# Computational Modelling of a Caged Methyl Cation: Structure, Energetics and Vibrational Analysis

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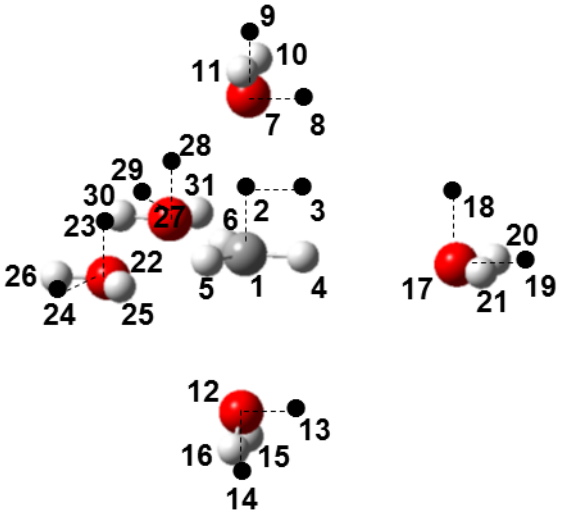
# Supporting Information

**Contents** **page**

**Table S1.** Z-matrix template for TS cage complexes.




```
C
X       1     c_1
X       2     c_1          1     c_90
H       1     v_CH         2     c_90         3     c_0
H       1     v_CH         2     c_90         3     c_120
H       1     v_CH         2     c_90         3   - c_120
O       1     c_Rax        4     c_90         3     c_0
X       7     c_1          1     c_90         4     c_0
X       7     c_1          8     c_90         1     c_180
H       7     v_HOax       9     v_Aax        8     c_90
H       7     v_HOax       9     v_Aax        8   - c_90
O       1     c_Rax        4     c_90         3     c_180
X      12     c_1          1     c_90         4     c_0
X      12     c_1         13     c_90         1     c_180
H      12     v_HOax      14     v_Aax       13     c_90
H      12     v_HOax      14     v_Aax       13   - c_90
O       1     c_Req        2     c_90         3     c_0
X      17     c_1          1     c_90         2     c_0
X      17     c_1         18     c_90         1     c_180
H      17     v_HOeq      19     v_Aeq       18     c_90
H      17     v_HOeq      19     v_Aeq       18   - c_90
O       1     c_Req        2     c_90         3     c_120
X      22     c_1          1     c_90         2     c_0
X      22     c_1         23     c_90         1     c_180
H      22     v_HOeq      24     v_Aeq       23     c_90
H      22     v_HOeq      24     v_Aeq       23   - c_90
O       1     c_Req        2     c_90         3   - c_120
X      27     c_1          1     c_90         2     c_0
X      27     c_1         28     c_90         1     c_180
H      27     v_HOeq      29     v_Aeq       28     c_90
H      27     v_HOeq      29     v_Aeq       28   - c_90
   Variables:
v_CH          1.1014
v_HOax        0.9664
v_Aax        55.0
v_HOeq        0.9656
v_Aeq        54.74
   Constants:
c_Rax         2.04          ! this is r_ax in the paper
c_Req         3.0           ! this is r_eq in the paper
c_0           0.0
c_1           1.0
c_90         90.0
c_120       120.0
c_180       180.0
```

**Table S2.** B3LYP/aug-cc-pVDZ optimised parameters for cage transition structures.

| Rax / Å | Req / Å | CH / Å | HOax / Å | Aax / ° | HOeq / Å | Aeq / ° |
|---|---|---|---|---|---|---|
| 2.04 | 3.0 | 1.08499 | 0.96469 | 54.6395 | 0.96596 | 52.277 |
| | 3.05 | 1.08591 | 0.96474 | 54.6675 | 0.96587 | 52.2825 |
| | 3.10 | 1.08664 | 0.96480 | 54.692 | 0.96579 | 52.287 |
| | 3.15 | 1.08719 | 0.96486 | 54.7135 | 0.96572 | 52.2915 |
| | 3.25 | 1.08790 | 0.96499 | 54.7475 | 0.96563 | 52.2985 |
| | 3.35 | 1.08220 | 0.96510 | 54.772 | 0.96556 | 52.302 |
| | 3.5 | 1.08817 | 0.96528 | 54.7945 | 0.96552 | 52.300 |
| | 3.75 | 1.08750 | 0.96554 | 54.8060 | 0.96551 | 52.2795 |
| | 4.0 | 1.08667 | 0.96576 | 54.8000 | 0.96553 | 52.251 |
| | 5.0 | 1.08502 | 0.96633 | 54.7275 | 0.96545 | 52.193 |
| 2.525 | 3.0 | 1.09642 | 0.96467 | 53.7425 | 0.96575 | 52.4315 |
| | 3.5 | 1.09693 | 0.96498 | 53.9960 | 0.96542 | 52.3712 |
| | 3.75 | 1.09561 | 0.96515 | 54.0535 | 0.96544 | 52.3275 |
| | 4.0 | 1.09436 | 0.96530 | 54.0862 | 0.96547 | 52.2835 |
| | 5.0 | 1.09205 | 0.96572 | 54.1055 | 0.96544 | 52.2005 |
| 3.0 | 3.0 | 1.10304 | 0.96505 | 52.9624 | 0.96574 | 52.5279 |
| | 3.5 | 1.10206 | 0.96519 | 53.1986 | 0.96541 | 52.4223 |
| | 3.75 | 1.10038 | 0.96528 | 53.2690 | 0.96543 | 52.3640 |
| | 4.0 | 1.09890 | 0.96536 | 53.3171 | 0.96546 | 52.3084 |
| | 5.0 | 1.09623 | 0.96565 | 53.3900 | 0.96544 | 52.2050 |
| 4.0 | 3.0 | 1.10865 | 0.96540 | 52.268 | 0.96592 | 52.600 |
| | 3.05 | 1.10891 | 0.96540 | 52.2755 | 0.96584 | 52.587 |
| | 3.10 | 1.10896 | 0.96540 | 52.2825 | 0.96577 | 52.574 |
| | 3.15 | 1.10888 | 0.96540 | 52.290 | 0.96572 | 52.561 |
| | 3.25 | 1.10841 | 0.96540 | 52.304 | 0.96564 | 52.5365 |
| | 3.35 | 1.10770 | 0.96540 | 52.317 | 0.96559 | 52.512 |
| | 3.5 | 1.10647 | 0.96541 | 52.335 | 0.96557 | 52.4745 |
| | 3.75 | 1.10428 | 0.96543 | 52.360 | 0.96562 | 52.409 |
| | 4.0 | 1.10220 | 0.96545 | 52.3745 | 0.96574 | 52.3505 |
| | 5.0 | 1.09738 | 0.96549 | 52.366 | 0.96623 | 52.2765 |

Continued on next page

| | | | | | | |
|---|---|---|---|---|---|---|
| 5.0 | 3.0 | 1.10998 | 0.96536 | 52.186 | 0.96608 | 52.530 |
| | 3.05 | 1.11018 | 0.96536 | 52.188 | 0.96600 | 52.587 |
| | 3.10 | 1.11019 | 0.96536 | 52.1895 | 0.96593 | 52.574 |
| | 3.15 | 1.11005 | 0.96536 | 52.191 | 0.96587 | 52.562 |
| | 3.25 | 1.10947 | 0.96536 | 52.194 | 0.96579 | 52.538 |
| | 3.35 | 1.10865 | 0.96536 | 52.1965 | 0.96575 | 52.515 |
| | 3.5 | 1.10722 | 0.96579 | 52.2005 | 0.96573 | 52.479 |
| | 3.75 | 1.10464 | 0.96378 | 52.205 | 0.96583 | 52.418 |
| | 4.0 | 1.10125 | 0.96619 | 52.2705 | 0.96568 | 52.346 |
| | 5.0 | 1.09721 | 0.96538 | 52.2125 | 0.96653 | 52.300 |

**Table S3.** Z-matrix template for RS cage complexes.

```
O
C       1     v_CO
H       2     v_CH      1     v_OCH
H       2     v_CH      1     v_OCH     3     c_120
H       2     v_CH      1     v_OCH     3   - c_120
H       1     v_HOax    2     c_Aax     3     c_90
H       1     v_HOax    2     c_Aax     3   - c_90
O       1     c_OO      6     c_Aax     2     c_0
H       8     v_HOax    2     c_Aax     3     c_90
H       8     v_HOax    2     c_Aax     3   - c_90
X       1     c_Rax     6     c_Aax     2     c_0
O      11     c_Req     1     c_90      3     c_0
H      12     c_HOeq   11     c_Aeq     1     c_90
H      12     c_HOeq   11     c_Aeq     1   - c_90
O      11     c_Req     1     c_90      3     c_120
H      15     c_HOeq   11     c_Aeq     1     c_90
H      15     c_HOeq   11     c_Aeq     1   - c_90
O      11     c_Req     1     c_90      3   - c_120
H      18     c_HOeq   11     c_Aeq     1     c_90
H      18     c_HOeq   11     c_Aeq     1   - c_90
  Variables:
v_CO        1.56677
v_CH        1.08504
v_OCH     102.0
  Constants:
c_OO        4.08          ! this is r_ax x 2
c_Rax       2.04          ! this is r_ax in the paper
c_Req       3.0           ! this is r_eq in the paper
c_HOax      0.96469
c_Aax     125.361
c_HOeq      0.96596
c_Aeq     127.723
c_0         0.0
c_90       90.0
c_120     120.0
```

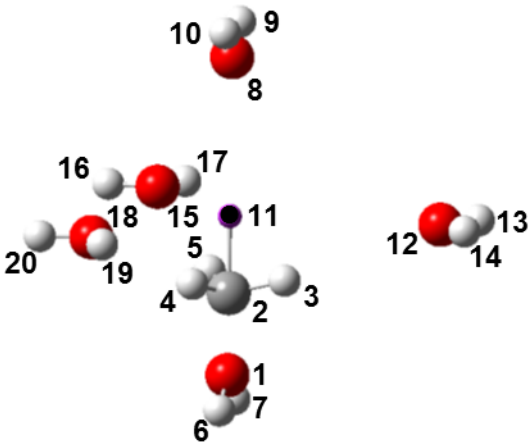


**Table S4.** B3LYP/aug-cc-pVDZ optimised parameters for cage reactant structures.

| $r_{ax}$ / Å | $r_{eq}$ / Å | CH / Å | CO / Å | HCOax / ° |
|---|---|---|---|---|
| 2.04 | 3.0 | 1.08609 | 1.583 | 102.249 |
| | 3.5 | 1.09039 | 1.563 | 102.825 |
| | 3.75 | 1.09010 | 1.568 | 103.174 |
| | 4.0 | 1.08959 | 1.563 | 103.428 |
| | 5.0 | 1.08850 | 1.553 | 103.953 |
| | ∞ | 1.08818 | 1.545 | 104.312 |
| 2.525 | 3.0 | 1.09287 | 1.569 | 103.831 |
| | 3.5 | 1.09420 | 1.563 | 104.185 |
| | 3.75 | 1.09359 | 1.557 | 104.375 |
| | 4.0 | 1.09289 | 1.551 | 104.552 |
| | 5.0 | 1.09166 | 1.540 | 104.935 |
| | ∞ | 1.09117 | 1.533 | 105.188 |
| 3.0 | 3.0 | 1.09513 | 1.565 | 104.472 |
| | 3.5 | 1.09452 | 1.554 | 104.631 |
| | 3.75 | 1.09384 | 1.547 | 104.713 |
| | 4.0 | 1.09322 | 1.543 | 104.811 |
| | 5.0 | 1.09224 | 1.532 | 105.058 |
| | ∞ | 1.09176 | 1.524 | 105.278 |
| 4.0 | 3.0 | 1.09343 | 1.553 | 105.079 |
| | 3.5 | 1.09303 | 1.542 | 105.0541 |
| | 3.75 | 1.09279 | 1.538 | 105.077 |
| | 4.0 | 1.09263 | 1.535 | 105.0771 |
| | 5.0 | 1.09222 | 1.528 | 105.156 |
| | ∞ | 1.09197 | 1.519 | 105.311 |
| 5.0 | 3.0 | 1.09208 | 1.537 | 105.199 |
| | 3.5 | 1.09213 | 1.532 | 105.196 |
| | 3.75 | 1.09213 | 1.531 | 105.198 |
| | 4.0 | 1.09206 | 1.530 | 105.181 |
| | 5.0 | 1.09210 | 1.525 | 105.219 |
| | ∞ | 1.09200 | 1.517 | 105.322 |

**Table S5.** B3LYP/aug-cc-pVDZ optimised bond lengths (Å) and angles (degrees) for unconstrained RS and TS with $r_{eq} = \infty$.

RS

| OC / Å | C···O / Å | CH / Å | $HO_{lg}$ / Å | $HO_{nuc}$ / Å | $COH_{lg}$ / ° | $HCO_{lg}$ / ° | $COH_{lg}$ / ° |
|---|---|---|---|---|---|---|---|
| 1.55219 | 2.67557 | 1.08941 | 0.97623 | 0.96626 | 113.943 | 104.854 | 127.807 |

TS

| $r_{ax}$ / Å | CH / Å | HO / Å | COH / ° |
|---|---|---|---|
| 1.98619 | 1.08388 | 0.96995 | 116.684 |

**Table S6.** B3LYP/aug-cc-pVDZ optimised energies for RS and TS structures (total energies in hartree, relative energies in kJ mol$^{-1}$).

| | | $r_{eq}$ | | | | | |
|---|---|---|---|---|---|---|---|
| $r_{ax}$ | | 3.0 | 3.5 | 3.75 | 4.0 | 5.0 | ∞ |
| 2.04 | $E_{RS}$ | -421.86098 | -421.86284 | -421.85963 | -421.85637 | -421.84710 | -192.49373 |
| | $E_{TS}$ | -421.85431 | -421.85515 | -421.85132 | -421.84755 | -421.83715 | -192.48296 |
| | $\Delta E^{‡}$ | 17.5 | 20.2 | 21.8 | 23.2 | 26.1 | 28.3 |
| 2.525 | $E_{RS}$ | -421.85795 | -421.85585 | -421.85265 | -421.84965 | -421.84143 | -192.48948 |
| | $E_{TS}$ | -421.83256 | -421.82884 | -421.82388 | -421.81939 | -421.80797 | -192.45370 |
| | $\Delta E^{‡}$ | 66.6 | 70.9 | 75.5 | 79.4 | 87.8 | 93.9 |
| 3.0 | $E_{RS}$ | -421.85239 | -421.84793 | -421.84511 | -421.84261 | -421.83569 | -192.48528 |
| | $E_{TS}$ | -421.81262 | -421.80504 | -421.79898 | -421.79371 | -421.78092 | -192.42612 |
| | $\Delta E^{‡}$ | 104 | 113 | 121 | 128 | 144 | 155 |
| 4.0 | $E_{RS}$ | -421.83788 | -421.83513 | -421.83379 | -421.83255 | -421.82869 | -192.48172 |
| | $E_{TS}$ | -421.79497 | -421.78306 | -421.77555 | -421.76925 | -421.75556 | -192.39894 |
| | $\Delta E^{‡}$ | 113 | 137 | 153 | 166 | 192 | 217 |
| 5.0 | $E_{RS}$ | -421.82682 | -421.82647 | -421.82614 | -421.82577 | -421.82411 | -192.48027 |
| | $E_{TS}$ | -421.78945 | -421.77622 | -421.76826 | -421.76244 | -421.74783 | -192.39280 |
| | $\Delta E^{‡}$ | 98 | 132 | 152 | 166 | 200 | 230 |
| unconstrained | | | | | | | |
| | $E_{RS}$ | -192.49915 | | | | | |
| | $E_{TS}$ | -192.48649 | | | | | |
| | $\Delta E^{‡}$ | 33.2 | | | | | |

**Table S7**. B3LYP/aug-cc-pVDZ average CH-bond stretching force constants (aJ $Å^{-2}$) for RS and TS.

| | | $rO_{eq}$ | | | | | |
|---|---|---|---|---|---|---|---|
| $rO_{ax}$ | | 3.0 | 3.5 | 3.75 | 4.0 | 5.0 | ∞ |
| 2.04 | $(CH)_{RS}$ | 5.763 | 5.620 | 5.633 | 5.654 | 5.708 | 5.730 |
| | $(CH)_{TS}$ | 5.863 | 5.752 | 5.779 | 5.812 | 5.888 | 5.926 |
| | $\Delta^{‡}$ | 0.100 | 0.132 | 0.146 | 0.158 | 0.180 | 0.196 |
| | $\Delta\Delta^{‡}_{eq}$ | -0.096 | -0.064 | -0.050 | -0.038 | -0.016 | |
| 2.525 | $(CH)_{RS}$ | 5.528 | 5.502 | 5.524 | 5.549 | 5.603 | 5.626 |
| | $(CH)_{TS}$ | 5.543 | 5.540 | 5.590 | 5.636 | 5.733 | 5.779 |
| | $\Delta^{‡}$ | 0.015 | 0.038 | 0.066 | 0.087 | 0.130 | 0.153 |
| | $\Delta\Delta^{‡}_{eq}$ | -0.138 | -0.115 | -0.087 | -0.066 | -0.023 | |
| 3.0 | $(CH)_{RS}$ | 5.467 | 5.496 | 5.518 | 5.540 | 5.580 | 5.600 |
| | $(CH)_{TS}$ | 5.320 | 5.376 | 5.440 | 5.495 | 5.605 | 5.654 |
| | $\Delta^{‡}$ | -0.147 | -0.120 | -0.078 | -0.045 | 0.025 | 0.054 |
| | $\Delta\Delta^{‡}_{eq}$ | -0.201 | -0.174 | -0.132 | -0.099 | -0.029 | |
| 4.0 | $(CH)_{RS}$ | 5.547 | 5.560 | 5.566 | 5.571 | 5.583 | 5.589 |
| | $(CH)_{TS}$ | 5.121 | 5.218 | 5.297 | 5.369 | 5.544 | 5.578 |
| | $\Delta^{‡}$ | -0.426 | -0.342 | -0.269 | -0.202 | -0.039 | -0.011 |
| | $\Delta\Delta^{‡}_{eq}$ | -0.415 | -0.331 | -0.258 | -0.191 | -0.028 | |
| 5.0 | $(CH)_{RS}$ | 5.629 | 5.608 | 5.602 | 5.600 | 5.590 | 5.587 |
| | $(CH)_{TS}$ | 5.071 | 5.184 | 5.275 | 5.388 | 5.541 | 5.597 |
| | $\Delta^{‡}$ | -0.558 | -0.424 | -0.327 | -0.212 | -0.049 | 0.010 |
| | $\Delta\Delta^{‡}_{eq}$ | -0.568 | -0.434 | -0.337 | -0.222 | -0.059 | |

**Table S8**. B3LYP/aug-cc-pVDZ unscaled harmonic frequencies (as wavenumbers, $cm^{-1}$) for internal vibrational modes of methyl cation in the centre a constrained cage (TS geometry). Values for CH stretching and in-plane bending (IP) are averages. Values shown in bold type are produced from the full 57 × 57 Hessian. Values shown in regular type are produced by eliminating all elements of the full 57 × 57 Hessian except for the 12 × 12 block corresponding to $Me^+$ alone but are identical to those from the full Hessian. Values in *italic* type result from projecting out the translational and rotational degrees of freedom from the 12 × 12 Hessian to obtain six pure vibrational modes for the internal degrees of freedom.

| mode | $r_{ax}$ / Å | $r_{eq}$ / Å | | | | | |
|---|---|---|---|---|---|---|---|
| | | 3.0 | 3.5 | 3.75 | 4.0 | 5.0 | ∞ |
| ⟨CH⟩ | 2.04 | **3245** | **3229** | **3239** | **3251** | **3278** | **3290** |
| | | 3245 | 3229 | 3239 | 3251 | 3278 | 3290 |
| | | *3261* | *3252* | *3263* | *3274* | *3299* | *3310* |
| | 2.525 | **3130** | **3159** | **3179** | **3196** | **3231** | **3247** |
| | | 3130 | 3159 | 3179 | 3196 | 3231 | 3247 |
| | | *3140* | *3171* | *3190* | *3207* | *3240* | *3254* |
| | 3 | **3054** | **3108** | **3134** | **3155** | **3194** | **3211** |
| | | 3054 | 3108 | 3134 | 3155 | 3194 | 3211 |
| | | *3063* | *3116* | *3141* | *3161* | *3198* | *3214* |
| | 4 | **2987** | **3059** | **3090** | **3116** | **3175** | **3188** |
| | | 2987 | 3059 | 3090 | 3116 | 3175 | 3188 |
| | | *2997* | *3066* | *3096* | *3118* | *3164* | *3188* |
| | 5 | **2969** | **3047** | **3083** | **3121** | **3174** | **3193** |
| | | 2969 | 3047 | 3083 | 3121 | 3174 | 3193 |
| | | *2980* | *3055* | *3088* | *3126* | *3176* | *3193* |
| | ∞ | **2956** | **3040** | **3080** | **3113** | **3177** | **3148** |
| | | 2954 | 3040 | 3080 | 3113 | 3177 | 3148 |
| | | *2966* | *3048* | *3086* | *3118* | *3178* | *3148* |
| ⟨IP⟩ | 2.04 | **1452** | **1427** | **1417** | **1410** | **1396** | **1390** |
| | | 1452 | 1427 | 1417 | 1410 | 1396 | 1390 |
| | | *1453* | *1433* | *1427* | *1423* | *1417* | *1414* |
| | 2.525 | **1452** | **1431** | **1420** | **1412** | **1399** | **1392** |
| | | 1452 | 1431 | 1420 | 1412 | 1399 | 1392 |
| | | *1437* | *1418* | *1412* | *1408* | *1403* | *1400* |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3 | **1462** | **1432** | **1420** | **1412** | **1399** | **1391** |
| | | 1462 | 1432 | 1420 | 1412 | 1399 | 1391 |
| | | *1433* | *1413* | *1408* | *1403* | *1398* | *1395* |
| | 4 | **1462** | **1431** | **1419** | **1413** | **1398** | **1394** |
| | | 1462 | 1431 | 1419 | 1413 | 1398 | 1394 |
| | | *1428* | *1409* | *1403* | *1395* | *1372* | *1393* |
| | 5 | **1461** | **1429** | **1417** | **1410** | **1397** | **1393** |
| | | 1461 | 1429 | 1417 | 1410 | 1397 | 1393 |
| | | *1426* | *1407* | *1401* | *1399* | *1394* | *1392* |
| | ∞ | **1460** | **1429** | **1417** | **1409** | **1397** | **1386** |
| | | 1461 | 1428 | 1417 | 1409 | 1397 | 1386 |
| | | *1425* | *1406* | *1401* | *1397* | *1394* | *1386* |
| OP (**UM**) | 2.04 | **1364** | **1330** | **1315** | **1304** | **1283** | **1272** |
| | | 1360 | 1324 | 1309 | 1298 | 1274 | 1263 |
| | | *810* | *735* | *705* | *681* | *629* | *599* |
| | 2.525 | **1387** | **1340** | **1321** | **1307** | **1279** | **1265** |
| | | 1360 | 1344 | 1325 | 1311 | 1283 | 1269 |
| | | *1213* | *1160* | *1139* | *1122* | *1089* | *1069* |
| | 3 | **1448** | **1406** | **1389** | **1376** | **1349** | **1335** |
| | | 1449 | 1407 | 1390 | 1377 | 1351 | 1338 |
| | | *1370* | *1333* | *1317* | *1304* | *1276* | *1260* |
| | 4 | **1486** | **1450** | **1432** | **1414** | **1351** | **1349** |
| | | 1486 | 1450 | 1432 | 1410 | 1351 | 1349 |
| | | *1454* | *1432* | *1419* | *1402* | *1341* | *1339* |
| | 5 | **1493** | **1453** | **1431** | **1387** | **1338** | **1313** |
| | | 1492 | 1453 | 1431 | 1387 | 1338 | 1313 |
| | | *1466* | *1443* | *1425* | *1383* | *1337* | *1313* |
| | ∞ | **1497** | **1453** | **1425** | **1397** | **1322** | **1429** |
| | | 1497 | 1453 | 1425 | 1397 | 1322 | 1429 |
| | | *1471* | *1443* | *1420* | *1395* | *1321* | *1428* |

**Table S9**. B3LYP/aug-cc-pVDZ unscaled harmonic frequencies (as wavenumbers, $cm^{-1}$) for methyl cation in the centre a constrained cage (TS geometry), as obtained from the reduced Hessian: all elements of the full 57 × 57 Hessian are eliminated except for the 12 × 12 block corresponding to $Me^+$ alone.

| mode | $r_{ax}$ / Å | $r_{eq}$ / Å | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 3.0 | 3.05 | 3.10 | 3.15 | 3.25 | 3.35 | 3.5 | 3.75 | 4.0 | 5.0 | ∞ |
| | 2.04 | | | | | | | | | | | |
| $T_z$ | | 260i | 261i | 263i | 264i | 267i | 271i | 276i | 283i | 288i | 300i | 307i |
| $T_x$ | | 284 | 270 | 258 | 248 | 229 | 214 | 199 | 185 | 183 | 186 | 97i |
| $R_z$ | | 293 | 303 | 308 | 306 | 294 | 284 | 288 | 240 | 201 | 90 | 44i |
| $T_y$ | | 341 | 330 | 322 | 318 | 313 | 305 | 271 | 272 | 269 | 272 | 274 |
| $R_y$ | | 1026 | 1029 | 1030 | 1030 | 1028 | 1024 | 1017 | 1006 | 998 | 983 | 924 |
| $R_x$ | | 1054 | 1057 | 1058 | 1058 | 1057 | 1054 | 1049 | 1040 | 1032 | 1017 | 1010 |
| OP | | 1360 | 1358 | 1355 | 1351 | 1343 | 1335 | 1324 | 1309 | 1298 | 1274 | 1263 |
| IP’ | | 1441 | 1439 | 1436 | 1433 | 1428 | 1423 | 1415 | 1405 | 1398 | 1384 | 1379 |
| IP” | | 1462 | 1460 | 1458 | 1455 | 1450 | 1445 | 1438 | 1428 | 1421 | 1407 | 1401 |
| CH | | 3105 | 3097 | 3092 | 3088 | 3083 | 3082 | 3084 | 3095 | 3107 | 3134 | 3146 |
| CH’ | | 3313 | 3307 | 3303 | 3300 | 3298 | 3298 | 3301 | 3311 | 3323 | 3349 | 3361 |
| CH” | | 3316 | 3309 | 3305 | 3302 | 3298 | 3298 | 3302 | 3312 | 3324 | 3350 | 3363 |

| mode | $r_{ax}$ / Å | $r_{eq}$ / Å | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 3.0 | 3.05 | 3.10 | 3.15 | 3.25 | 3.35 | 3.5 | 3.75 | 4.0 | 5.0 | ∞ |
| | 2.525 | | | | | | | | | | | |
| $T_z$ | | 207i | | | | | | 211 | 216i | 221i | 230i | 236i |
| $T_x$ | | 241 | | | | | | 138 | 120 | 114 | 121 | 146i |
| $R_z$ | | 372 | | | | | | 317 | 269 | 223 | 105 | 27i |
| $T_y$ | | 264 | | | | | | 176 | 163 | 161 | 167 | 171 |
| $R_y$ | | 592 | | | | | | 594 | 574 | 558 | 530 | 465 |
| $R_x$ | | 630 | | | | | | 627 | 610 | 596 | 570 | 560 |
| OP | | 1360 | | | | | | 1344 | 1325 | 1311 | 1283 | 1269 |
| IP’ | | 1441 | | | | | | 1427 | 1416 | 1408 | 1395 | 1386 |
| IP” | | 1462 | | | | | | 1434 | 1424 | 1416 | 1403 | 1398 |
| CH | | 3105 | | | | | | 3016 | 3035 | 3052 | 3087 | 3102 |
| CH’ | | 3313 | | | | | | 3230 | 3251 | 3268 | 3303 | 3319 |
| CH” | | 3316 | | | | | | 3231 | 3252 | 3269 | 3304 | 3319 |
| | 3.0 | | | | | | | | | | | |
| $T_z$ | | 150i | | | | | | 149i | 156i | 162i | 173i | 180i |
| $T_x$ | | 220 | | | | | | 98 | 74 | 65 | 77 | 174i |
| $R_z$ | | 411 | | | | | | 407 | 282 | 234 | 112 | 22i |
| $T_y$ | | 229 | | | | | | 121 | 102 | 98 | 107 | 114 |
| $R_y$ | | 400 | | | | | | 335 | 382 | 357 | 309 | 223 |
| $R_x$ | | 427 | | | | | | 432 | 407 | 385 | 343 | 327 |
| OP | | 1449 | | | | | | 1407 | 1390 | 1377 | 1351 | 1338 |
| IP’ | | 1460 | | | | | | 1430 | 1418 | 1410 | 1397 | 1386 |
| IP” | | 1463 | | | | | | 1433 | 1422 | 1414 | 1400 | 1395 |
| CH | | 2926 | | | | | | 2967 | 2992 | 3012 | 3051 | 3068 |
| CH’ | | 3118 | | | | | | 3178 | 3204 | 3226 | 3265 | 3281 |
| CH” | | 3119 | | | | | | 3178 | 3205 | 3227 | 3266 | 3283 |

| mode | $r_{ax}$ / Å | $r_{eq}$ / Å | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 3.0 | 3.05 | 3.10 | 3.15 | 3.25 | 3.35 | 3.5 | 3.75 | 4.0 | 5.0 | ∞ |
| | 4.0 | | | | | | | | | | | |
| $T_z$ | | 41i | 20i | 21 | 31 | 37 | 35 | 19 | 38i | 62i | 75 | 96i |
| $T_x$ | | 205 | 184 | 166 | 149 | 119 | 93 | 59 | 37i | 173i | 364i | 29i |
| $R_z$ | | 440 | 437 | 430 | 422 | 403 | 382 | 349 | 293 | 240 | 104 | 50 |
| $T_y$ | | 207 | 186 | 168 | 152 | 122 | 98 | 67 | 23 | 23i | 33 | 65 |
| $R_y$ | | 303 | 319 | 328 | 332 | 332 | 324 | 305 | 263 | 68 | 483i | 75 |
| $R_x$ | | 309 | 324 | 334 | 338 | 338 | 331 | 313 | 275 | 236 | 133 | 108 |
| OP | | 1486 | 1483 | 1480 | 1476 | 1469 | 1461 | 1450 | 1432 | 1410 | 1398 | 1349 |
| IP’ | | 1462 | 1458 | 1455 | 1452 | 1445 | 1439 | 1430 | 1418 | 1411 | 1399 | 1393 |
| IP” | | 1462 | 1459 | 1456 | 1452 | 1446 | 1439 | 1431 | 1419 | 1414 | 1351 | 1395 |
| CH | | 2863 | 2864 | 2868 | 2873 | 2885 | 2899 | 2918 | 2945 | 2967 | 3027 | 3041 |
| CH’ | | 3048 | 3054 | 3062 | 3070 | 3087 | 3105 | 3129 | 3162 | 3190 | 3247 | 3261 |
| CH” | | 3049 | 3055 | 3062 | 3071 | 3088 | 3105 | 3129 | 3163 | 3191 | 3250 | 3262 |
| | 5.0 | | | | | | | | | | | |
| $T_z$ | | 56 | 67 | 74 | 78 | 81 | 81 | 77 | 65 | 47 | 22i | 44i |
| $T_x$ | | 201 | 181 | 162 | 145 | 113 | 88 | 50 | 39i | 48i | 24i | 92 |
| $R_z$ | | 450 | 445 | 439 | 430 | 410 | 388 | 354 | 296 | 241 | 103 | 25i |
| $T_y$ | | 202 | 181 | 162 | 146 | 115 | 89 | 52 | 36i | 46i | 21i | 26 |
| $R_y$ | | 306 | 322 | 331 | 336 | 336 | 328 | 309 | 269 | 225 | 109 | 33 |
| $R_x$ | | 306 | 322 | 331 | 336 | 336 | 328 | 310 | 269 | 225 | 112 | 29 |
| OP | | 1492 | 1489 | 1486 | 1482 | 1474 | 1466 | 1453 | 1431 | 1387 | 1338 | 1313 |
| IP’ | | 1461 | 1457 | 1454 | 1451 | 1444 | 1437 | 1429 | 1417 | 1410 | 1397 | 1393 |
| IP | | 1461 | 1458 | 1454 | 1451 | 1444 | 1437 | 1429 | 1417 | 1410 | 1397 | 1395 |
| CH | | 2845 | 2847 | 2851 | 2857 | 2870 | 2884 | 2904 | 2934 | 2972 | 3027 | 3048 |
| CH’ | | 3031 | 3037 | 3046 | 3055 | 3074 | 3093 | 3119 | 3157 | 3196 | 3248 | 3265 |
| CH” | | 3031 | 3038 | 3046 | 3055 | 3074 | 3093 | 3119 | 3157 | 3196 | 3248 | 3266 |

| mode | $r_{ax}$ / Å | $r_{eq}$ / Å |
|---|---|---|
| | | ∞ |
| | ∞ | |
| OP | | 1428 |
| IP’ | | 1386 |
| IP” | | 1386 |
| CH | | 3011 |
| CH’ | | 3217 |
| CH” | | 3217 |

**Table S10**. B3LYP/aug-cc-pVDZ unscaled force constants for methyl cation in the centre a constrained cage (TS geometry), as obtained from the reduced Hessian, for OP (/aJ rad$^{-2}$), $T_z$ (/aJ Å$^{-2}$) and the interaction force constant OP/$T_z$ between them (aJ rad$^{-1}$Å$^{-1}$).

| $r_{ax}$ / Å | term | $r_{eq}$ / Å | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 3.0 | 3.05 | 3.10 | 3.15 | 3.25 | 3.35 | 3.5 | 3.75 | 4.0 | 5.0 | ∞ |
| 2.04 | OP | 0.121 | 0.120 | 0.118 | 0.116 | 0.111 | 0.107 | 0.101 | 0.093 | 0.086 | 0.074 | 0.067 |
| | $T_z$ | *0.018* | *0.017* | *0.017* | *0.017* | *0.017* | *0.017* | *0.017* | *0.015* | *0.015* | *0.013* | *0.012* |
| | OP/$T_z$ | **0.122** | **0.122** | **0.123** | **0.123** | **0.123** | **0.124** | **0.124** | **0.125** | **0.125** | **0.126** | **0.127** |
| 2.525 | OP | 0.279 | | | | | | 0.256 | 0.246 | 0.238 | 0.223 | 0.215 |
| | $T_z$ | *-0.016* | | | | | | *-0.018* | *-0.019* | *-0.021* | *-0.023* | *-0.024* |
| | OP/$T_z$ | **0.061** | | | | | | **0.061** | **0.061** | **0.061** | **0.062** | **0.063** |
| 3.0 | OP | 0.361 | | | | | | 0.341 | 0.332 | 0.325 | 0.309 | 0.301 |
| | $T_z$ | *-0.011* | | | | | | *-0.011* | *-0.013* | *-0.014* | *-0.016* | *-0.017* |
| | OP/$T_z$ | **0.031** | | | | | | **0.029** | **0.029** | **0.029** | **0.029** | **0.030** |
| 4.0 | OP | 0.411 | 0.410 | 0.409 | 0.408 | 0.405 | 0.402 | 0.397 | 0.388 | 0.378 | 0.342 | 0.341 |
| | $T_z$ | *0.0004* | *0.00004* | *0.0005* | *0.0008* | *0.0009* | *0.0008* | *0.0005* | *-0.001* | *-0.002* | *-0.003* | *-0.004* |
| | OP/$T_z$ | **0.012** | **0.011** | **0.010** | **0.009** | **0.008** | **0.007** | **0.006** | **0.005** | **0.005** | **0.004** | **0.005** |
| 5.0 | OP | 0.418 | 0.418 | 0.417 | 0.416 | 0.412 | 0.409 | 0.403 | 0.391 | 0.367 | 0.340 | 0.327 |
| | $T_z$ | *0.002* | *0.003* | *0.003* | *0.004* | *0.004* | *0.004* | *0.003* | *0.002* | *0.001* | *-0.0003* | *-0.0009* |
| | OP/$T_z$ | **0.009** | **0.008** | **0.007** | **0.006** | **0.005** | **0.004** | **0.002** | **0.001** | **0.001** | **0.0005** | **0.0007** |
| ∞ | OP | 0.422 | | | | | | 0.404 | 0.389 | 0.373 | 0.332 | |
| | $T_z$ | *0.003* | | | | | | *0.005* | *0.004* | *0.003* | *0.001* | |
| | OP/$T_z$ | **0.008** | | | | | | **0.001** | **0.0003** | **-0.0002** | **-0.0001** | |

**Table S11.** B3LYP/aug-cc-pVDZ electrostatic potential (ESP) and atomic polar tensor (APT) charges for cage transition structures.

| | | ESP | | | APT | | |
|---|---|---|---|---|---|---|---|
| $r_{ax}$ / Å | $r_{eq}$ / Å | $\langle q_H \rangle$ | $q_C$ | $q_{Me}$ | $\langle q_H \rangle$ | $q_C$ | $q_{Me}$ |
| 2.04 | 3 | 0.941 | -1.723 | 1.049 | 0.159 | 0.721 | 1.197 |
| | 3.05 | 0.931 | -1.724 | 1.035 | 0.150 | 0.741 | 1.192 |
| | 3.1 | 0.916 | -1.729 | 1.020 | 0.142 | 0.760 | 1.186 |
| | 3.15 | 0.916 | -1.740 | 1.007 | 0.135 | 0.776 | 1.182 |
| | 3.25 | 0.827 | -1.511 | 0.972 | 0.123 | 0.805 | 1.174 |
| | 3.35 | 0.733 | -1.258 | 0.941 | 0.113 | 0.829 | 1.168 |
| | 3.5 | 0.640 | -1.012 | 0.907 | 0.102 | 0.856 | 1.162 |
| | 3.75 | 0.484 | -0.583 | 0.870 | 0.089 | 0.887 | 1.154 |
| | 4 | 0.417 | -0.406 | 0.845 | 0.082 | 0.905 | 1.150 |
| | 5 | 0.299 | -0.095 | 0.802 | 0.071 | 0.931 | 1.145 |
| 2.525 | 3 | 0.608 | -0.782 | 1.043 | 0.212 | 0.523 | 1.158 |
| | 3.5 | 0.464 | -0.448 | 0.944 | 0.150 | 0.666 | 1.116 |
| | 3.75 | 0.380 | -0.232 | 0.909 | 0.136 | 0.698 | 1.107 |
| | 4 | 0.333 | -0.103 | 0.895 | 0.128 | 0.717 | 1.100 |
| | 5 | 0.293 | 0.003 | 0.849 | 0.115 | 0.743 | 1.089 |
| 3 | 3 | 0.349 | -0.019 | 1.028 | 0.244 | 0.414 | 1.145 |
| | 3.5 | 0.269 | 0.163 | 0.971 | 0.182 | 0.564 | 1.110 |
| | 3.75 | 0.238 | 0.245 | 0.952 | 0.168 | 0.597 | 1.100 |
| | 4 | 0.223 | 0.275 | 0.940 | 0.158 | 0.617 | 1.093 |
| | 5 | 0.227 | 0.226 | 0.909 | 0.144 | 0.645 | 1.077 |
| 4 | 3 | 0.214 | 0.347 | 0.989 | 0.266 | 0.307 | 1.106 |
| | 3.05 | 0.206 | 0.368 | 0.985 | 0.257 | 0.328 | 1.100 |
| | 3.1 | 0.196 | 0.392 | 0.980 | 0.249 | 0.348 | 1.095 |
| | 3.15 | 0.188 | 0.412 | 0.977 | 0.241 | 0.367 | 1.091 |
| | 3.25 | 0.174 | 0.450 | 0.971 | 0.228 | 0.399 | 1.082 |
| | 3.35 | 0.168 | 0.465 | 0.969 | 0.216 | 0.427 | 1.075 |
| | 3.5 | 0.156 | 0.498 | 0.965 | 0.201 | 0.460 | 1.063 |
| | 3.75 | 0.146 | 0.515 | 0.958 | 0.177 | 0.499 | 1.031 |
| | 4 | 0.147 | 0.504 | 0.946 | 0.145 | 0.416 | 0.851 |
| | 5 | 0.172 | 0.360 | 0.876 | 0.103 | 0.119 | 0.428 |
| 5 | 3 | 0.211 | 0.345 | 0.979 | 0.269 | 0.287 | 1.095 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 3.05 | 0.199 | 0.369 | 0.975 | 0.260 | 0.309 | 1.088 |
| 3.1 | 0.192 | 0.396 | 0.970 | 0.251 | 0.329 | 1.082 |
| 3.15 | 0.182 | 0.419 | 0.966 | 0.243 | 0.348 | 1.076 |
| 3.25 | 0.166 | 0.462 | 0.959 | 0.228 | 0.381 | 1.064 |
| 3.35 | 0.158 | 0.481 | 0.957 | 0.214 | 0.410 | 1.053 |
| 3.5 | 0.145 | 0.514 | 0.951 | 0.195 | 0.444 | 1.030 |
| 3.75 | 0.136 | 0.529 | 0.938 | 0.162 | 0.474 | 0.959 |
| 4 | 0.146 | 0.448 | 0.887 | 0.131 | 0.382 | 0.776 |
| 5 | 0.161 | 0.338 | 0.822 | 0.113 | 0.342 | 0.682 |

**Full citation for reference 15**

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