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The Effect of Steric Repulsion on the Torsional Potential of *n*-Butane: a Theoretical Study

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Supplementary Data

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Table S1. Experimentally determined and calculated (MP2/6-31G(d)) bond lengths (d/Å), bond angles (τ/°), and torsional angles (φ/°) for *anti*, *anticlinal* (*ac*), *gauche* and *syn* conformations of *n*-butane and geometry changes accompanying the rotation.

Conformation	exp[a]	*anti*	*ac*	*gauche*	*syn*	*anti* → *ac*	*anti* → *gauche*	*anti* → *syn*
d_{C1C2}	1.531(2)	1.526	1.527	1.527	1.529	0.000	0.001	0.003
d_{C2C3}	1.531(2)	1.527	1.543	1.530	1.553	0.017	0.003	0.027
d_{C1H}[b]	1.117(5)	1.094	1.094	1.094	1.094	0.000	0.000	0.000
d_{C1H}[c]	1.117(5)	1.095	1.094	1.095	1.093	0.000	0.000	-0.002
d_{C1H}[c]	1.117(5)	1.095	1.095	1.093	1.093	0.000	-0.002	-0.002
d_{C2H}[d]	1.117(5)	/	1.096	1.097	1.095	-0.002	-0.001	-0.002
d_{C2H}[e]	1.117(5)	1.097	1.097	1.098	/	-0.001	0.000	/
τ_{CCC}	113.8(4)	112.9	112.9	113.9	116.4	0.0	1.0	3.5
τ_{HC1C2}[b]	111.0(5)	111.5	111.7	111.0	109.9	0.1	-0.5	-1.6
τ_{HC1C2}[c]	111.0(5)	110.8	110.8	110.7	111.9	0.0	-0.1	1.0
τ_{HC1C2}[c]	111.0(5)	110.8	110.7	111.7	111.9	-0.2	0.9	1.0
τ_{HC2C3}[d]	111.0(5)	/	110.2	108.8	109.1	1.2	-0.3	0.0
τ_{HC2C3}[e]	111.0(5)	109.1	109.5	109.1	/	0.4	0.0	/
φ_{CCCC}	65(6)[f]	180.0	120.0	63.7	0.0			

[a] Electron diffraction (from ref. 26 in the manuscript). [b] *Anti* to the CC bond on the other carbon. [c] *Gauche* to the CC bond on the other carbon. [d] *Anti* or *anticlinal* to the CC bond on the other carbon. [e] *Gauche* or *syn* to the CC bond on the other carbon. [f] For *gauche* conformer.

Table S2. Comparison of EDA results for binding interactions between two ethyl radicals in the optimized *syn* (φ = 0°), *gauche* (φ = 63.7°), *anticlinal* (*ac*, φ = 120°) and *anti* (φ = 180°) conformations and energy changes occuring upon rotations, for different methods.[a,b] Values are in kcal/mol.

φ_{CCCC}/°	method	ΔE	ΔE_{prep}	ΔE_{int}	ΔE_{elstat}	ΔE_{ex+rep}	ΔE_{pol}	ΔE_{disp}
syn	MP2/6-31G(d)	-83.87	19.14	-103.01	-146.57	205.70	-135.20	-26.94
	MP2/6-311++G(d,p)	-86.14	18.85	-104.99	-145.56	206.72	-135.73	-30.42
	B3LYP/6-31G(d)	-80.73	19.72	-100.45	-141.17	218.91	-154.15	-24.04
	B3LYP/6-311++G(d,p)	-78.35	20.96	-99.31	-138.86	220.38	-156.94	-23.89
gauche	MP2/6-31G(d)	-88.97	16.67	-105.64	-156.77	219.88	-142.01	-26.74
	MP2/6-311++G(d,p)	-91.19	16.52	-107.71	-155.61	220.91	-142.69	-30.32
	B3LYP/6-31G(d)	-85.58	17.60	-103.18	-150.66	233.49	-161.88	-24.13
	B3LYP/6-311++G(d,p)	-83.23	18.89	-102.12	-148.25	234.83	-164.72	-23.98
ac	MP2/6-31G(d)	-86.21	17.48	-103.69	-151.88	212.86	-137.96	-26.71
	MP2/6-311++G(d,p)	-88.61	17.29	-105.90	-151.00	213.91	-138.57	-30.24
	B3LYP/6-31G(d)	-83.04	18.32	-101.35	-145.85	225.61	-157.32	-23.79
	B3LYP/6-311++G(d,p)	-80.84	19.58	-100.42	-143.92	227.38	-160.25	-23.63
anti	MP2/6-31G(d)	-89.65	16.16	-105.81	-158.46	222.04	-142.93	-26.46
	MP2/6-311++G(d,p)	-91.80	16.02	-107.82	-157.23	222.84	-143.55	-29.88
	B3LYP/6-31G(d)	-86.40	17.09	-103.49	-152.49	235.88	-162.95	-23.93
	B3LYP/6-311++G(d,p)	-84.07	18.39	-102.46	-149.98	237.03	-165.75	-23.76
anti → *ac*	MP2/6-31G(d)	3.44	1.32	2.12	6.58	-9.18	4.97	-0.25
	MP2/6-311++G(d,p)	3.19	1.27	1.92	6.23	-8.93	4.98	-0.36
	B3LYP/6-31G(d)	3.36	1.22	2.14	6.64	-10.27	5.63	-0.14
	B3LYP/6-311++G(d,p)	3.23	1.19	2.04	6.06	-9.65	5.50	0.13
anti → *gauche*	MP2/6-31G(d)	0.68	0.51	0.17	1.69	-2.16	0.92	-0.28
	MP2/6-311++G(d,p)	0.61	0.50	0.11	1.62	-1.93	0.86	-0.44
	B3LYP/6-31G(d)	0.81	0.50	0.31	1.83	-2.39	1.07	-0.20
	B3LYP/6-311++G(d,p)	0.84	0.50	0.34	1.73	-2.20	1.03	-0.22
anti → *syn*	MP2/6-31G(d)	5.78	2.98	2.80	11.89	-16.34	7.73	-0.48
	MP2/6-311++G(d,p)	5.67	2.84	2.83	11.67	-16.12	7.82	-0.54
	B3LYP/6-31G(d)	5.67	2.63	3.04	11.32	-16.97	8.80	-0.11
	B3LYP/6-311++G(d,p)	5.72	2.57	3.15	11.12	-16.65	8.81	-0.13

[a] ΔE = total binding energy, ΔE_{prep} = preparation energy, ΔE_{int} = interaction energy, ΔE_{elstat} = electrostatic energy, ΔE_{ex+rep} = exchange repulsion energy, ΔE_{pol} = polarization energy, ΔE_{disp} = dispersion energy. [b] All interaction energy terms are corrected for the BSSE by using the CP method.

Absolute energies (a.u.) and x, y, z coordinates (Å) for the optimized *anti* and *gauche* conformers, and for *anticlinal* (*ac*) and *syn* transition structures

anti-butane

E = -157.8260363621 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.703090	1.823478	0.000000
2	1	0	0.188420	2.212894	0.883993
3	1	0	0.188420	2.212894	-0.883993
4	1	0	1.720724	2.225097	0.000000
5	6	0	0.703090	0.297149	0.000000
6	1	0	1.248650	-0.071831	-0.877794
7	1	0	1.248650	-0.071831	0.877794
8	6	0	-0.703090	-0.297149	0.000000
9	1	0	-1.248650	0.071831	0.877794
10	1	0	-1.248650	0.071831	-0.877794
11	6	0	-0.703090	-1.823478	0.000000
12	1	0	-0.188420	-2.212894	0.883993
13	1	0	-1.720724	-2.225097	0.000000
14	1	0	-0.188420	-2.212894	-0.883993

gauche-butane

E = -157.8249506385 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.586116	1.452996	-0.560321
2	1	0	-0.354922	2.010886	-0.606989
3	1	0	0.710159	0.925002	-1.509273
4	1	0	1.401122	2.177979	-0.477405
5	6	0	0.586116	0.491597	0.626313
6	1	0	1.527309	-0.072965	0.641109
7	1	0	0.561224	1.071822	1.556602
8	6	0	-0.586116	-0.491597	0.626313
9	1	0	-0.561224	-1.071822	1.556602
10	1	0	-1.527309	0.072965	0.641109
11	6	0	-0.586116	-1.452996	-0.560321
12	1	0	-1.401122	-2.177979	-0.477405
13	1	0	-0.710159	-0.925002	-1.509273
14	1	0	0.354922	-2.010886	-0.606989

ac-butane

E = -157.8202719035 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.693749	1.692968	-0.330225
2	1	0	0.009220	2.388332	0.165265
3	1	0	0.367506	1.588404	-1.369935
4	1	0	1.689813	2.146165	-0.333919
5	6	0	0.693749	0.337836	0.373192
6	1	0	1.420675	-0.319375	-0.119489
7	1	0	1.053712	0.464613	1.400275
8	6	0	-0.693749	-0.337836	0.373192
9	1	0	-1.053712	-0.464613	1.400275
10	1	0	-1.420675	0.319375	-0.119489
11	6	0	-0.693749	-1.692968	-0.330225
12	1	0	-1.689813	-2.146165	-0.333919
13	1	0	-0.367506	-1.588404	-1.369935
14	1	0	-0.009220	-2.388332	0.165265

syn-butane

E = -157.8163393912 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	1.457778	-0.648391
2	1	0	-0.883802	1.193175	-1.234502
3	1	0	0.883802	1.193175	-1.234502
4	1	0	0.000000	2.544863	-0.524528
5	6	0	0.000000	0.776574	0.720944
6	1	0	0.871993	1.134602	1.279106
7	1	0	-0.871993	1.134602	1.279106
8	6	0	0.000000	-0.776574	0.720944
9	1	0	0.871993	-1.134602	1.279106
10	1	0	-0.871993	-1.134602	1.279106
11	6	0	0.000000	-1.457778	-0.648391
12	1	0	0.000000	-2.544863	-0.524528
13	1	0	-0.883802	-1.193175	-1.234502
14	1	0	0.883802	-1.193175	-1.234502