Nimag= -2816.47

O	9.292102	13.373332	0.376549
O	8.117879	12.694552	0.444526
H	9.971018	12.675087	0.426571
C	8.913661	13.256353	4.083888
C	9.597286	12.572897	5.124813
C	9.550377	14.360299	3.449813
H	9.100432	11.724825	5.583890
H	9.029288	14.852707	2.634068
C	10.838365	13.012937	5.544400
C	10.806180	14.766031	3.863126
H	11.348104	12.503774	6.356246
H	11.291262	15.604947	3.374318
C	11.450528	14.103720	4.913872
H	12.432304	14.433075	5.238605
O	7.708838	12.880173	3.751347
H	7.779725	12.736213	2.108903

Phenoxyl/phenol

TS E= -614.015521288

Nimag= -1972.86

C	0.255755	0.785203	2.167383
C	0.514079	-0.565682	2.017184
C	0.066275	1.594561	1.044655
H	0.657257	-1.217776	2.873059
H	-0.134143	2.654131	1.167173
C	0.625937	-1.139881	0.715945
C	0.109383	1.035887	-0.243594
H	-0.061108	1.668455	-1.109500
C	0.392041	-0.302423	-0.414594
H	0.461860	-0.757102	-1.397577
H	0.207056	1.217754	3.161881
O	0.973170	-2.381703	0.552120
H	2.019079	-2.568428	1.112959
C	3.382683	-0.313201	0.728576
C	3.550961	1.048136	0.909655
C	3.319415	-1.189436	1.852630
H	3.563525	1.709312	0.048722
C	3.696284	1.574394	2.195435
C	3.507516	-0.634911	3.153149
H	3.826039	2.643131	2.332730
H	3.475694	-1.316108	3.997451
C	3.700529	0.720748	3.311198
H	3.836519	1.136284	4.305086
H	3.275634	-0.748388	-0.260048
O	3.055039	-2.454157	1.710450

TSconstrained E= -614.008717050

Nimag= -2961.75

C	-0.526575	0.939161	1.767128
C	0.115596	-0.274904	1.613643
C	-0.900674	1.693343	0.648970
H	0.404976	-0.876315	2.470092
H	-1.412827	2.640911	0.779623
C	0.419094	-0.760166	0.309981
C	-0.616583	1.221844	-0.639708
H	-0.908178	1.809423	-1.504750
C	0.037544	0.019077	-0.816069
H	0.279395	-0.366671	-1.800642
H	-0.750519	1.306050	2.764013
O	1.023048	-1.897127	0.124370
H	1.580537	-2.294460	1.094229

C	3.879585	-4.202352	2.660135
C	4.418020	-5.467137	2.533470
C	2.765698	-3.815734	1.866100
H	5.266457	-5.756282	3.145947
C	3.881340	-6.378571	1.614209
C	2.223135	-4.754561	0.943397
H	4.311659	-7.369981	1.518475
H	1.369142	-4.455820	0.343072
C	2.787486	-6.010220	0.822521
H	2.372303	-6.719637	0.113368
H	4.279651	-3.472467	3.355758
O	2.263453	-2.624197	2.007533

TSdistance E= -613.871131778

Nimag= -617.88

C	-1.821567	0.644199	1.576901
C	-1.270780	-0.617142	1.547066
C	-1.650280	1.513407	0.486796
H	-1.380559	-1.315979	2.369899
H	-2.087204	2.506472	0.518746
C	-0.522004	-1.065341	0.401111
C	-0.919181	1.112882	-0.643740
H	-0.798359	1.800330	-1.475105
C	-0.359943	-0.144033	-0.694243
H	0.212072	-0.488770	-1.549493
H	-2.389800	0.973788	2.441098
O	-0.039312	-2.232913	0.350663
H	1.996326	-2.354655	1.158065
C	5.171661	-0.408564	1.193868
C	5.655315	0.854407	1.451430
C	4.447359	-1.138135	2.202677
H	6.205628	1.396551	0.688784
C	5.438285	1.449525	2.705142
C	4.236886	-0.493150	3.473232
H	5.822357	2.445921	2.899547
H	3.683701	-1.048251	4.223819
C	4.728999	0.770627	3.709745
H	4.571993	1.248865	4.671515
H	5.318228	-0.900384	0.237764
O	4.026656	-2.310856	1.986839

Benzyl/toluene

Toluene E= -271.433220704

C	0.239360	0.778340	2.158199
C	0.535647	-0.571985	1.999172
C	0.042034	1.586755	1.041315
H	0.685140	-1.199381	2.874761
H	-0.192097	2.639717	1.163127
C	0.642690	-1.138991	0.726737
C	0.142914	1.033331	-0.231961
H	-0.013955	1.653580	-1.109478
C	0.439538	-0.318458	-0.384747
H	0.513273	-0.745917	-1.381895
H	0.158353	1.199418	3.155938
H	2.082549	-2.736929	0.552706
C	0.995591	-2.595816	0.559570
H	0.605854	-2.993395	-0.381372
H	0.591307	-3.198302	1.377794

Benzyl E= -270.779437967

C	0.250516	0.768019	2.157730
C	0.468714	-0.589296	1.999848
C	0.086177	1.592721	1.041345
H	0.596022	-1.227452	2.870264
H	-0.084791	2.656670	1.169031
C	0.530978	-1.174381	0.709181
C	0.143126	1.038674	-0.240575
H	0.015786	1.675056	-1.111162
C	0.360893	-0.317515	-0.408410
H	0.404354	-0.744865	-1.406697
H	0.206984	1.193592	3.155793
C	0.752730	-2.558111	0.543287
H	0.799380	-3.001936	-0.443711
H	0.881190	-3.209394	1.399274

TS E= -542.191988051

Nimag= -1518.32

C	0.203890	1.070675	1.857984
C	0.349203	-0.297707	2.038190
C	0.092555	1.601723	0.572874
H	0.456080	-0.705105	3.040304
H	-0.018601	2.672443	0.431959
C	0.389520	-1.170764	0.937922
C	0.122335	0.748924	-0.529399
H	0.029780	1.154201	-1.532816
C	0.271115	-0.620846	-0.349444
H	0.301992	-1.282828	-1.211785
H	0.188401	1.728357	2.721918
H	2.025274	-2.663835	1.107550
C	3.534112	-0.035805	0.779611
C	3.590354	1.257073	1.280988
C	3.557554	-1.145888	1.640734
H	3.558330	2.100742	0.598079

C	3.673670	1.473784	2.656539
C	3.646179	-0.910973	3.023024
H	3.715300	2.485289	3.048673
H	3.663400	-1.759449	3.703180
C	3.705463	0.383492	3.524534
H	3.776452	0.543996	4.596395
H	3.449087	-0.199761	-0.291601
C	0.668668	-2.594889	1.121888
H	0.380791	-3.252685	0.301587
H	0.433022	-3.005976	2.103931
C	3.374040	-2.500986	1.121416
H	3.712253	-3.313723	1.764505
H	3.629659	-2.650152	0.071981

TSconstrained E= -542.186897300

Nimag= -1508.71

C	-0.174468	1.079813	1.553748
C	0.169487	-0.244308	1.795162
C	-0.253698	1.557484	0.246469
H	0.228353	-0.612815	2.816398
H	-0.523947	2.591582	0.057598
C	0.438556	-1.125593	0.735514
C	0.014470	0.696435	-0.816649
H	-0.047530	1.059247	-1.838314
C	0.358419	-0.627645	-0.575018
H	0.564994	-1.295885	-1.407491
H	-0.384274	1.742711	2.387925
H	2.205302	-2.500929	1.099994
C	4.050926	-4.364800	2.787208
C	4.395329	-5.687392	3.036269
C	3.972083	-3.873903	1.473946
H	4.456351	-6.044725	4.059923
C	4.665258	-6.553939	1.978082
C	4.242875	-4.760689	0.419325
H	4.935878	-7.586857	2.172794
H	4.184946	-4.397641	-0.603928
C	4.587295	-6.083300	0.668171
H	4.798464	-6.750507	-0.162216
H	3.843075	-3.692266	3.615885
C	0.861244	-2.504898	0.992254
H	0.721034	-3.210393	0.172462
H	0.577551	-2.921637	1.959375
C	3.549216	-2.496204	1.209052
H	3.834228	-2.084596	0.240130
H	3.687919	-1.786216	2.025232

Methoxyl/methanol

Methanol E= -115.6547578

C	-0.046785	0.658091	0.000000
H	-1.091646	0.973590	0.000000
H	0.437523	1.077763	0.891937
H	0.437523	1.077763	-0.891937
O	-0.046785	-0.753213	0.000000
H	0.871595	-1.051960	0.000000

Methoxyl E= -114.9889688

C	-0.009738	-0.577810	0.000000
H	1.056999	-0.867510	0.000000
H	-0.460335	-1.006509	0.905992
H	-0.460335	-1.006509	-0.905992
O	-0.009738	0.793424	0.000000

TS E= -230.635760987

Nimag= -1809.67

O	1.332618	-0.130554	0.490813
H	2.006671	-0.077235	1.433628
O	2.820453	-0.518371	2.133057
C	2.132974	-0.394625	-0.621739
H	2.947898	0.328781	-0.738231
H	2.543247	-1.414321	-0.599874
H	1.470766	-0.324514	-1.494450
C	2.464528	-1.824683	2.472053
H	1.463109	-1.889868	2.912409
H	2.536189	-2.506190	1.612401
H	3.200238	-2.155100	3.216786

TSconstrained E= -230.632333659

Nimag= -1919.88

O	0.960432	-0.045941	0.251547
H	1.945154	-0.341033	0.788183
O	2.655988	-0.405712	1.702259
C	1.197810	1.228113	-0.271960
H	1.237602	1.990276	0.517303
H	2.111196	1.274492	-0.877214
H	0.336824	1.459693	-0.912867
C	2.360812	-1.630059	2.308469
H	1.383071	-1.610488	2.807539
H	2.400772	-2.471557	1.606299
H	3.124879	-1.778940	3.082874