**Supplementary Material**

Table 1-S. Frequencies, ν and IR intensities, I, in $cm^{-1}$ and km/mol, respectively.

$C_5^{2-}$

| | B3LYP | | MP2 | |
|---|---|---|---|---|
| | ν | I | ν | I |
| $\nu_1(a_g)$ | 1552 | 0.0 | 1489.2 | 0.0 |
| $\nu_2(a_g)$ | 682 | 0.0 | 713 | 0.0 |
| $\nu_3(b_{3g})$ | 645 | 0.0 | 673 | 0.0 |
| $\nu_4(a_u)$ | 172 | 0.0 | 182 | 0.0 |
| $\nu_5(b_{1u})$ | 1590 | 7.8 | 1571 | 6.2 |
| $\nu_6(b_{1u})$ | 563 | 137.3 | 739 | 119.3 |
| $\nu_7(b_{2u})$ | 807 | 147.0 | 871 | 151.4 |
| $\nu_8(b_{2u})$ | 363 | 1.5 | 356 | 0.6 |
| $\nu_9(b_{3u})$ | 535 | 79.2 | 543 | 67.1 |

Table 2-S. HOMO, LUMO, hardness, η, chemical potential, μ, and electrophilicity, ω, in atomic units. These values are from the B3LYP calculations.

| | HOMO | LUMO | η | μ | ω |
|---|---|---|---|---|---|
| $C_5^{2-}$ | 0.15718 | 0.26461 | 0.10743 | 0.210895 | 0.207003 |
| $C_5Li^-$ | -0.0223 | 0.05931 | 0.08161 | 0.018505 | 0.002098 |
| $C_5Na^-$ | -0.01237 | 0.04646 | 0.05883 | 0.017045 | 0.002469 |
| $C_5K^-$ | -0.00371 | 0.03964 | 0.04335 | 0.017965 | 0.003723 |
| $C_5Li_2$ | -0.20542 | -0.04059 | 0.16483 | -0.12301 | 0.045896 |
| $C_5Na_2$ | -0.17288 | -0.03984 | 0.13304 | -0.10636 | 0.042515 |
| $C_5K_2$ | -0.14947 | -0.03029 | 0.11918 | -0.08988 | 0.033892 |

Table 3-S. Frequencies, ν and IR intensities, I, in $cm^{-1}$ and km/mol, respectively.

| $C_5Li^-$ | | | | | $C_5Li_2$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | B3LYP | | MP2 | | | B3LYP | | MP2 | |
| | ν | I | ν | I | | ν | I | ν | I |
| $\nu_1(a_1)$ | 1590 | 4.6 | 1534 | 0.5 | $\nu_1(a_g)$ | 1626 | 0.0 | 1572 | 0 |
| $\nu_2(a_1)$ | 874 | 132.9 | 932 | 118.8 | $\nu_2(a_g)$ | 736 | 0.0 | 762 | 0 |
| $\nu_3(a_1)$ | 719 | 0.2 | 751 | 2.1 | $\nu_3(a_g)$ | 480 | 0.0 | 489 | 0 |
| $\nu_4(a_1)$ | 554 | 65.9 | 569 | 87.5 | $\nu_4(b_{2g})$ | 286 | 0.0 | 267 | 0 |
| $\nu_5(a_1)$ | 402 | 4.9 | 401 | 8.0 | $\nu_5(b_{3g})$ | 678 | 0.0 | 699 | 0 |
| $\nu_6(a_2)$ | 220 | 0.0 | 231 | 0.0 | $\nu_6(b_{3g})$ | 477 | 0.0 | 499 | 0 |
| $\nu_7(b_1)$ | 507 | 46.6 | 520 | 43.2 | $\nu_7(a_u)$ | 286 | 0.0 | 285 | 0 |
| $\nu_8(b_1)$ | 224 | 22.6 | 215 | 26.2 | $\nu_8(b_{1u})$ | 928 | 108.0 | 982 | 0 |
| $\nu_9(b_2)$ | 1611 | 14.9 | 1596 | 13.3 | $\nu_9(b_{1u})$ | 569 | 261.4 | 579 | 266.2 |
| $\nu_{10}(b_2)$ | 682 | 16.7 | 818.8 | 30.4 | $\nu_{10}(b_{1u})$ | 415 | 45.7 | 409 | 50.5 |
| $\nu_{11}(b_2)$ | 635 | 5.1 | 675 | 2.0 | $\nu_{11}(b_{2u})$ | 1641 | 10.4 | 1626.6 | 9.2 |
| $\nu_{12}(b_2)$ | 527 | 55.0 | 556 | 44.7 | $\nu_{12}(b_{2u})$ | 729 | 37.3 | 879.2 | 36.7 |
| | | | | | $\nu_{13}(b_{2u})$ | 406 | 99.9 | 425.2 | 98.2 |
| | | | | | $\nu_{14}(b_{3u})$ | 479 | 44.9 | 493 | 42.2 |
| | | | | | $\nu_{15}(b_{3u})$ | 174 | 114.0 | 167.2 | 119.7 |

Table 4-S. Frequencies, ν and IR intensities, I, in $cm^{-1}$ and km/mol, respectively.(Only with B3LYP)

| | $C_5Na^-$ | | $C_5K^-$ | | | $C_5Na_2$ | | $C_5K_2$ | |
|---|---|---|---|---|---|---|---|---|---|
| | ν | I | ν | I | | ν | I | ν | I |
| $\nu_1(a_1)$ | 1576 | 241.8 | 1569 | 479.8 | $\nu_1(a_g)$ | 1619 | 0 | 1616 | 0 |
| $\nu_2(a_1)$ | 851 | 239.7 | 836 | 339.2 | $\nu_2(a_g)$ | 717 | 0 | 701 | 0 |
| $\nu_3(a_1)$ | 686 | 22.7 | 684 | 9.6 | $\nu_3(a_g)$ | 250 | 0 | 179 | 0 |
| $\nu_4(a_1)$ | 417 | 1.4 | 398 | 3 | $\nu_4(b_{2g})$ | 225 | 0 | 175 | 0 |
| $\nu_5(a_1)$ | 295 | 5.2 | 230 | 2.8 | $\nu_5(b_{3g})$ | 690 | 0 | 663 | 0 |
| $\nu_6(a_2)$ | 191 | 0 | 181 | 0 | $\nu_6(b_{3g})$ | 310 | 0 | 278 | 0 |
| $\nu_7(b_1)$ | 519 | 44.8 | 518 | 37.5 | $\nu_7(a_u)$ | 248 | 0 | 227 | 0 |
| $\nu_8(b_1)$ | 159 | 4.8 | 122 | 3.6 | $\nu_8(b_{1u})$ | 882 | 181.2 | 873 | 140 |
| $\nu_9(b_2)$ | 1619 | 11.3 | 1614 | 13.4 | $\nu_9(b_{1u})$ | 459 | 34.1 | 432 | 28 |
| $\nu_{10}(b_2)$ | 695 | 55.8 | 702 | 29.3 | $\nu_{10}(b_{1u})$ | 311 | 81.4 | 250 | 104 |
| $\nu_{11}(b_2)$ | 598 | 8.9 | 571 | 19.5 | $\nu_{11}(b_{2u})$ | 1646 | 10.7 | 1637 | 13.6 |
| $\nu_{12}(b_2)$ | 527 | 55 | 293 | 15.8 | $\nu_{12}(b_{2u})$ | 687 | 67.8 | 669 | 46.4 |
| | | | | | $\nu_{13}(b_{2u})$ | 208 | 56.3 | 160 | 57.5 |
| | | | | | $\nu_{14}(b_{3u})$ | 502 | 38.2 | 507 | 29.4 |
| | | | | | $\nu_{15}(b_{3u})$ | 82 | 65.1 | 53.4 | 55.8 |

Table 5-S. Results of the topological analysis of the electronic density. ρ, L and ε are the density, laplacian ($-1/4\nabla^2\rho$) and ellipticity at the critical points, respectively. All quantities are in atomic units.

| | $C_1$-$C_2$ | | | $C_1$-$C_3$ | | | $C_2$-$C_3$ | | | $C_2$-M | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ρ | L | ε | ρ | L | ε | ρ | L | ε | ρ | L | ε |
| $C_5^{2-}$ | 0.228 | 0.032 | 1.999 | --- | --- | --- | 0.358 | 0.282 | 0.030 | --- | --- | --- |
| $C_5Li^-$ | 0.231 | 0.034 | 1.886 | 0.226 | 0.017 | 3.456 | 0.359 | 0.285 | 0.036 | 0.040 | -0.053 | 0.507 |
| $C_5Na^-$ | 0.237 | 0.038 | 1.367 | 0.226 | 0.017 | 5.120 | 0.361 | 0.288 | 0.032 | 0.028 | -0.037 | 0.214 |
| $C_5K^-$ | 0.235 | 0.046 | 1.491 | 0.223 | -0.008 | 18.307 | 0.361 | 0.290 | 0.034 | 0.028 | -0.026 | 0.145 |
| $C_5Li_2$ | 0.232 | 0.028 | 2.531 | --- | --- | --- | 0.357 | 0.279 | 0.039 | 0.034 | -0.045 | 0.583 |
| $C_5Na_2$ | 0.232 | 0.032 | 2.222 | --- | --- | --- | 0.358 | 0.281 | 0.034 | 0.025 | -0.033 | 0.241 |
| $C_5K_2$ | 0.230 | 0.028 | 2.398 | --- | --- | --- | 0.360 | 0.288 | 0.034 | 0.025 | -0.032 | 0.141 |

Table 6-S. Population of the basins of the ELF(r).

| System | Basin, Population |
|---|---|
| $CH_4$ | V(C-H), 1.40; V(C), 1.05 |
| $CAl_4^{2-}$ | V(C-Al), 1.75; V(Al), 2.49 |
| $C_5^{2-}$ | V($C_1$-$C_2$), 1.48; V($C_2$-$C_3$), 2.61; V(C), 2.63 |
| $C_5Li^-$ | V($C_1$-$C_2$), 1.43; V($C_1$-$C_3$), 1.49; V($C_2$-$C_3$), 2.60; V($C_2$), 2.67; V($C_3$), 2.56 |
| $C_5Na^-$ | V($C_1$-$C_2$), 1.42; V($C_1$-$C_3$), 1.55; V($C_2$-$C_3$), 2.60; V($C_2$), 2.64; V($C_3$), 2.57 |
| $C_5K^-$ | V($C_1$-$C_2$), 1.42; V($C_1$-$C_3$), 1.54; V($C_2$-$C_3$), 2.59; V($C_2$), 2.63; V($C_3$), 2.55 |
| $C_5Li_2$ | V($C_1$-$C_2$), 1.48; V($C_2$-$C_3$), 2.61; V($C_2$), 2.62 |
| $C_5Na_2$ | V($C_1$-$C_2$), 1.48; V($C_2$-$C_3$), 2.62; V($C_2$), 2.60 |
| $C_5K_2$ | V($C_1$-$C_2$), 1.48; V($C_2$-$C_3$), 2.60; V($C_2$), 2.60 |

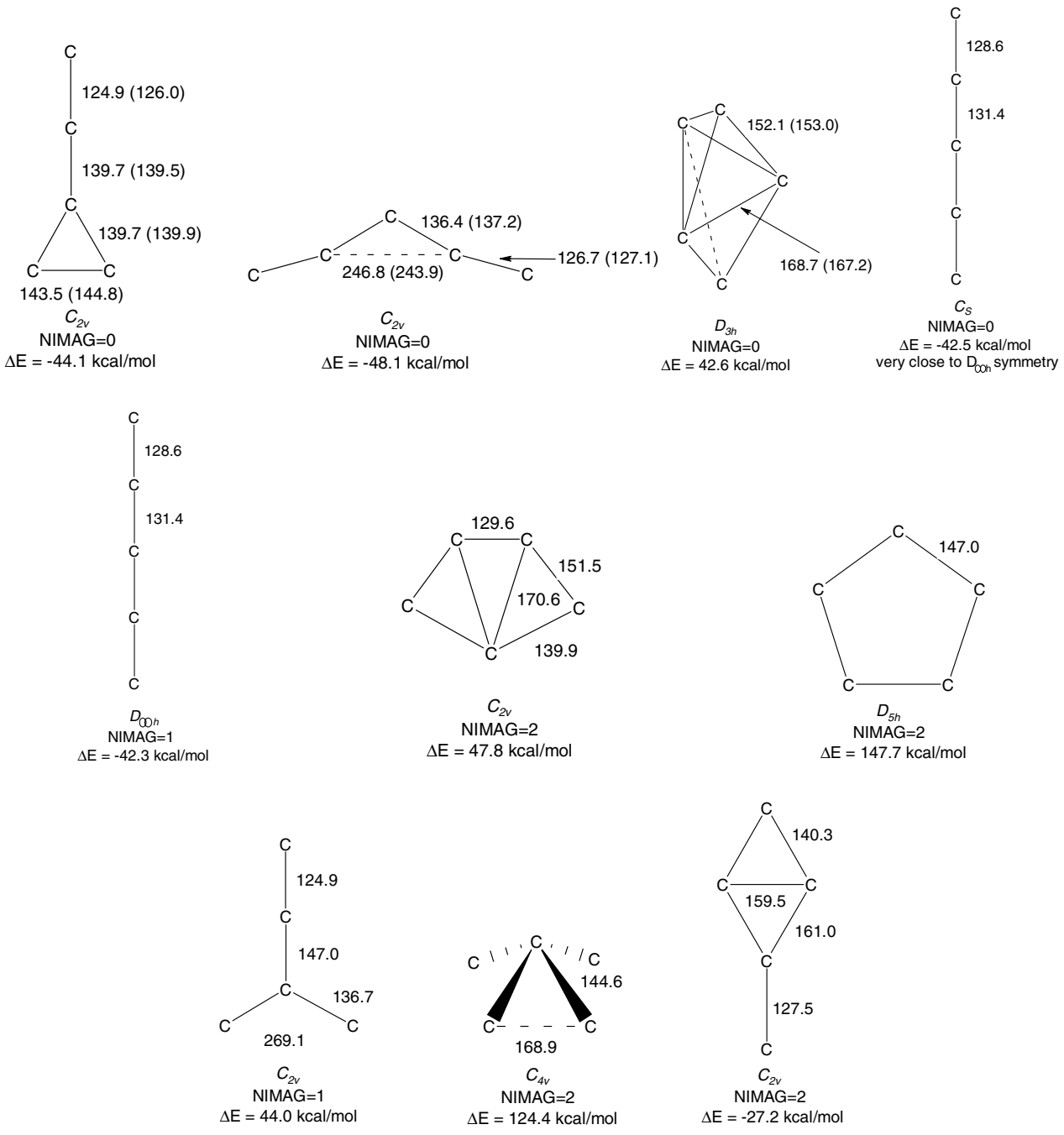



Figure 1-S. Stationary points on B3LYP potential energy surface of planar $C_5^{2-}$. NIMAG is the number of imaginary frequencies and the energy difference, ΔE, is with respect to the planar structure 1 and it includes the zero point energy correction. The local minima were further optimized with MP2 and the corresponding bond lengths are in parenthesis.

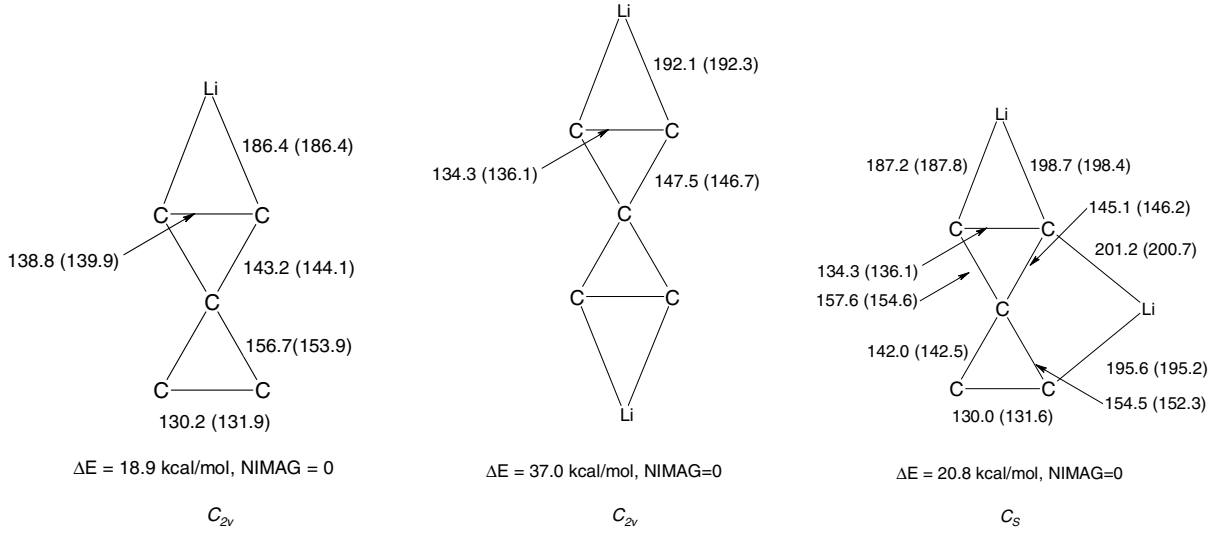



Figure 2-S. Stationary points on B3LYP potential energy surface of planar $C_5Li^-$ and $C_5Li_2$. NIMAG is the number of imaginary frequencies and the energy difference, ΔE, is with respect to the planar structure 2 and 3, respectively, and it includes the zero point energy correction. The local minima were further optimized with MP2 and the corresponding bond lengths are in parenthesis.

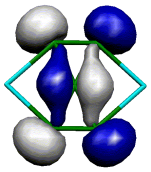
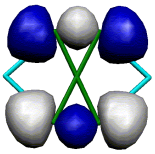
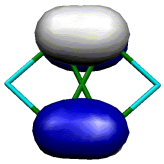
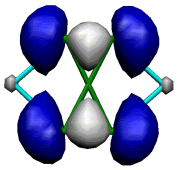
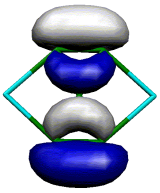
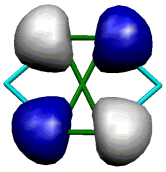
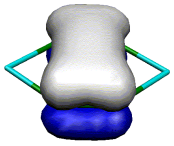
| | Symmetry | DFT |
|---|---|---|
|  | **4 $b_{1u}$** | **-0.20542** |
|  | **4 $b_{2u}$** | **-0.26425** |
|  | **1 $b_{1g}$** | **-0.26635** |
|  | **6 $a_g$** | **-0.28810** |
|  | **3 $b_{2u}$** | **-0.36695** |
|  | **2 $b_{3g}$** | **-0.37092** |
|  | **1 $b_{3u}$** | **-0.39300** |

Figure 3-S. Seven highest occupied molecular orbitals of $C_5Li_2$ obtained with B3LYP/6-311++G(2df) level of theory. $|\varphi| = 0.05$ a.u.