The Importance of Correlated Motions on the Low Barrier Rotational Potentials of Crystalline Molecular Gyroscopes

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SUPPORTING INFORMATION

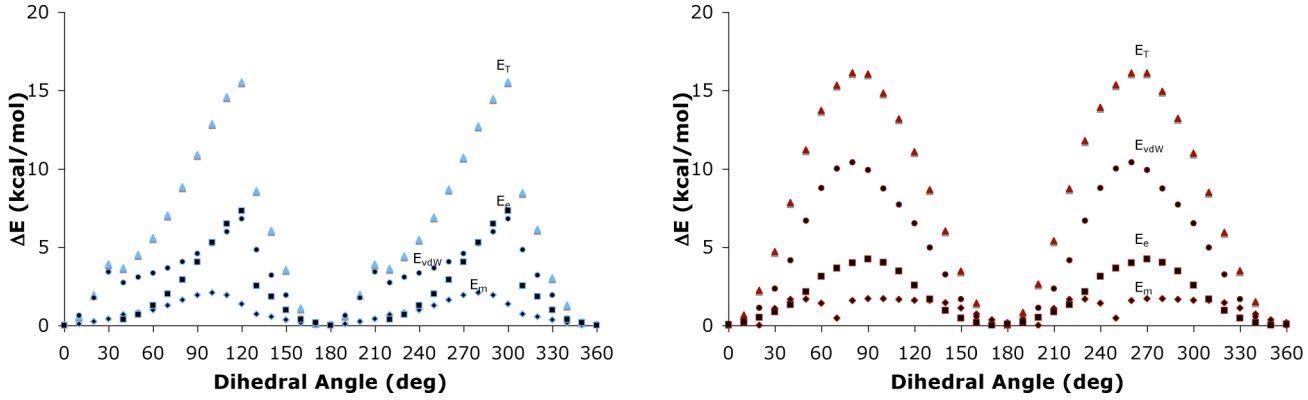
SI 1. Raw rotational energy profile data for **M-1A** and **M-1B** using *constraint sets I - IV*.

	Energy (kcal/mol)							
	M-1A				**M-1B**			
Dihedral Angle (deg)	*Constraint Set I*	*Constraint Set II*	*Constraint Set III*	*Constraint Set IV*	*Constraint Set I*	*Constraint Set II*	*Constraint Set III*	*Constraint Set IV*
0	3406.00	2910.06	2865.24	1087.76	3368.26	2903.50	2843.13	2891.95
10	3407.12	2910.60	2865.80	1087.88	3369.19	2904.27	2843.91	2892.61
20	3409.56	2911.95	2867.16	1088.49	3371.55	2906.26	2845.75	2894.19
30	3413.23	2914.08	2869.22	1087.58	3375.25	2909.38	2848.54	2896.66
40	3417.91	2916.74	2869.04	1087.92	3380.22	2913.53	2852.07	2899.79
50	3423.44	2917.32	2869.77	1088.52	3386.57	2918.43	2855.75	2903.15
60	3430.26	2919.30	2870.74	1089.46	3394.49	2923.10	2858.63	2905.66
70	3438.80	2921.72	2872.16	1091.03	3404.09	2926.69	2860.27	2907.28
80	3449.26	2924.68	2874.06	1093.21	3415.34	2927.90	2860.63	2908.07
90	3461.72	2928.16	2876.30	1095.65	3428.05	2926.94	2860.51	2907.99
100	3476.12	2931.84	2878.63	1098.09	3438.82	2924.38	2859.80	2906.77
110	3489.38	2934.87	2880.66	1099.70	3398.11	2921.39	2857.81	2905.12
120	3426.46	2919.98	2882.19	1100.35	3391.73	2918.34	2855.16	2903.04
130	3419.70	2917.57	2871.67	1092.18	3385.52	2915.11	2852.38	2900.61
140	3414.31	2915.26	2869.39	1090.83	3379.41	2911.57	2849.51	2897.97
150	3410.27	2913.10	2867.37	1089.15	3374.38	2908.16	2846.78	2895.41
160	3407.56	2911.39	2865.81	1087.61	3370.79	2905.47	2844.63	2893.38
170	3406.16	2910.33	2864.91	1086.77	3368.76	2903.87	2843.38	2892.20
180	3406.02	2910.06	2864.72	1086.70	3368.28	2903.50	2843.15	2891.97
190	3407.17	2910.62	2865.35	1087.13	3369.35	2904.42	2844.05	2892.77
200	3409.55	2911.98	2866.72	1087.46	3371.93	2906.65	2846.12	2894.59
210	3413.07	2914.08	2868.72	1087.60	3375.95	2910.10	2849.18	2897.34
220	3417.52	2916.71	2869.01	1087.98	3381.35	2914.59	2852.89	2900.67
230	3422.75	2917.26	2869.69	1088.60	3388.20	2919.44	2856.31	2903.74
240	3429.08	2919.23	2870.66	1089.64	3396.50	2923.59	2858.82	2905.87
250	3436.89	2921.63	2872.08	1091.37	3406.12	2926.74	2860.27	2907.31
260	3446.31	2924.58	2873.97	1093.69	3416.79	2927.89	2860.62	2908.06
270	3457.29	2928.03	2876.22	1096.13	3427.75	2927.05	2860.53	2908.06
280	3469.70	2931.66	2878.56	1098.31	3436.23	2924.33	2859.88	2906.90
290	3483.25	2934.74	2880.62	1099.75	3396.72	2921.18	2857.72	2905.16
300	3426.52	2935.88	2882.17	1100.36	3390.77	2918.08	2854.98	2902.93
310	3419.99	2917.74	2871.85	1092.16	3384.97	2914.85	2852.21	2900.44
320	3414.67	2915.44	2869.59	1090.79	3379.29	2911.43	2849.41	2897.89
330	3410.57	2913.27	2867.55	1089.11	3374.48	2908.17	2846.78	2895.43
340	3407.74	2911.51	2865.92	1087.64	3370.93	2905.55	2844.69	2893.46
350	3406.21	2910.38	2864.95	1086.81	3368.84	2903.92	2843.41	2892.26
360	3406.00	2910.06	2864.70	1086.67	3368.26	2903.49	2843.12	2891.94

SI 2. Potential Energy Profiles and Energetic Breakdown.

The type and magnitude of the forces acting on a rotator are analyzable from the molecular mechanics calculation. The energy profiles of **M-1A** and **M-1B** using *constraint set IV* are decomposed into their

constituent mechanical (E_m) (stretch, bend, and torsion), van der Waals or steric (E_{vdW}), and electrostatic (E_e) energies. The results are shown below.



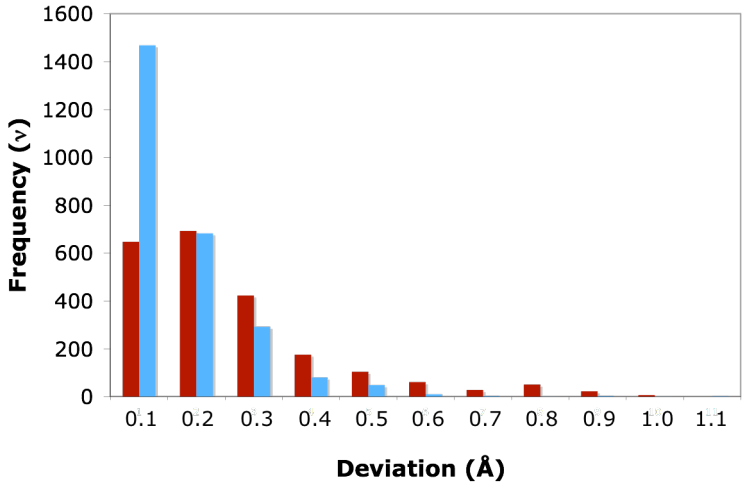
Caption: Rotational potential energy profiles (triangles) and energetic breakdown into the van der Waals (E_{vdW}) (circles), electrostatic (E_e) (squares), and mechanical (sum of the stretch, bend, and torsion strain terms) (E_m) (diamonds) for the clathrate **M-1A** (left) and desolvated **M-1B** (right) rotors using *constraint set IV*.

The E_{vdw} and E_e contributions to the rotational energy profile for **M-1A** are close in magnitude, and they are both far greater than E_m. It should be noted that the electrostatic contribution in aromatic systems arise from the quadrupolar nature of their structures, with electrostatic potentials that vary from positive in the center of the ring, to negative on the edges. The E_{vdw} and E_e terms at the maxima account for 44 and 47% of the barrier height, respectively. The shapes of these traces are very different. The E_e trace climbs nearly exponentially from the minimum to the maximum and then drops off in a similar fashion. The E_{vdw} trace is non-monotonic as there is a slight kink in the profile occurring at 30 and 210°. The same kink is found in the overall trace. The E_m contribution has a nearly sinusoidal trace with a maximum that is displaced by -20° from the overall maxima. The abrupt decrease in energy after the maxima and the kink in the profile just described may be the outcome of hysteresis, *i.e.* the profile may not represent the lowest energy pathway to rotation. Indeed, if the profile is obtained by rotation in the opposite direction the maxima shift to 70 and 250° with barrier heights of about 20 kcal/mol, as described in the computational method section. However molecular dynamics runs at the minimum and

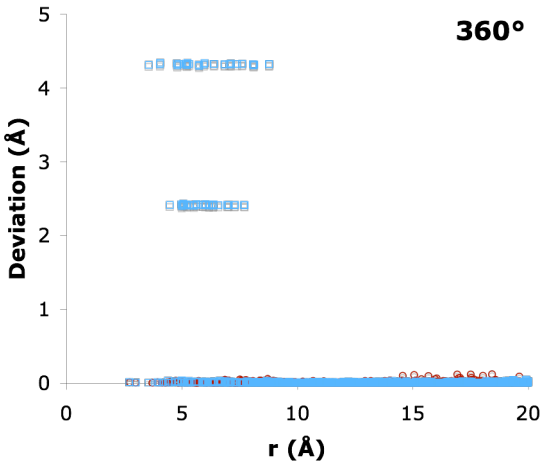
maximum of this profile did not locate a lower energy structure than was found from the dihedral drive as shown.

A similar analysis of **M-1B** reveals a barrier that is 65% E_{vdw} and 21% E_e. Thus, the **M-1B** has a larger steric contribution for the barrier and a smaller electrostatic contribution compared to **M-1A**. The similar magnitudes of these energy terms for **M-1A** thus results from a relatively low steric contribution and a slightly larger electrostatic contribution illuminated by comparison to the case of **M-1B**. Although the steric contribution dominates the profile in this case, the electrostatic contribution is still larger than the mechanical one. All the traces, but that of E_m are essentially sinusoidal, and the maximum of E_e is displaced by 10° with respect to the overall maximum.

SI 3. Frequency (ν) of data points versus deviation (Å) of the calculated equilibrium structure at 0° dihedral angle from the X-ray structure for **M-1A** (blue) and **M-1B** (red). The frequency data is collected in data ranges of 0.1 Å.



SI 4. Deviation (Å) from calculated 0° equilibrium structure at 360° dihedral angle versus distance (Å) from the center-of-mass of the models **M-1A** (blue squares) and **M-1B** (red circles).


360°
Deviation (Å)
r (Å)
0
1
2
3
4
5
0
5
10
15
20