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Contribution of high-energy conformations to NMR chemical shifts, a DFT-BOMD study

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Supplementary Information

Content

SI1- Basis set effects on calculated NMR isotropic shieldings

Table SI1- NMR isotropic ^{13}C shielding of the optimized conformers using aug-cc-pVDZ and aug-cc-pVTZ (PW91 method); the corresponding TMS σ_{ref} values are 187.6 and 179.4 ppm, respectively.

	Properties	A (αα)	B (αγ)	C (αβ)	D (βγ)	E (ββ)	F (γγ)
aug-cc-pVTZ	σ_1	107.4	108.9	105.0	111.4	101.9	102.1
	σ_2	98.3	99.0	94.6	99.0	100.7	100.6
	σ_3	109.0	109.3	107.4	110.7	100.4	104.5
	$\sigma_1-\sigma_2$	9.1	9.9	10.4	12.4	1.2	1.5
	$\sigma_3-\sigma_2$	10.7	10.3	12.8	11.7	-0.3	3.9
aug-cc-pVDZ	σ_1	120.1	121.4	117.4	123.6	112.1	112.2
	σ_2	109.7	110.5	106.2	110.5	114.3	114.6
	σ_3	121.2	121.2	119.6	122.4	112.8	116.9
	$\sigma_1-\sigma_2$	10.5	10.9	11.2	13.1	-2.2	-2.4
	$\sigma_3-\sigma_2$	10.7	10.7	13.4	11.9	-1.5	-2.3

SI2. Relative energies of glycerol isomer types

Table SI2: Relative energies ΔE and free energies (ΔG) (kcal/mol) of the six most stable glycerol conformers obtained with DZVP and TZVP basis sets, respectively. Corrections for zero point energy and thermal population are included in ΔE.

Isomer	ΔE (DZVP)	ΔG (DZVP)	ΔE (TZVP)	ΔG (TZVP)
Isomer type A (αα)	2.4	0.9	0.9	0.0
Isomer type B (αγ)	1.9	1.0	1.1	0.7
Isomer type C (αβ)	4.3	2.7	3.3	2.2
Isomer type D (βγ)	3.5	1.9	2.2	1.4
Isomer type E (ββ)	4.5	3.2	4.1	3.3
Isomer type F (γγ)	0.0	0.0	0.0	0.5

SI3. Transition states activation energies

Table SI3: Low-lying transition states activation energy (ΔE^*) calculated with DZVP and TZVP basis sets. All values are given in kcal/mol.

Interchange reaction	ΔE^* (DZVP)	ΔE^* (TZVP)
F (γγ) ---> D (βγ)	1.2	1.8

D (βγ) ---> C (αβ)	6.0	5.6
B (αγ) ---> C (αβ)	3.6	2.4
A (αα) ---> C (αβ)	3.6	2.4
A (αα) ---> B (αγ)	3.7	3.9
F (γγ) ---> B (αγ)	3.7	3.7

SI4. Cartesian coordinates of glycerol transition state structures

Below are listed the Cartesian coordinates (in Å) of the transition state (TS) structures (see main text) The corresponding TS structures are given in Figure 2.

1) F --> D

C	0.642807	-0.835624	0.755625
O	0.639237	-1.581366	-0.499399
C	0.375752	0.665432	0.497444
H	-0.309217	-1.612712	-0.765748
O	1.389002	1.210741	-0.390648
H	1.544845	0.504723	-1.060580
H	1.663101	-0.944839	1.172395
H	0.503118	1.216660	1.451857
H	-0.112213	-1.245021	1.460053
C	-1.061328	0.951492	-0.072071
O	-1.872429	-0.275564	-0.077228
H	-2.756178	-0.038966	-0.426497
H	-0.934424	1.341055	-1.102908
H	-1.562621	1.726030	0.552112

2) F--> B

C	-1.459959	-0.188484	-0.603713
O	-1.761706	-0.602709	0.764766
C	-0.041360	0.424902	-0.696554
H	-1.206495	-1.385496	0.974710
O	0.115342	1.470645	0.304157
H	-0.435102	1.176555	1.068871
H	-2.219295	0.582348	-0.839272
H	0.063334	0.933964	-1.675296
H	-1.555327	-1.037942	-1.316851
C	1.099610	-0.678214	-0.564236
O	2.024088	-0.433314	0.514466
H	1.852650	0.497550	0.784623
H	0.638444	-1.674654	-0.385169
H	1.652942	-0.726627	-1.527196

3) A --> B

C	1.218473	-0.717880	0.278230
O	2.474525	-0.033957	0.065985

C	0.058434	-0.037504	-0.478075
H	2.284899	0.916923	0.222264
O	-0.008828	1.343516	-0.026858
H	-0.962448	1.511447	0.143572
C	-1.301961	-0.812823	-0.240437
O	-2.364135	0.060932	0.256108
H	-2.448675	-0.087984	1.220346
H	1.362789	-1.753810	-0.094360
H	-1.666959	-1.223243	-1.201286
H	-1.133343	-1.650238	0.468233
H	0.958559	-0.749905	1.366342
H	0.291597	-0.030155	-1.564896

4) B --> C

C	1.057095	-0.776602	-0.377072
O	2.328390	-0.580057	0.280710
C	-0.024491	0.187430	0.158706
H	2.415311	0.393459	0.388452
O	0.459855	1.572636	0.056677
H	0.508178	1.798406	-0.898082
H	-0.149682	0.027008	1.246526
H	0.752279	-1.826068	-0.183635
C	-1.411967	-0.034614	-0.530600
O	-2.440608	-0.527439	0.365550
H	-2.630821	0.178405	1.018316
H	-1.329140	-0.813737	-1.315884
H	-1.718121	0.924430	-1.005222
H	1.154455	-0.631965	-1.483465

5) A --> C

C	1.059082	-0.776830	-0.376027
O	2.329840	-0.576587	0.281698
C	-0.024530	0.185814	0.158225
H	2.414254	0.397246	0.388720
O	0.457311	1.571835	0.054970
H	0.505305	1.796774	-0.900003
H	-0.150027	0.026484	1.246171
H	0.756474	-1.826642	-0.181066
C	-1.411278	-0.039300	-0.531428
O	-2.441778	-0.524531	0.366799
H	-2.631361	0.185863	1.014882
H	-1.328278	-0.823771	-1.311371
H	-1.715799	0.916896	-1.012971
H	1.156412	-0.633604	-1.482627

6) D --> C

C	0.000000	0.000000	0.000000

O	0.000000	0.000000	1.446427
C	1.475026	0.000000	-0.466963
H	-0.728590	-0.613984	1.696313
O	1.585267	0.004137	-1.921027
H	1.303433	0.889623	-2.231941
H	1.967127	-0.933713	-0.125131
C	-0.797133	-1.233592	-0.602949
O	-1.526597	-1.977644	0.424192
H	-0.984945	-2.757891	0.663496
H	-1.563818	-0.870205	-1.314410
H	-0.090713	-1.890667	-1.147639
H	2.001558	0.866828	-0.007735
H	-0.488841	0.935679	-0.364338