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SUPPORTING INFORMATION

Title: Carbolithiation of Simple Terminal and Strained Internal Alkenes by the Naphthalene and the Biphenyl Dianion: New Modes of Reactivity of Highly Reduced Organic Species in Solution
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Table S1 shows the so-called gross population from the HOMO and the Mulliken charge on the carbon atoms in the arene dianions $\mathbf{I^{-2}}$-$\mathbf{III^{-2}}$. The gross population, N_i, on atom i out of the M comprising each molecule is calculated as:

$$N_i = n_{ii} + \sum_{j \neq i} n_{ij} \tag{S1}$$

with

$$n_{ij} = \sum_{k=1}^{m_i} \sum_{l=1}^{m_j} C_k^{(i)} S_{kl}^{(ij)} C_l^{(j)} \tag{S2}$$

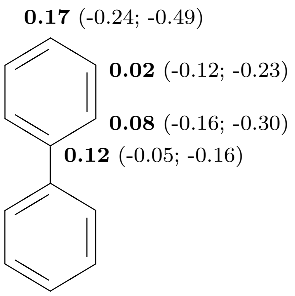
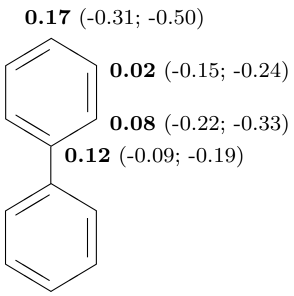
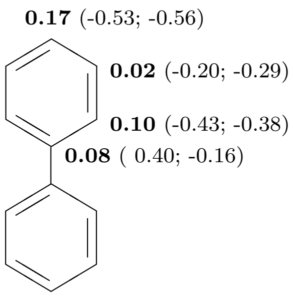
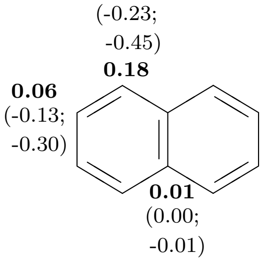
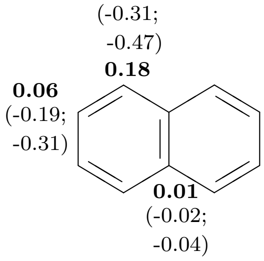
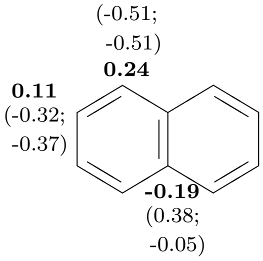
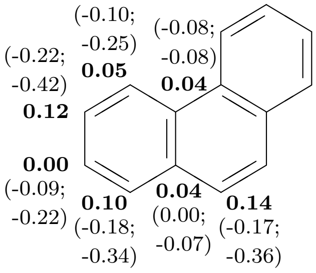
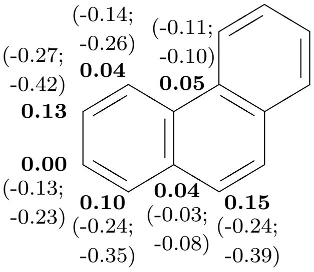
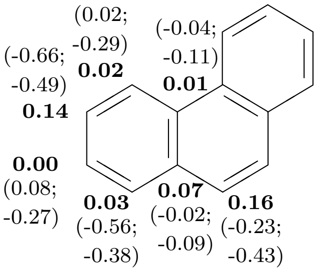
where m_i is the number of atomic orbitals centered on the i-th atom, $C_k^{(i)}$ represents the coefficient of the HOMO corresponding to the k-th atomic orbital centered on atom i, and $S_{kl}^{(ij)}$ is the overlap matrix between the k-th atomic orbital on atom i and the l-th one centered on atom j. Since $n_{ij} = n_{ji}\ \forall i, j$ the gross population corresponds to split each overlap population between atoms i and j, $n_{ij} + n_{ji}$, into two identical parts, each ascribed to one of the two atoms. As a consequence of the normalization condition of the molecular orbitals and, in particular, of the HOMO we have that:

$$\sum_{i=1}^{M} N_i = 1. \tag{S3}$$

Recall that, for an orthonormal basis set, $S_{kl}^{(ij)} = \delta_{kl}\delta_{ij}$, and N_i reduces to the sum of the squares of the coefficients for the atomic orbitals centered on the i-th atom (only real orbitals are considered for simplicity). On the other hand, when a non-orthogonal basis set is used, as in the calculations performed in this work, Eq. (S2) appropriately considers the non-zero overlap between different atomic orbitals. The Mulliken population on each atom is obtained by summing the gross population for that atom corresponding to each occupied molecular orbital. The Mulliken charge is obtained by adding the nuclear charge to the Mulliken population. Atomic charges derived from the so-called Natural Population Analysis (NPA) (see Ref. 1 and references therein) have also been reported in Table S1 for completeness. It can be seen that both population analysis yield the same relative ordering of the charges in the carbon atoms. The same ordering for the atomic charges and HOMO populations was also found from PM3 calculations performed in the preliminary communication,[2] giving strong support to the theoretical explanation for the reactivity of $\mathbf{I^{-2}}$-$\mathbf{III^{-2}}$.

Different types of geometries (planar and non-planar) and spin multiplicities (singlet and triplet) have been tested for each molecule but only those results corresponding to the lowest true minima found in the potential energy hypersurface (as confirmed by the corresponding vibrational analysis) have been depicted in Table S1, which always correspond to the singlet state. We note, however, that for the calculation corresponding to the naphthalene dianion using the 6-31+G(d,p) basis set and the PCM model to represent the THF solvent we have not been able to localize a true minimum, and the results presented in Table S1 for this case correspond to the optimized geometry that attains the lowest energy among the set of geometries and multiplicities tested. According to the vibrational frequencies this geometry corresponds to a first-order saddle point. However, geometry optimizations starting at a distorted molecular geometry along the mode corresponding to the imaginary frequency always revert to this geometry. Notwithstanding this, the N_i values obtained in this case confirm the conclusions gathered from the rest of calculations. The Gaussian03 program[3] was used for all the calculations performed in this work.

Table S1: HOMO atomic contributions (bold face) and population analysis (in parenthesis; first entry: Mulliken charges, second entry: NPA charges) of arene dianions $\mathbf{I^{-2}}$-$\mathbf{III^{-2}}$ from B3LYP calculations. The entry below each figure is the point group the optimized geometry of the molecule belongs to.

Molecule	Gas phase	THF	
	6-311G(d,p)	6-311G(d,p)	6-31+G(d,p)
Biphenyl$^{(-2)}$	 C_{2h}	 C_{2h}	 C_2
Naphthalene$^{(-2)}$	 D_{2h}	 D_{2h}	 C_{2h}
Phenantrene$^{(-2)}$	 C_2	 C_2	 C_2

References

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