**Conformational Equilibrium Study of calix[4]tetraloranes using Density Functional Theory and Molecular Dynamics Simulations**

SUPPLEMENTARY INFORMATION

Table S1. Optimized Structures of calix[4]tetrolarenes at B97D/6-31G\* level of approximation

|  |  |
| --- | --- |
| 4a | 4b |
| cone | cone |
| partial cone | partial cone |
| 1,2-alternate | 1,2-alternate |
| 1,3-alt | 1,3-alt |

Table S2: Dipole moments (in Debye) of calix[4]tetrolarenes conformers along various components

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **4a\_cone** | **wB97XD/6-31 G(d)** | *X=*2.7844 | *Y=*-0.7566 | *Z=* 3.2087 | µ= 4.3152 |
| **wB97XD/6-31+G(d)** | *X=*0.8542 | *Y=*-2.3004 | *Z=* 1.4351 | µ= 2.8427 |
| **B97D/6-31G(d)** | *X=*0.7402 | *Y=*-2.0926 | *Z=* 1.2472 | µ= 2.5460 |
| **B97D/6-31+ G(d)** | *X=*0.7776 | *Y=*-2.2360 | *Z=* 1.9396 | µ= 3.0605 |
| **B3LYP/6-31 G(d)** | *X=*2.6654 | *Y=*-0.7862 | *Z=* 3.0353 | µ= 4.1153 |
| **B3LYP/6-31+ G(d)** | *X=*0.6492 | *Y=*-2.2174 | *Z=* 2.1518 | µ= 3.1573 |
| **CAMB3LYP/6-31 G(d)** | *X=*0.6122 | *Y=*-2.2690 | *Z=* 2.1700 | µ= 3.1987 |
| **CAMB3LYP/6-31+ G(d)** | *X=*0.7113 | *Y=*-2.3003 | *Z=* 2.1258 | µ= 3.2120 |
| **4a\_partial-cone** | **wB97XD/6-31 G(d)** | *X=*-5.2295 | *Y=*-0.2743 | *Z=* -2.9376 | µ=6.0044 |
| **wB97XD/6-31+G(d)** | *X=*-5.2038 | *Y=* 0.3050 | *Z=* 3.0243 | µ= 6.0266 |
| **B97D/6-31G(d)** | *X=*-2.5467 | *Y=*-2.7507 | *Z=*1.0042 | µ=3.8808 |
| **B97D/6-31+ G(d)** | *X=*3.0190 | *Y=* 2.5973 | *Z=*0.3890 | µ=4.0015 |
| **B3LYP/6-31 G(d)** | *X=*-2.5450 | *Y=*-1.7150 | *Z=* -0.6764 | µ=3.1426 |
| **B3LYP/6-31+ G(d)** | *X=*2.5372 | *Y=* 1.5315 | *Z=* -0.4957 | µ=3.0048 |
| **CAMB3LYP/6-31 G(d)** | *X=*2.6196 | *Y=*1.7372 | *Z=* -0.7343 | µ=3.2279 |
| **CAMB3LYP/6-31+ G(d)** | *X=* 2.5497 | *Y=* 1.7016 | *Z=*-0.6776 | µ= 3.1394 |
| **4a\_1,3-Alter** | **wB97XD/6-31 G(d)** | *X=*1.1960 | *Y=*-0.0503 | *Z=*1.7106 | µ=2.0879 |
| **wB97XD/6-31+G(d)** | *X=*1.3863 | *Y=*-0.1900 | *Z=*1.5484 | µ=2.0870 |
| **B97D/6-31G(d)** | *X=*1.3161 | *Y=*-0.1214 | *Z=*1.6022 | µ=2.0770 |
| **B97D/6-31+ G(d)** | *X=*1.4724 | *Y=*-0.1053 | *Z=*1.4753 | µ=2.0870 |
| **B3LYP/6-31 G(d)** | *X=*0.7713 | *Y=*-0.0251 | *Z=*1.3283 | µ=1.5362 |
| **B3LYP/6-31+ G(d)** | *X=*0.8779 | *Y=*-0.0974 | *Z=*1.3149 | µ=1.5840 |
| **CAMB3LYP/6-31 G(d)** | *X=*0.8939 | *Y=*-0.0545 | *Z=*1.3732 | µ=1.6394 |
| **CAMB3LYP/6-31+ G(d)** | *X=*0.8939 | *Y=*-0.0545 | *Z=*1.3732 | µ=1.6394 |
| **4a\_1,2-Alter** | **wB97XD/6-31 G(d)** | *X=*2.9884 | *Y=*-2.5671 | *Z=* -2.0256 | µ=4.4299 |
| **wB97XD/6-31+G(d)** | *X=*2.8041 | *Y=*-2.5036 | *Z=* -2.1688 | µ=4.3399 |
| **B97D/6-31G(d)** | *X=*2.9538 | *Y=*-2.2839 | *Z=* -1.8059 | µ=4.1476 |
| **B97D/6-31+ G(d)** | *X=*2.7624 | *Y=*-2.2643 | *Z=* -1.9876 | µ=4.0876 |
| **B3LYP/6-31 G(d)** | *X=*0.9643 | *Y=*-3.9190 | *Z=* -1.8535 | µ=4.4412 |
| **B3LYP/6-31+ G(d)** | *X=*0.8458 | *Y=*-3.6295 | *Z=* -1.9593 | µ=4.2104 |
| **CAMB3LYP/6-31 G(d)** | *X=*3.0256 | *Y=*-2.7276 | *Z=* -1.9694 | µ=4.5246 |
| **CAMB3LYP/6-31+ G(d)** | *X=*2.9132 | *Y=*-2.4618 | *Z=* -2.0506 | µ=4.3304 |
|  |  |  |  |  |  |
| **4b\_cone** | **wB97XD/6-31 G(d)** | *X=*-1.0326 | *Y=*-4.3175 | *Z=*1.3209 | µ=4.6316 |
| **wB97XD/6-31+G(d)** | *X=*-1.0525 | *Y=*-4.3116 | *Z=* 1.3216 | µ= 4.6308 |
| **B97D/6-31G(d)** | *X=* 0.4395 | *Y=* -4.6868 | *Z=* -0.3463 | µ=4.7201 |
| **B97D/6-31+ G(d)** | *X=* -0.0427 | *Y=* -4.6650 | *Z=* -0.8113 | µ=4.7352 |
| **B3LYP/6-31 G(d)** | *X=*0.7162 | *Y=*-2.1845 | *Z=*0.5845 | µ=2.3721 |
| **B3LYP/6-31+ G(d)** | *X=*-2.9836 | *Y=*-0.8895 | *Z=* 1.9324 | µ= 3.6643 |
| **CAMB3LYP/6-31 G(d)** | *X=*0.0541 | *Y=*-4.6780 | *Z=*-0.2777 | µ=4.6865 |
| **CAMB3LYP/6-31+ G(d)** | *X=* 0.0696 | *Y=*-4.7649 | *Z=*-0.3100 | µ= 4.7755 |
| **4b\_partial-cone** | **wB97XD/6-31 G(d)** | *X=*1.4526 | *Y=*-1.5593 | *Z=* -3.9943 | µ=4.5272 |
| **wB97XD/6-31+G(d)** | *X=* 1.2876 | *Y=* -1.5004 | *Z=* -4.0337 | µ=4.4921 |
| **B97D/6-31G(d)** | *X=*1.7396 | *Y=*-1.6896 | *Z=* -3.6685 | µ=4.3976 |
| **B97D/6-31+ G(d)** | *X=* 1.5463 | *Y=* -1.6989 | *Z=* -3.6959 | µ=4.3517 |
| **B3LYP/6-31 G(d)** | *X=*1.1563 | *Y=*-1.5173 | *Z=* -3.4143 | µ=3.9111 |
| **B3LYP/6-31+ G(d)** | *X=* 1.2602 | *Y=* -1.4634 | *Z=* -3.2296 | µ=3.7630 |
| **CAMB3LYP/6-31 G(d)** | *X=*0.9524 | *Y=*-1.6020 | *Z=* -3.6883 | µ=4.1324 |
| **CAMB3LYP/6-31+ G(d)** | *X=* 1.2245 | *Y=* -1.5347 | *Z=* -3.5392 | µ=4.0473 |
| **4b\_1,3-Alter** | **wB97XD/6-31 G(d)** | *X=*-1.2997 | *Y=*-1.3759 | *Z=* -2.0281 | µ=2.7741 |
| **wB97XD/6-31+G(d)** | *X=*1.3445 | *Y=* 1.4734 | *Z=* -1.7879 | µ=2.6787 |
| **B97D/6-31G(d)** | *X=* 0.8788 | *Y=* 1.5495 | *Z=* -1.9212 | µ=2.6200 |
| **B97D/6-31+ G(d)** | *X=*1.0205 | *Y=*1.3871 | *Z=*-1.7288 | µ=2.4401 |
| **B3LYP/6-31 G(d)** | *X=*0.4820 | *Y=* 1.9861 | *Z=* -0.8335 | µ=2.2072 |
| **B3LYP/6-31+ G(d)** | *X=*0.4968 | *Y=* 2.0951 | *Z=*-0.4047 | µ=2.1909 |
| **CAMB3LYP/6-31 G(d)** | *X=*1.0322 | *Y=* 1.5287 | *Z=* -1.8413 | µ=2.6063 |
| **CAMB3LYP/6-31+ G(d)** | *X=*0.5632 | *Y=* 2.0515 | *Z=* -1.0215 | µ=2.3600 |
| **4b\_12Alter** | **wB97XD/6-31 G(d)** | *X=*1.8457 | *Y=* 0.2026 | *Z=*2.4010 | µ=3.0352 |
| **wB97XD/6-31+G(d)** | *X=*1.9297 | *Y=* 0.1957 | *Z=*2.3246 | µ=3.0275 |
| **B97D/6-31G(d)** | *X=* 1.7313 | *Y=* 0.3271 | *Z=* 2.0860 | µ= 2.7305 |
| **B97D/6-31+ G(d)** | *X=* 1.7741 | *Y=* 0.3205 | *Z=* 2.2240 | µ= 2.8629 |
| **B3LYP/6-31 G(d)** | *X=*2.2962 | *Y=* 0.2991 | *Z=*2.2754 | µ=3.2465 |
| **B3LYP/6-31+ G(d)** | *X=* 2.0124 | *Y=* 0.3325 | *Z=* 2.3693 | µ= 3.1263 |
| **CAMB3LYP/6-31 G(d)** | *X=*2.1384 | *Y=* 0.1782 | *Z=*2.3314 | µ=3.1686 |
| **CAMB3LYP/6-31+ G(d)** | *X=*2.1859 | *Y=* 0.2454 | *Z=*2.2273 | µ=3.1304 |

X,Y,Z indicates the components whereas µ designates the total dipole moment.

Table S3. Structural comparison of 4b at various level of theories

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | B97D/6-31d | B97D/6-31+d | CAMB3LYP/6-31+d | CAMB3LYP/6-31d | WB97XD/6-31+d | WB97XD/6-31d | B3LYP/6-31d | B3LYP/6-31+d |
| B97D/6-31d |  | 0.1545 | 0.2612 | 0.1867 | 0.5155 | 0.5149 | 0.9883 | 0.9883 |
| B97D/6-31+d | 0.1545 |  | 0.2070 | 0.2202 | 0.5743 | 0.5775 | 0.9797 | 0.9797 |
| CAMB3LYP/6-31+d | 0.2612 | 0.2070 |  | 0.1658 | 0.5871 | 0.5990 | 0.9242 | 0.9242 |
| CAMB3LYP/6-31d | 0.1867 | 0.2202 | 0.1658 |  | 0.5423 | 0.5469 | 0.9372 | 0.9372 |
| WB97XD/6-31+d | 0.5155 | 0.5743 | 0.5871 | 0.5423 |  | 0.0468 | 1.1234 | 1.1234 |
| WB97XD/6-31d | 0.5149 | 0.5775 | 0.5990 | 0.5469 | 0.0468 |  | 1.1305 | 1.1305 |
| B3LYP/6-31d | 0.9883 | 0.9797 | 0.9242 | 0.9372 | 1.1234 | 1.1305 |  | 0.00 |
| B3LYP/6-31+d | 0.9883 | 0.9797 | 0.9242 | 0.9372 | 1.1234 | 1.1305 | 0.00 |  |

Table S4. Energetics of the components and the anionic complexes computed at B97D/6-31G\* level

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **components** | **Etotal** | **Enthalpy** | **Gibbs energy** | **ZPE** |
| Cl- | -460.25685304 | -460.254493 | -460.271876 | -460.256853 |
| F- | -99.70360519 | -99.701245 | -99.717764 | -99.703605 |
| 4a cone | -2754.75379913 | -2753.866805 | -2754.014589 | -2753.925273 |
| 4a cone-Cl- | -3215.07019336 | -3214.183995 | -3214.339523 | -3214.244933 |
| 4a cone-F- | -2854.63793590 | -2853.753030 | -2853.905156 | -2853.813068 |

\*energies are represented in a.u.

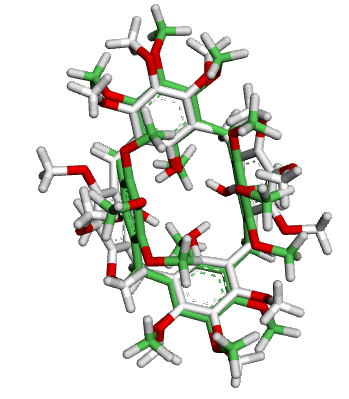


Figure S1. Superimposed Structure (**4a** in *cone* conformer) of experimental and theoretically predicted B97D/6-31+d Level

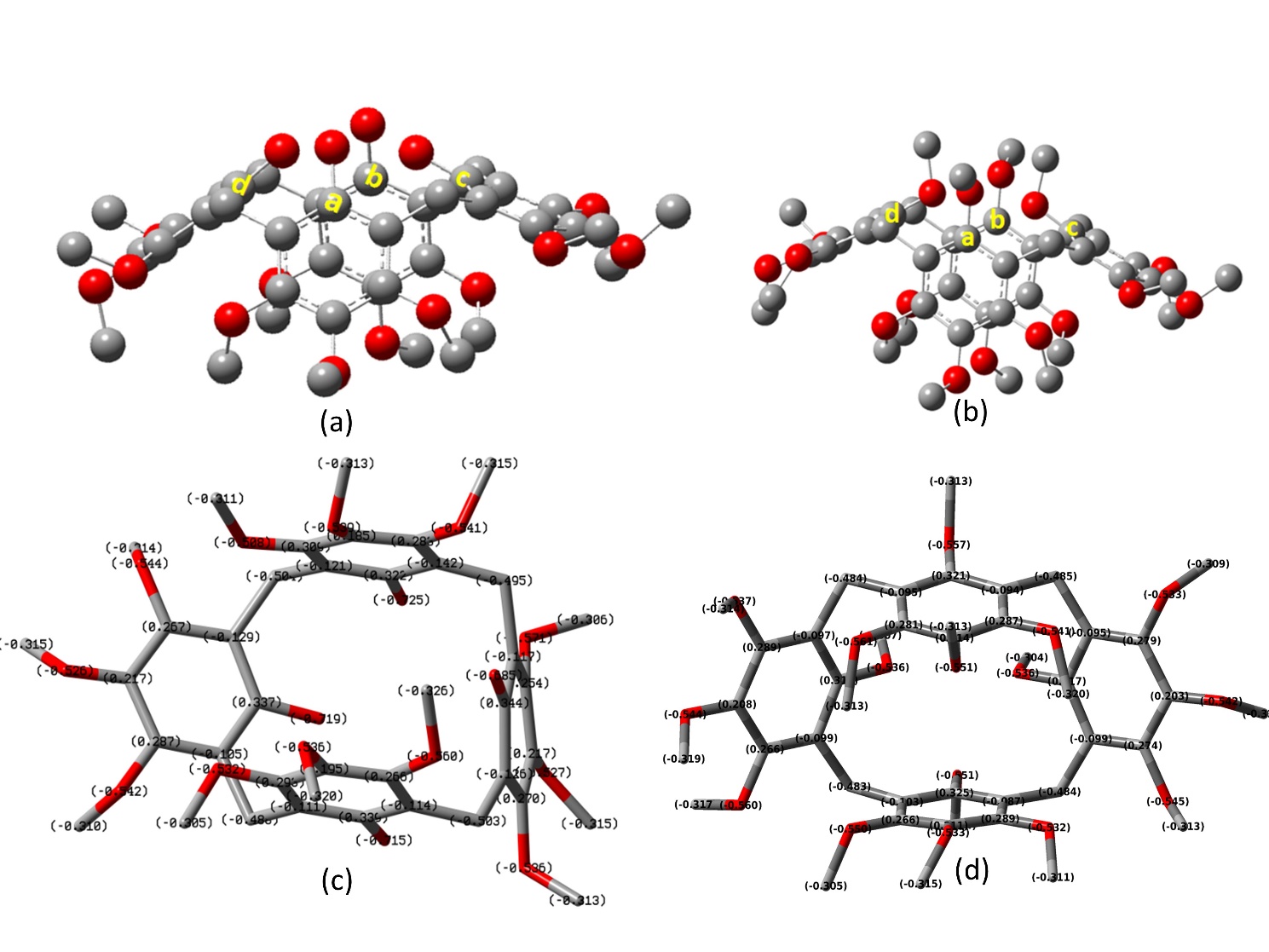


Figure S2. Naming scheme for NBO charges of cone conformer of 4a and 4b

|  |  |
| --- | --- |
| 4a\_13Alternate | 4a\_partial-cone |
| 4a\_12Alternate | 4a\_cone |
| 4b\_12Alternate | 4b\_13Alternate |
| 4b\_partial-cone | I:\4b cone1 nbo.tif  4b\_cone |

Figure S3. NBO charges of conformer of 4a and 4b

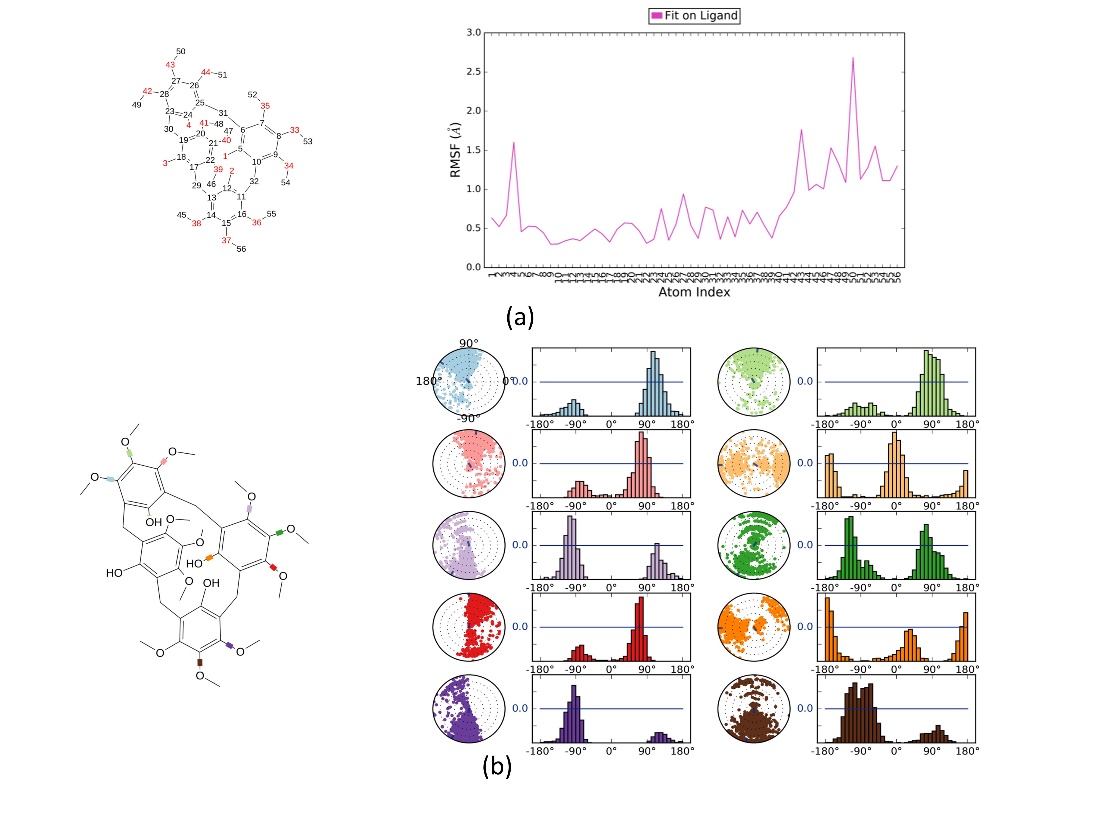


Figure S4. MD properties of 4a

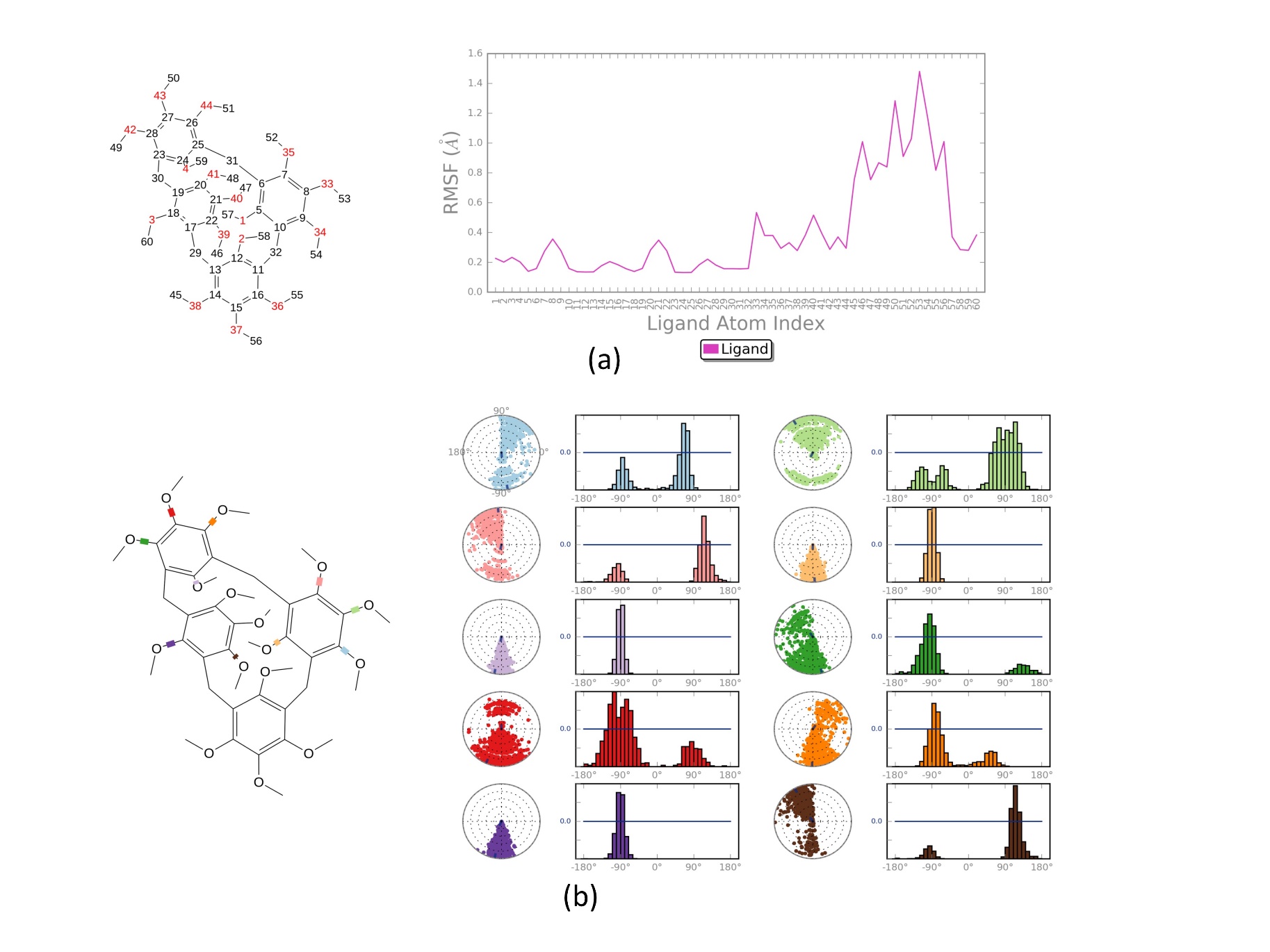


Figure S5. MD properties of 4b

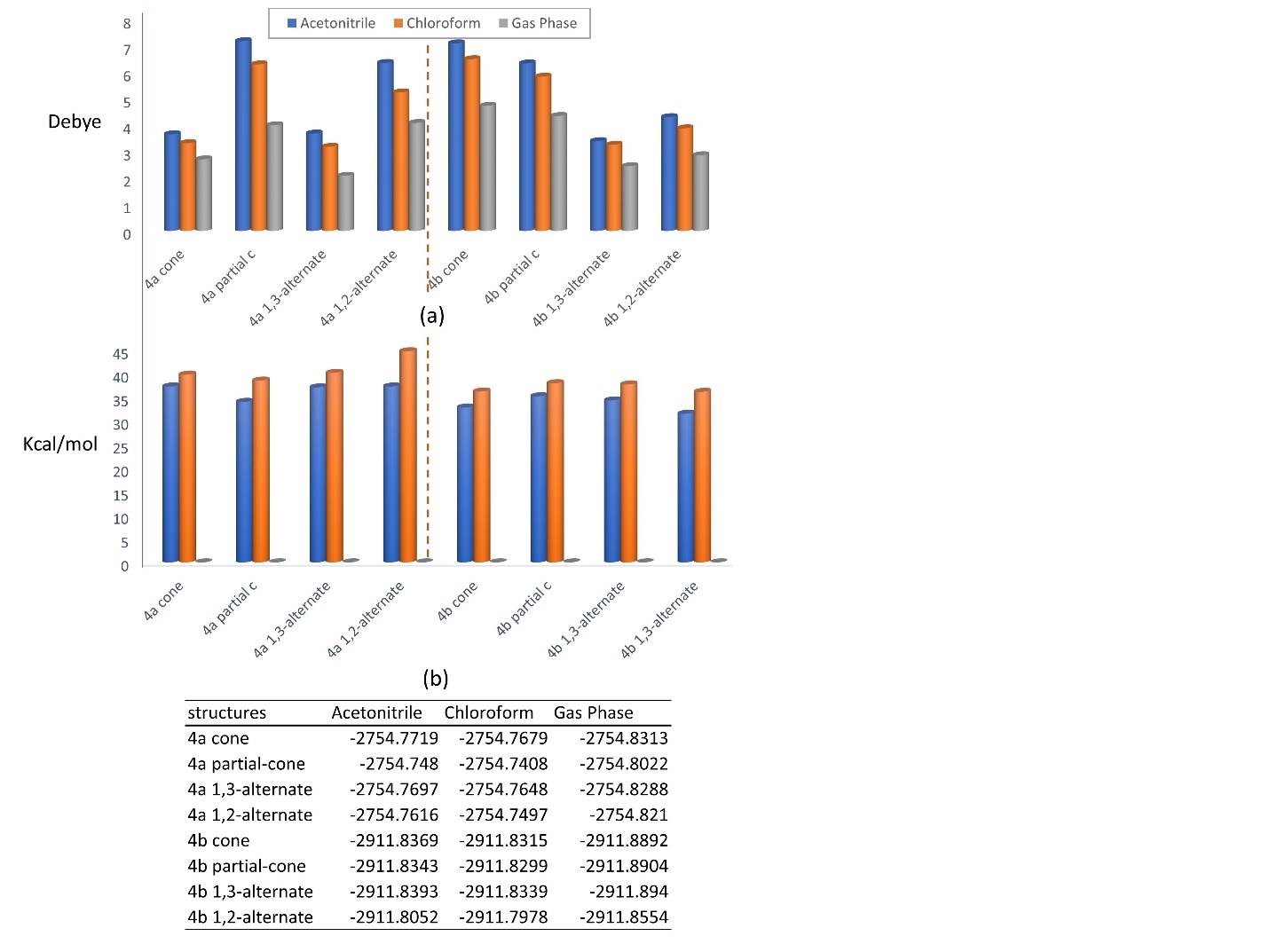


Figure S6. Solvation properties of calix[4]tetrolarenes (a) Dipole moments of conformers, (b) Energy difference of solvation phase and the gas phase (solvation energy)