Supporting Information

Table S1: Description of conformers for guest molecules studied and their number count in parentheses. The conformers are show in Newman projection in Figures S1 to S6

Molecule	Conformer 1	Conformer 2	Conformer 3	Conformer 4	5
2-methylbutane $(C_\delta H_3)_2C_\gamma HC_\beta H_2C_\alpha H_3$	anti (2)	gauche (1)	NA	NA	
2-methylpentane $(C_\varepsilon H_3)_2C_\delta HC_\gamma H_2C_\beta H_2C_\alpha H_3$	α-anti, ε-anti (2)	α-anti, ε-gauche (1)	α-gauche, ε-anti (4)	α-gauche, ε-gauche (2)	
3-methylpentane $C_\alpha H_3C_\beta H_2C_\gamma H(C_\delta H_3)C_\beta H_2C_\alpha H_3$	anti, anti (1)	anti, gauche (CH_3--CH_3) (2)	anti, gauche (CH_3--H) (2)	gauche, gauche I (2)	gauche, gauche II (2)
2,2-dimethylbutane $(C_\delta H_3)_3C_\gamma C_\beta H_2C_\alpha H_3$	anti	NA	NA	NA	
2,3-dimethylbutane $(C_\alpha H_3)_2C_\beta HC_\beta H(C_\alpha H_3)_2$	anti, anti (1)	anti, gauche (2)	NA	NA	
n-pentane $C_\alpha H_3C_\beta H_2C_\gamma H_2C_\beta H_2C_\alpha H_3$	anti, anti (1)	anti, gauche (2)	gauche, gauche 1	gauche, gauche 2	
n-hexane $C_\alpha H_3C_\beta H_2C_\gamma H_2C_\gamma H_2C_\beta H_2C_\alpha H_3$	anti, anti, anti (1)	anti, gauche, anti (4)	anti, anti, gauche (4)	gauche, anti, gauche (8)	
methylcyclopentane $C_\alpha H_3$-$(C_\beta H(C_\gamma H_2C_\delta H_2)_2)$	equatorial (1)	axial (1)	NA	NA	
methylcyclohexane $C_\alpha H_3$-$(C_\beta H(C_\gamma H_2C_\delta H_2)_2C_\varepsilon H_2)$	equatorial (1)	axial (1)	NA	NA	

Table S2: Relative energies ($kJ \cdot mol^{-1}$), Boltzmann distribution probabilities, and longest C-C distance (Å) for the conformers of the guest molecules studied in this work. In each case, the energy is calculated relative to the all anti conformer.

molecules	Conformer 1	Conformer 2	Conformer 3	Conformer 4
2-methylbutane $(CH_3)_2CHCH_2CH_3$	-197.8293454 0.911 3.9230	+3.72 0.089 3.1667	NA	NA
2-methylpentane $(CH_3)_2CHCH_2CH_2CH_3$	-237.1535889 0.761 5.0712	+4.08 0.063 4.5757	+3.4 0.173 4.5580	+10.69 0.003 4.8506
3-methylpentane $CH_3CH_2CH(CH_3)CH_2CH_3$	-237.1520259 - 5.1694	+0.65 - 4.5271	+3.28 - 3.9261	-
2,2-dimethylbutane $(CH_3)_3CCH_2CH_3$	-237.1526923 1.000 3.9280	NA	NA	NA
2,3-dimethylbutane $(CH_3)_2CHCH(CH_3)_2$	-237.1513116 0.328 3.9371	-0.05 0.672 3.9149	NA	NA
n-pentane $CH_3CH_2CH_2CH_2CH_3$	-197.8298791 0.662 5.1186	+3.59 0.273 4.6149	+6.94 0.0623 3.9229	+14.03 0.003 3.4859
n-hexane $CH_3CH_2CH_2CH_2CH_2CH_3$	-237.1542222 - 6.4601	+3.54 - 5.6051	+6.86 - 5.0890	-
methylcyclopentane CH_3-$(CH(CH_2CH_2)_2)$	-235.9377729 0.894 3.8435	+4.84 0.106 3.1878	NA	NA
methylcyclohexane CH_3-$(CH(CH_2CH_2)_2CH_2)$	-275.2707517 0.980 4.4098	+8.84 0.020 3.8159	NA	NA

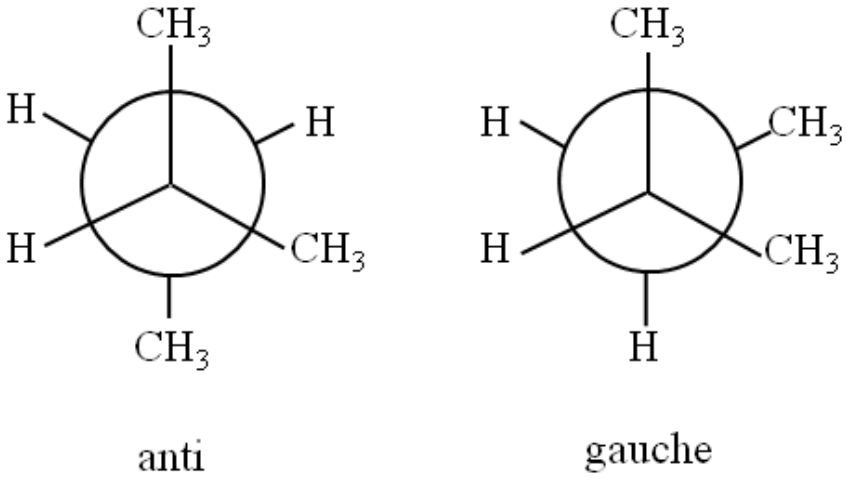


Figure S1. The two conformers of 2-methylbutane.

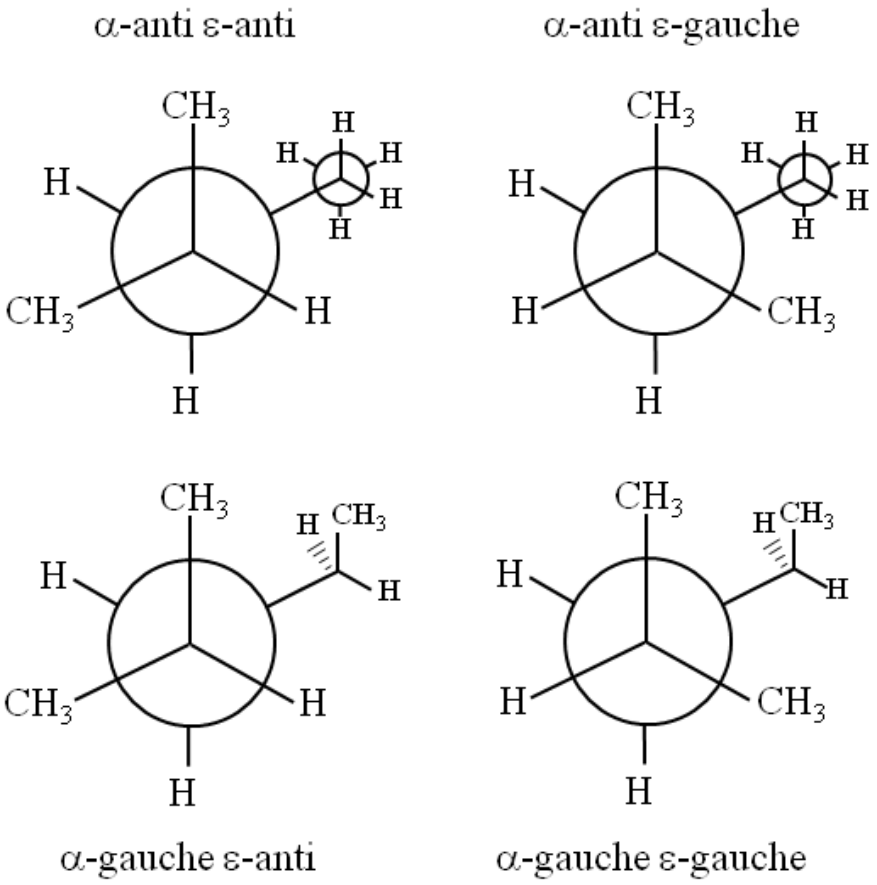


Figure S2. The four conformers of 2-methylpentane.

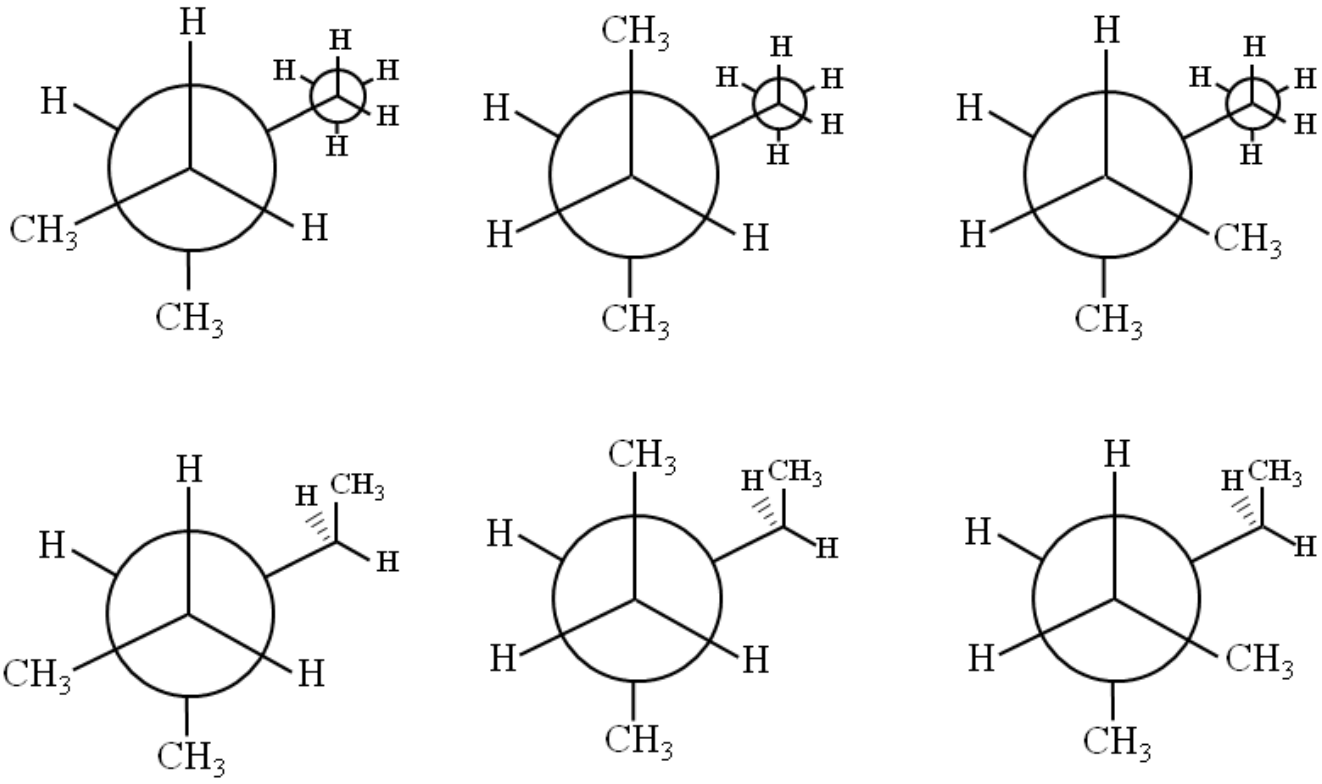


Figure S3. The conformers of 3-methylpentane

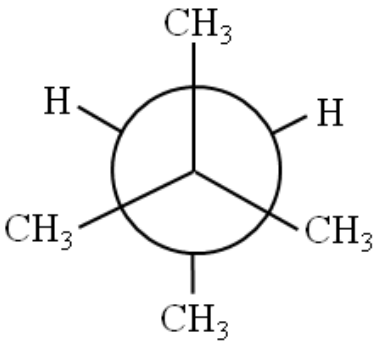


Figure S4. The conformer of 2,2-dimethylbutane

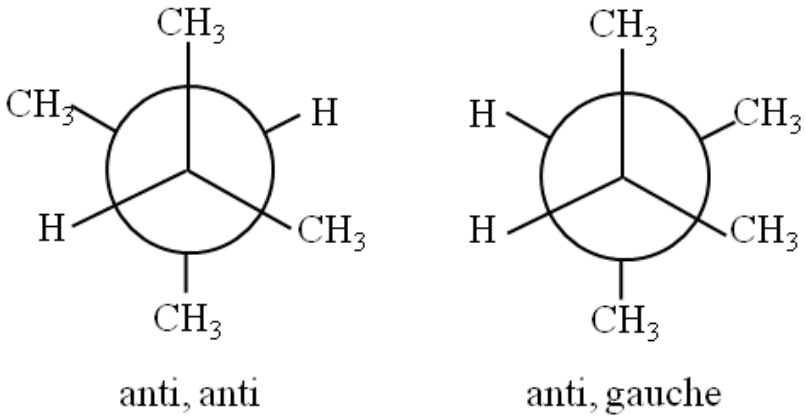


Figure S5. The two conformer of 2,3-dimethylbutane.

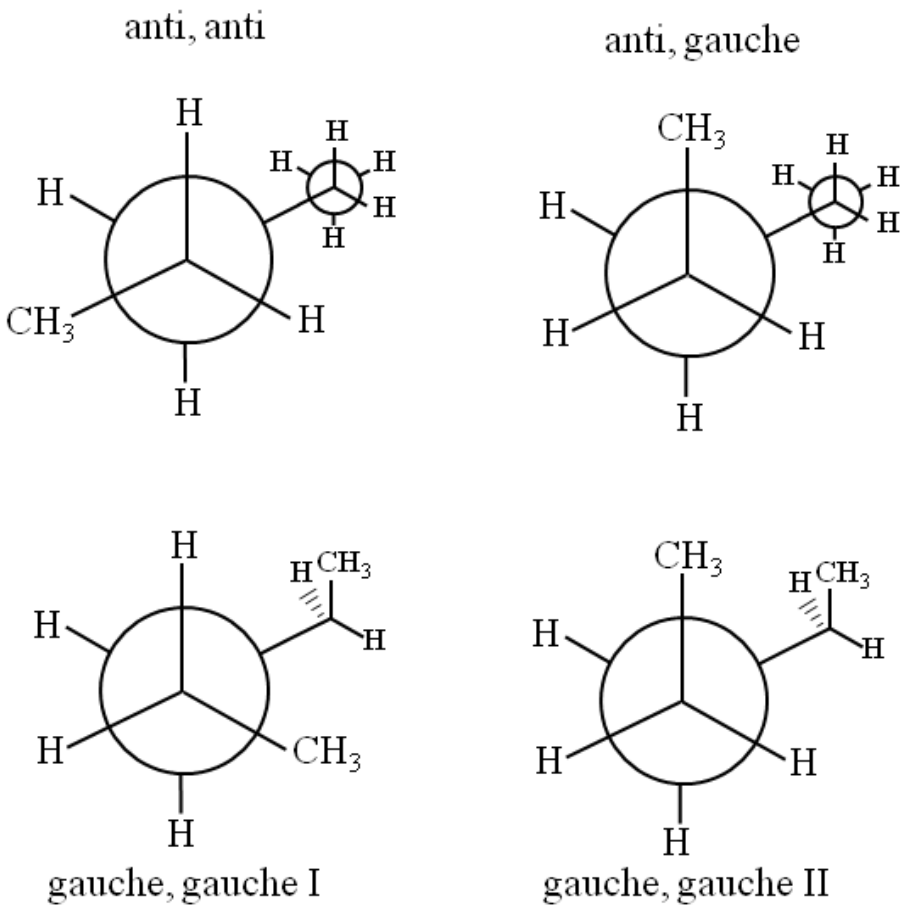


Figure S6. The conformers of n-pentane.

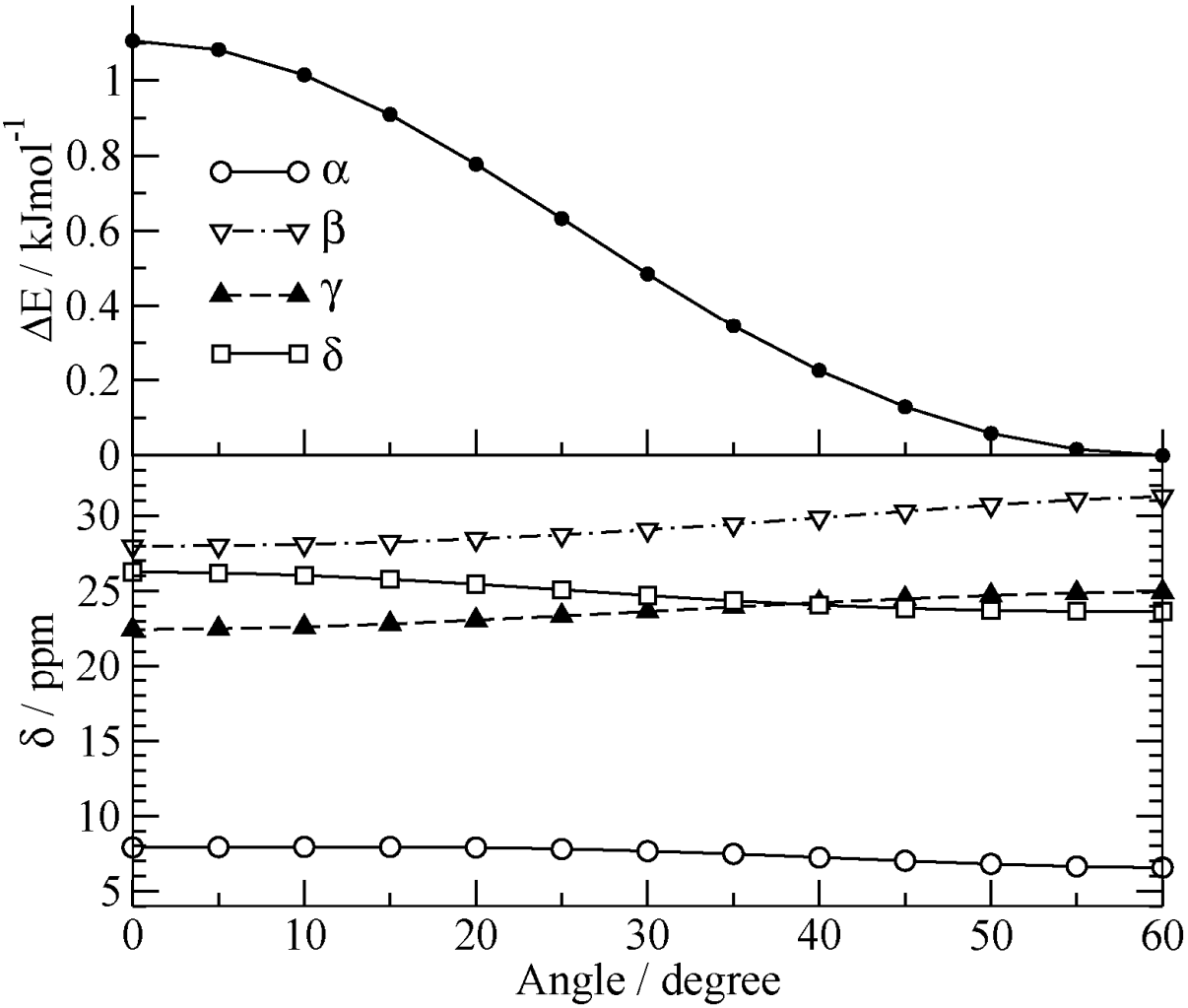
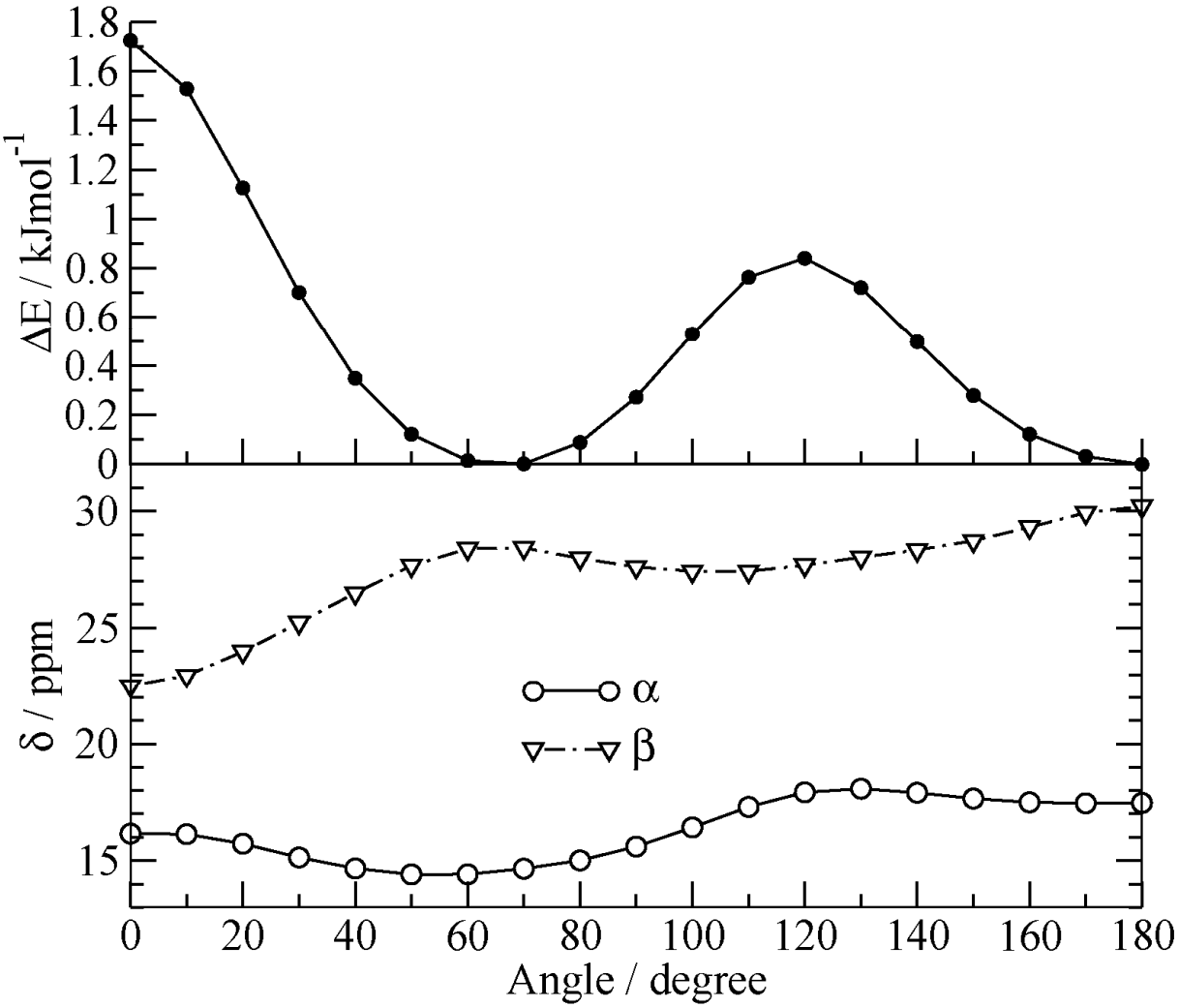

ΔE / kJmol-1
1
0.8
0.6
0.4
0.2
0
α
β
γ
δ
δ / ppm
30
25
20
15
10
5
0
10
20
30
40
50
60
Angle / degree

Figure S7


ΔE / kJmol-1
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1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
δ / ppm
30
25
20
15
α
β
0
20
40
60
80
100
120
140
160
180
Angle / degree

Figure S8.