

**Table S1.** Calculated conformational energies, for the 1,3-dap conformers.

| Conformer <sup>a</sup> | CCSD(T)                               |                                       | mPW1PW                                |                                       | wB97XD                                |                                       | M06-2X                                |                                       |
|------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
|                        | $\Delta E$<br>(kJ.mol <sup>-1</sup> ) | $\Delta E$<br>(kJ.mol <sup>-1</sup> ) | $\Delta G$<br>(kJ.mol <sup>-1</sup> ) | $\Delta G$<br>(kJ.mol <sup>-1</sup> ) | $\Delta E$<br>(kJ.mol <sup>-1</sup> ) | $\Delta G$<br>(kJ.mol <sup>-1</sup> ) | $\Delta E$<br>(kJ.mol <sup>-1</sup> ) | $\Delta G$<br>(kJ.mol <sup>-1</sup> ) |
| GGG'G                  | 0.00                                  | 0.00                                  | 0.00                                  | 0.00                                  | 0.00                                  | 0.00                                  | 0.00                                  | 0.00                                  |
| TG'GG'                 | 4.11                                  | 1.03                                  | 0.64                                  | 2.58                                  | 1.31                                  | 3.50                                  | 2.14                                  |                                       |
| TGGG'                  | 3.56                                  | 4.04                                  | 2.30                                  | 2.95                                  | 0.63                                  | 2.00                                  | 0.66                                  |                                       |
| TTTT                   | 6.29                                  | 5.39                                  | 3.52                                  | 6.22                                  | 3.48                                  | 7.82                                  | 6.44                                  |                                       |
| GGGG'                  | 1.14                                  | 4.28                                  | 3.67                                  | 2.91                                  | 1.66                                  | 0.41                                  | 0.29                                  |                                       |
| GG'G'G                 | 1.26                                  | 5.94                                  | 3.11                                  | 4.62                                  | 2.81                                  | 3.88                                  | 2.59                                  |                                       |
| TTGG'                  | 3.64                                  | 6.44                                  | 2.56                                  | 6.43                                  | 2.91                                  | 6.86                                  | 2.78                                  |                                       |
| TTTG                   | 5.52                                  | 6.65                                  | 2.74                                  | 6.77                                  | 2.55                                  | 7.91                                  | 2.83                                  |                                       |
| TGTT                   | 7.52                                  | 6.41                                  | 3.04                                  | 6.31                                  | 1.98                                  | 7.88                                  | 2.68                                  |                                       |
| GTGG'                  | 4.21                                  | 6.92                                  | 3.57                                  | 6.28                                  | 2.52                                  | 6.13                                  | 2.35                                  |                                       |
| TGTG                   | 6.40                                  | 7.25                                  | 3.84                                  | 6.45                                  | 2.24                                  | 7.36                                  | 2.93                                  |                                       |
| TGGT                   | 7.83                                  | 6.54                                  | 6.09                                  | 4.85                                  | 4.20                                  | 6.23                                  | 4.31                                  |                                       |
| RMSD <sup>b</sup>      |                                       | 2.281                                 | 2.417                                 | 1.853                                 | 2.894                                 | 1.733                                 | 2.485                                 |                                       |

<sup>a</sup> See Figure 1; <sup>b</sup> Root-mean-square deviation