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Electronic Supplementary Information

Playing with isomerism and N substitution in pentalenedione derivatives for organic electrode batteries: how high are the stakes?

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S1. Computational details

1. Calculation of the reduction potential

The protocol used for the theoretical prediction of the standard redox potentials in solution with implicit solvent model (SMD) involves the Born-Haber cycle shown in Scheme S1.

$$\begin{tikzcd}
\mathbf{P}_{\mathbf{(g)}} \arrow[d, "\Delta G^{*}_{\mathrm{solv}}"] & + & \mathbf{e}^{-} \arrow[r, "\mathrm{EA}_{\mathrm{gas}}"] \arrow[d, "\Delta G = 0"] & \mathbf{P}_{\mathbf{(g)}}^{-\cdot} \arrow[d, "\Delta G^{*}_{\mathrm{solv}}"] \\
\mathbf{P}_{\mathbf{(solv)}} & + & \mathbf{e}^{-} \arrow[r, "\Delta G^{0}_{\mathrm{red\,(solv)}}"] & \mathbf{P}_{\mathbf{(solv)}}^{-\cdot}
\end{tikzcd}$$

Scheme S1. Thermodynamic cycle used for the estimation of the standard state free energy difference relative to the one-electron reduction process in solution, $\Delta G^{0}_{red\,(solv)}$.

In this thermodynamic cycle, $\Delta G^{0}_{red\,(solv)}$ can be written as:

$$\Delta G^{0}_{\mathrm{red\,(solv)}} = G_{\mathrm{298K,\,solv}}(Q^{-\cdot}) - G_{\mathrm{298K,\,solv}}(Q) = \mathrm{EA}_{\mathrm{gas}} + \Delta G^{*}_{\mathrm{solv},Q^{-\cdot}} - \Delta G^{*}_{\mathrm{solv},Q} \qquad (1)$$

where $\mathrm{EA}_{\mathrm{gas}}$ corresponds to the electron affinity in gas-phase at 298 K, $\Delta G^{*}_{\mathrm{solv},Q}$ and $\Delta G^{*}_{\mathrm{solv},Q^{-\cdot}}$ are respectively the solvation free energies of the compound and of its reduced counterpart. The solvation effects were calculated by using Ethylene Carbonate as solvent.

2. QTAIM energy analysis

Atomic energies were obtained as minus the integrated kinetic energy density within each atomic basin. A single scaling value was applied to each integrated kinetic energy to correct for the virial ratio[1], which was, however, in all cases only marginally different from two (as required for the exact wavefunction of a system at equilibrium, where no net forces act on the nuclei). Three, probably minor, not exactly quantifiable and, within Kohn-Sham DFT, unavoidable approximations were made by proceeding in this way. First, one has to remind that Kohn-Sham (KS) orbitals provide only the non-interacting electrons part of the kinetic energy density, the remaining part being hidden into and dealt with through the exchange-correlation energy term, although in an unknown manner. We are therefore assuming that the kinetic energies of the non-interacting electron system marginally differ from those in the "real" system. This is a quite commonly adopted practice in literature, where it has also been shown 2 that QTAIM energy analyses based on KS DFT orbitals faithfully reproduce those obtained through Hartree-Fock (HF) MOs (these latter MOs reconstruct indeed the "true" kinetic energy of a system, though within the HF mean-field approximation).[3] Secondly, the "virial ratio" correction we applied also implicitly include the departure of the kinetic energy of the non-interacting electrons system from its "exact" value. Finally, by using a single value to scale each atomic or atomic group energy, we tacitly assume that the atoms and atomic groups' energies of a system are, in percentage, all similarly affected by the approximations leading to a global virial ratio different from two.

S2. Electron and electron spin/charge populations, energetic and geometric features

Table S1 : Reduction potential, V, (in V *vs.* Li$^+$/Li) and free energies values, G, for the initial (I) and reduced (R) forms of the pentalenedione derivatives. Corresponding ΔG(R-I) changes from reduced to initial forms are also reported.

System	Red. Pot., (V *vs.* Li$^+$/Li)	G (I) (Hartree)	G (R) (Hartree)	ΔG(R-I) (Hartree)
1,5_N (0,0)	**2.17**	-457.6161	-457.7497	-0.1335
1,5_N (3)	2.47	-473.6544	-473.7989	-0.1445
1,5_N (4)	2.48	-473.6733	-473.8182	-0.1449
1,5_N (6)	2.53	-473.6683	-473.8149	-0.1466
1,5_N (2)	2.63	-473.6628	-473.8129	-0.1501
1,5_N (3,4)	2.78	-489.7137	-489.8695	-0.1557
1,5_N (3,6)	2.96	-489.7006	-489.8629	-0.1623
1,5_N (3,2)	3.08	-489.6683	-489.8351	-0.1668
1,5_N (4,6)	2.86	-489.7212	-489.8798	-0.1587
1,5_N (4,2)	2.99	-489.7140	-489.8775	-0.1635
1,5_N (2,6)	2.94	-489.7119	-489.8736	-0.1616
1,2_N (0,0)	**2.37**	-457.6177	-457.7583	-0.1406
1,2_N (4)	2.70	-473.6678	-473.8205	-0.1527
1,2_N (5)	2.79	-473.6590	-473.8152	-0.1562
1,2_N (6)	2.80	-473.6604	-473.8171	-0.1567
1,2_N (3)	2.86	-473.6633	-473.8220	-0.1587
1,2_N (4,6)	3.14	-489.7151	-489.8840	-0.1689
1,2_N (4,3)	3.22	-489.7143	-489.8861	-0.1718
1,2_N (4,5)	3.38	-489.6769	-489.8546	-0.1777
1,2_N (5,6)	3.14	-489.6817	-489.8508	-0.1692
1,2_N (3,5)	3.28	-489.7002	-489.8745	-0.1743
1,2_N (3,6)	3.39	-489.6970	-489.8751	-0.1781
1,6_N (0,0)	**2.78**	-457.5951	-457.7510	-0.1559
1,6_N (2)	3.07	-473.6481	-473.8144	-0.1663
1,6_N (3)	3.09	-473.6396	-473.8067	-0.1672
1,6_N (2,5)	3.37	-489.6999	-489.8773	-0.1774
1,6_N (2,4)	3.37	-489.6891	-489.8668	-0.1777
1,6_N (2,3)	3.58	-489.6559	-489.8410	-0.1852
1,6_N (3,4)	3.38	-489.6853	-489.8630	-0.1777
1,6_N (2,5)	3.37	-489.6999	-489.8773	-0.1774
1,6_N (2,4)	3.37	-489.6891	-489.8668	-0.1777
1,4_N (0,0)	**2.82**	-457.5883	-457.7455	-0.1572
1,4_N (2)	3.12	-473.6462	-473.8144	-0.1682
1,4_N (3)	3.13	-473.6291	-473.7977	-0.1686
1,4_N (2,5)	3.39	-489.6994	-489.8775	-0.1781
1,4_N (2,6)	3.41	-489.6852	-489.8642	-0.1790
1,4_N (2,3)	3.63	-489.6499	-489.8369	-0.1870
1,4_N (3,6)	3.39	-489.6669	-489.8453	-0.1784

Fig. S1: Free energy changes upon CH replacement(s) by Nitrogen(s) ($\Delta G_{CH\rightarrow N}$) in the Initial (I) and reduced (R) forms for the singly and doubly N-substituted 1,2 (top, left), 1,4 (top right), 1,5 (bottom, left), 1,6 (bottom, right) pentalenedione derivatives.

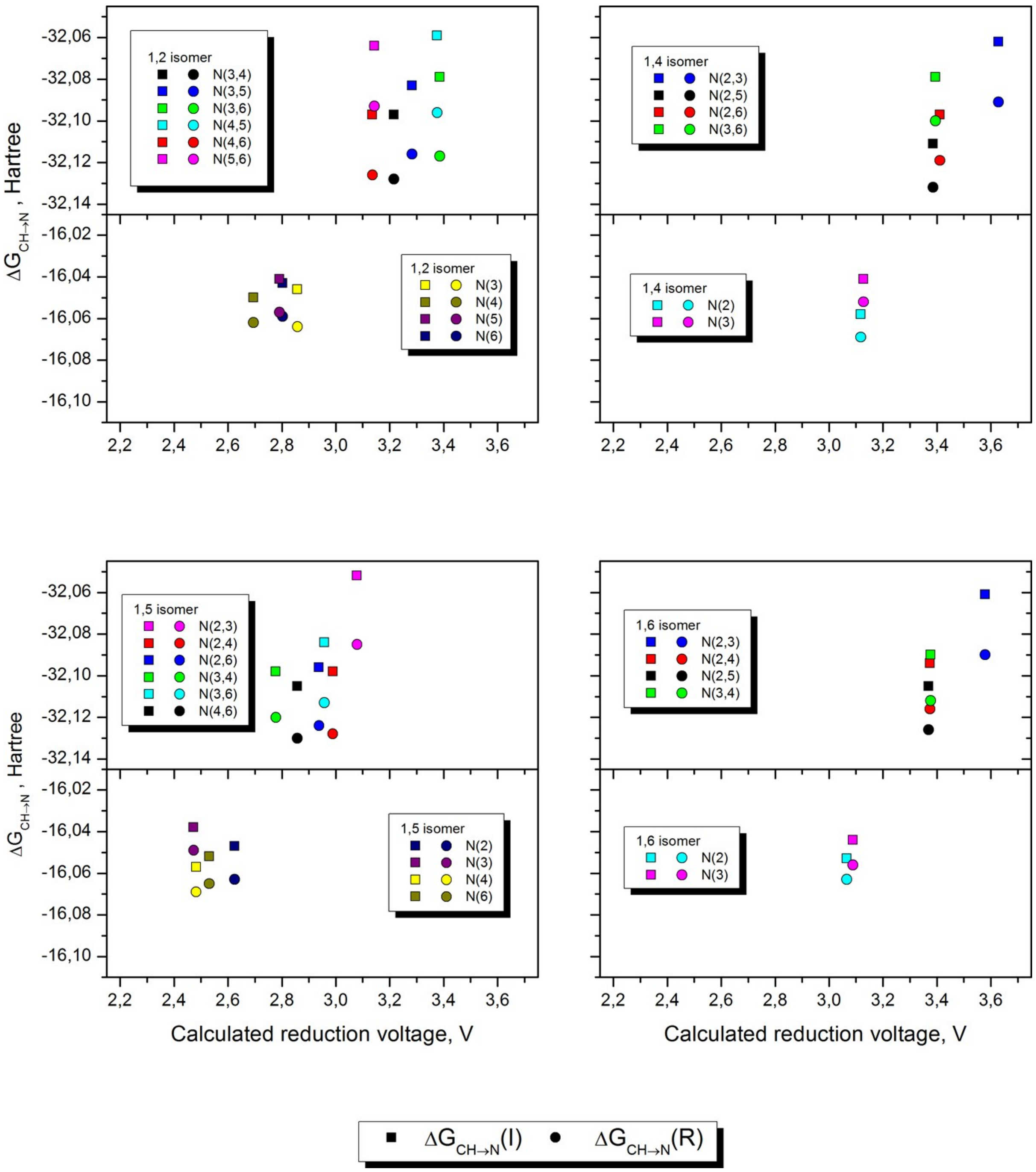


Table S2 : 1,2_N(4,5), 1,2_N(5,6) and 1,4_N(2,3) pentalenedione derivatives: calculated N-N bond distances in the initial and reduced forms.

System	N—N bond, Initial molecule (Å)	N—N bond, Reduced molecule (Å)
1,2_N(4,5)	1.29	1.38
1,2_N(5,6)	1.45	1.37
1,4_N(2,3)	1.26	1.32

Table S3 : 1,2 and 1,4 pentalenedione derivatives including parent, singly and doubly substituted compounds with two neighbouring N atoms in one ring: Reduction potentials V, (in V *vs.* Li$^+$/Li), subsystem energy changes from reduced to initial forms for ring 1 (R1) plus ring 2 (R2) (ΔE(R1+R2)) oxygen atoms ΔE(O_{1+x})and nitrogen atoms ΔE(N) as well as total energy variations for the whole molecule (ΔE_{TOT}), Spin density population values (*S*) on O and N atoms in the reduced forms, *i.e.* *S*(O_1+O_X) and *S*(N), respectively. Total net atomic charge variation for N atoms upon reduction (ΔQ(N)) is also displayed.

System	Red. Pot., V	ΔE(R1+R2)^a	$\Delta E(O_{1+x})^{a,b}$	ΔE(N)^a	$\Delta E_{TOT}{}^a$	$S(O_{1+}O_x)^b$	*S*(N)	ΔQ(N)
1,2_N(0)	2.37	-0.212	0.074	-	-0.138	0.130	-	-
1,2_N(4)	2.70	-0.215	0.066	0.057	-0.149	0.130	0.047	-0.062
1,2_N(5)	2.79	-0.231	0.076	0.046	-0.155	0.153	0.118	-0.071
1,2_N(6)	2.80	-0.221	0.067	0.030	-0.154	0.141	0.073	-0.096
1,2_N(4,5)	3.38	-0.238	0.062	-0.234	-0.176	0.150	0.276	-0.605
1,2_N(5,6)	3.14	-0.227	0.061	0.200	-0.167	0.157	0.110	+0.059
1,4_N(0)	2.82	-0.288	0.134	-	-0.155	0.394	-	
1,4_N(2)	3.12	-0.286	0.120	0.068	-0.166	0.354	-0.002	-0.049
1,4_N(3)	3.13	-0.297	0.131	0.018	-0.167	0.387	-0.000	-0.084
1,4_N(2,3)	3.63	-0.306	0.120	-0.189	-0.185	0.374	0.237	-0.555

a) All energies are in Hartree (Ha). *b*) O_x is the second oxygen other than O_1.

Table S4 : Bader net atomic charges for the doubly substituted compounds with two neighbouring N atoms in one ring for the 1,2 and 1,4 isomers, in initial and reduced forms. Data for their parent compounds and their related singly N-substituted pentalenedione derivatives, as well as an example system with no contiguous nitrogen atoms (1,2_N(3,6)) are also reported for the sake of comparison.

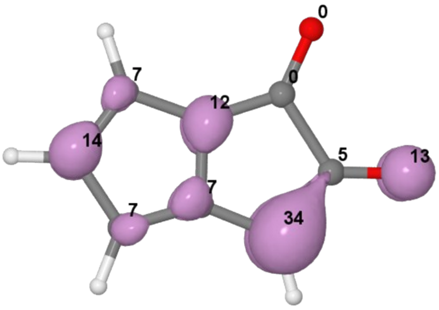
System	N_x, initial^a	N_x, reduced^a	N_y, initial^a	N_y, reduced^a
1,2_N(4)	-1.175	-1.237	-	-
1,2_N(5)	-1.144	-1.215	-	-
1,2_N(6)	-1.146	-1.242	-	-
1,2_N(3,6)	-1.087	-1.115	-1.091	-1.193
1,2_N(4,5)	-0.461	-0.765	-0.432	-0.733
1,2_N(5,6)	-0.778	-0.741	-0.783	-0.761
1,4_N(2)	-1.160	-1.209	-	-
1,4_N(3)	-1.161	-1.245	-	-
1,4_N(2,3)	-0.308	-0.582	-0.352	-0.633

a) x and y labels are listed in increasing numerical order.

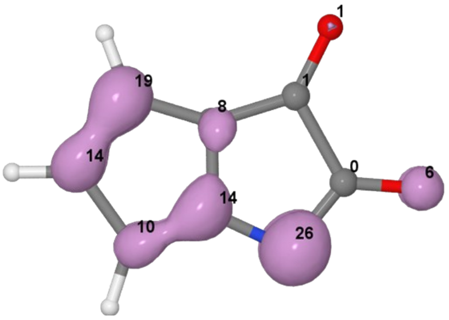
S3. Spin density patterns for all reduced molecules

The spin density patterns for the reduced forms of the singly and doubly N-substituted pentalenedione derivatives are displayed in this section. An isocontour value of 0.0075 electron (magenta: positive; light blue: negative) was used to plot the spin density distribution isosurface. Bader's atomic spin density populations (in hundredths of an electron) are presented as well.

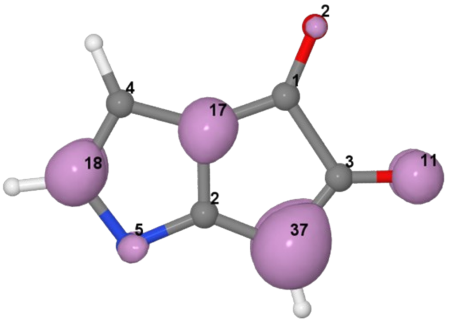
S.3.1. Isomer 1,2



1,2_N(0,0)



1,2_N(3)



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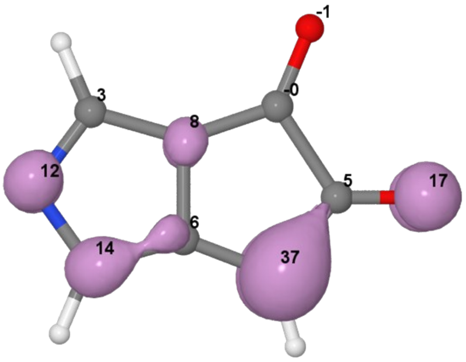
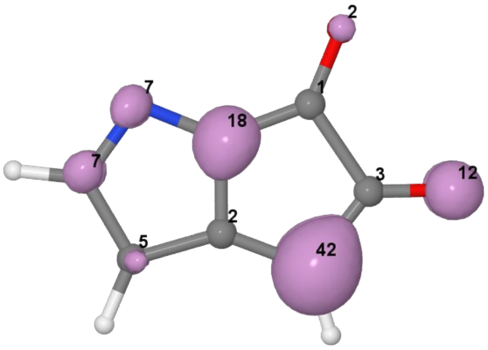
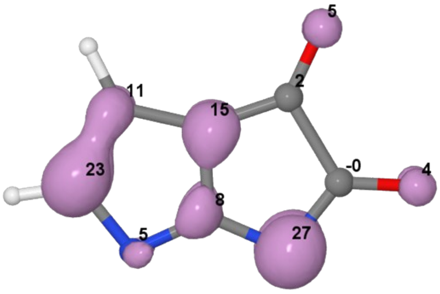


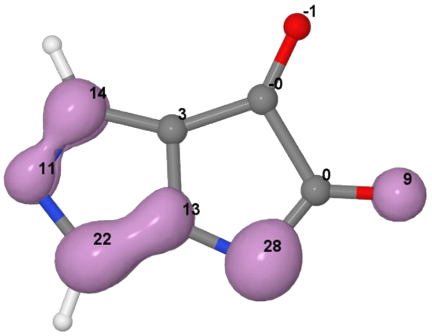
1,2_N(5)



1,2_N(6)



1,2_N(3,4)



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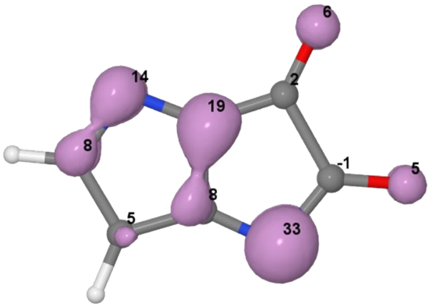

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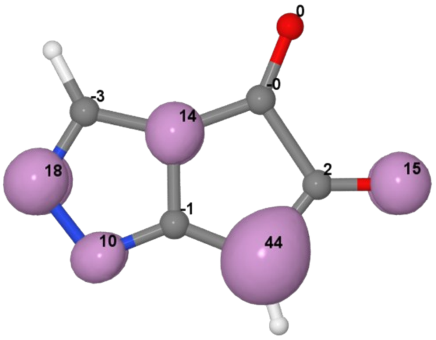
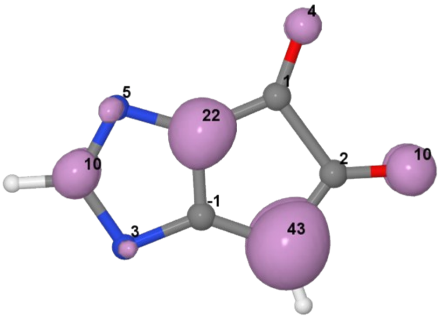


1,2_N(4,5)



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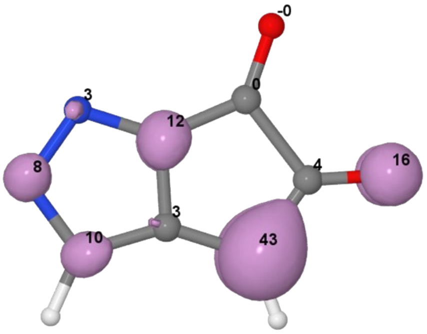
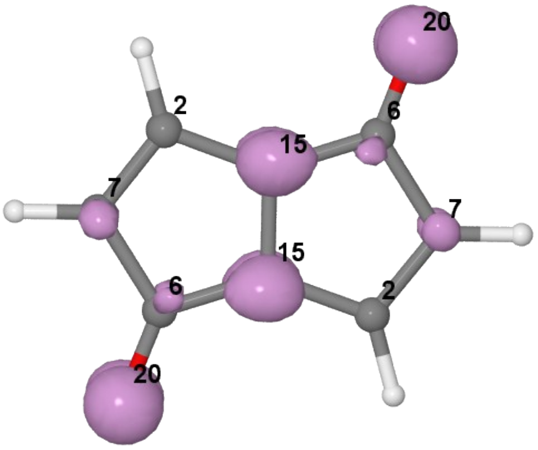
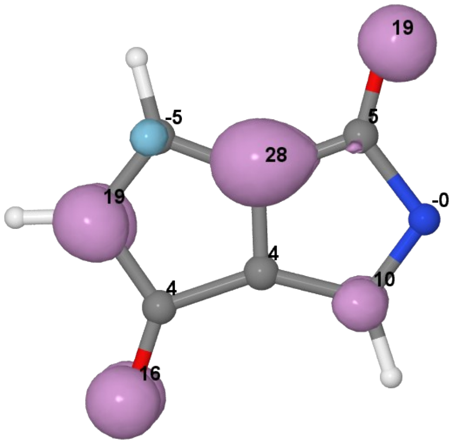


1,2_N(5,6)

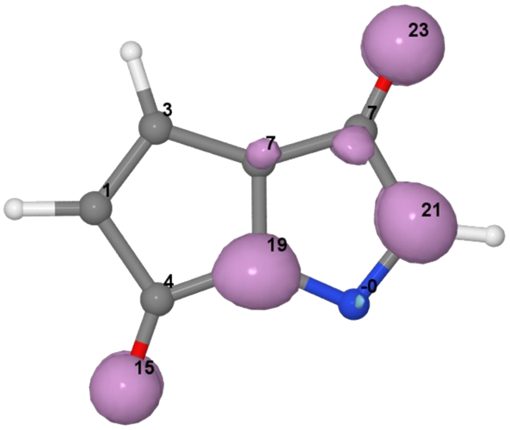
S.3.2. Isomer 1,4



1,4_N(0,0)



1,4_N(2)



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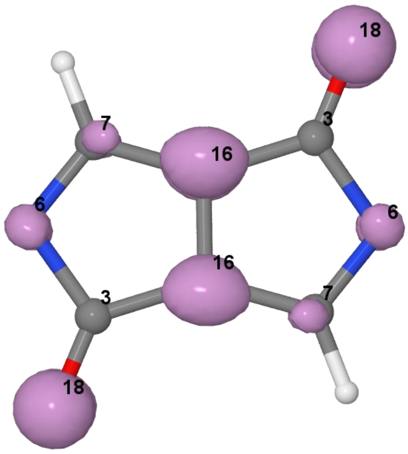

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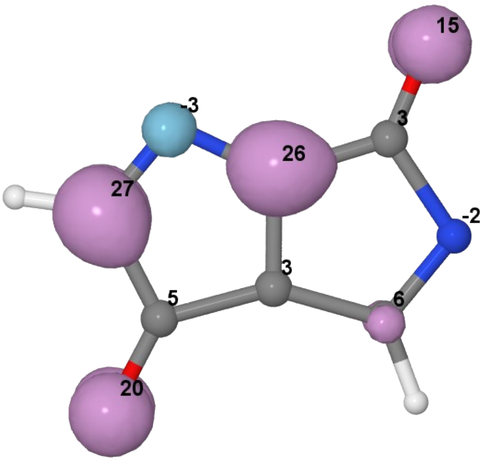

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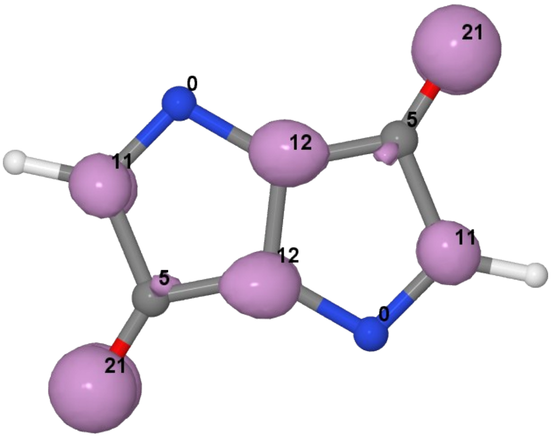

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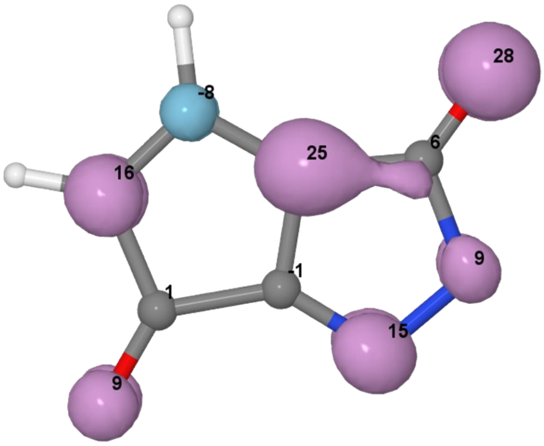
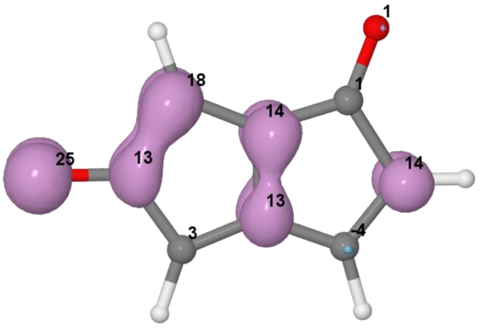


1,4_N(2,3)

S.3.3. Isomer 1,5



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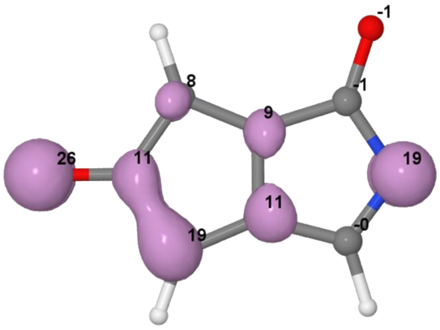

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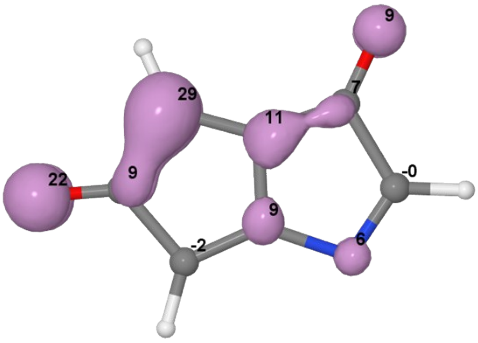

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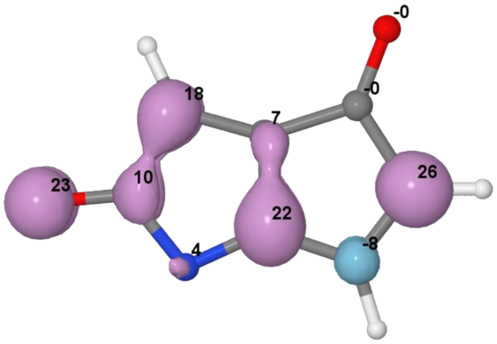

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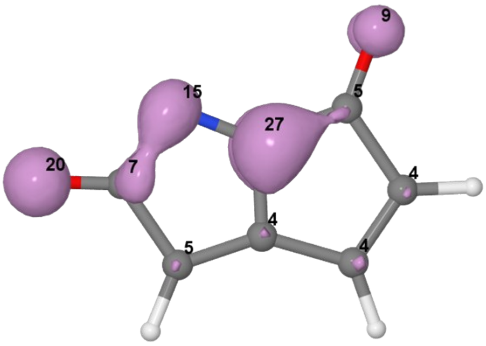

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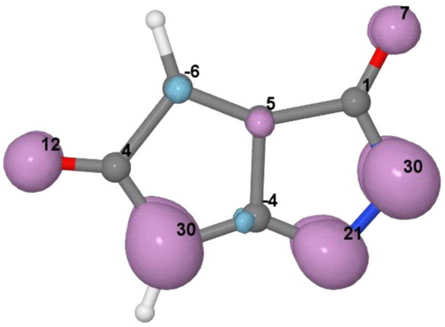

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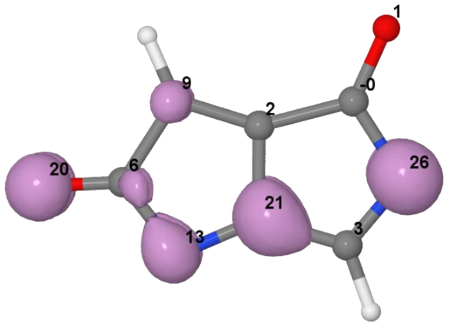

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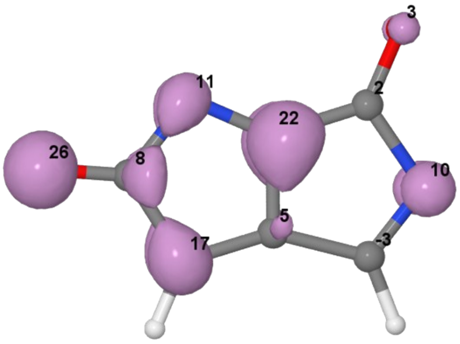

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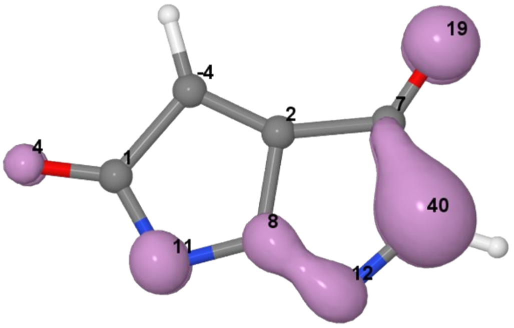

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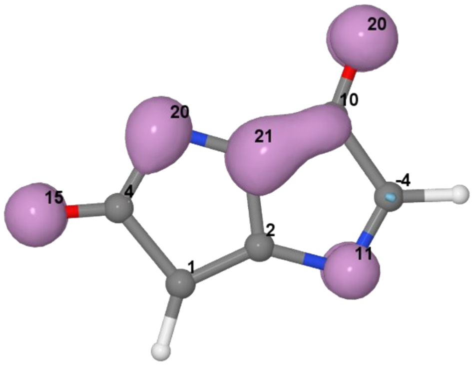

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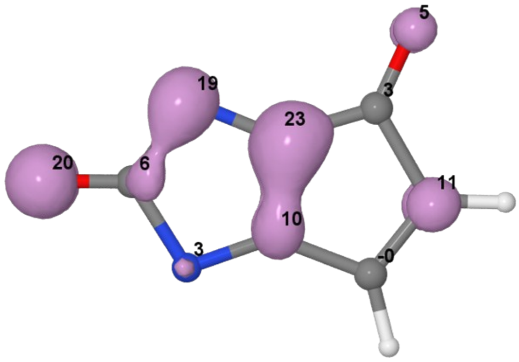
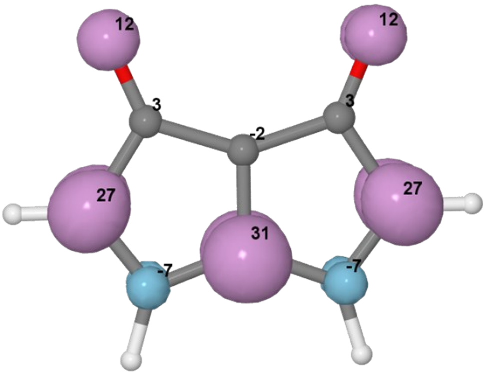


1,5_N(4,6)

S.3.4. Isomer 1,6



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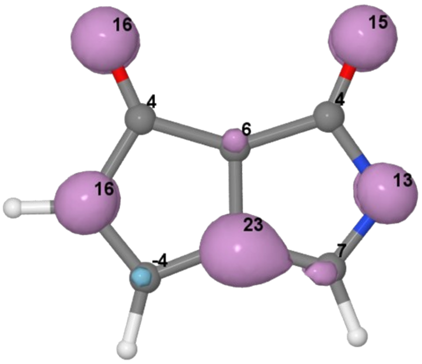

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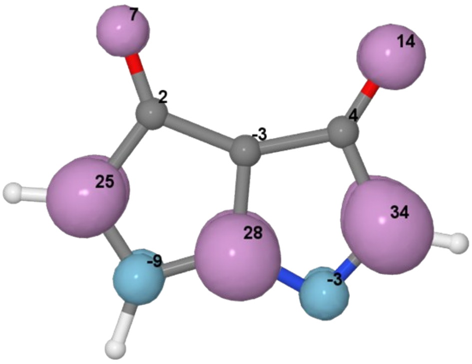

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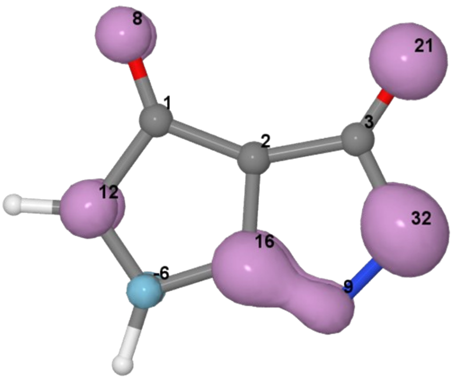

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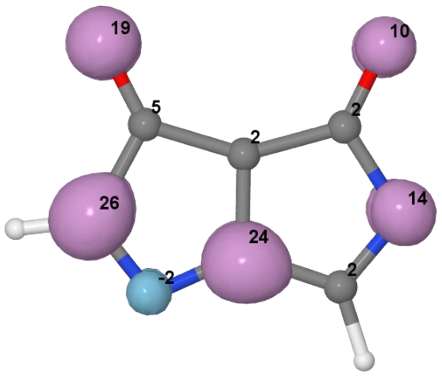
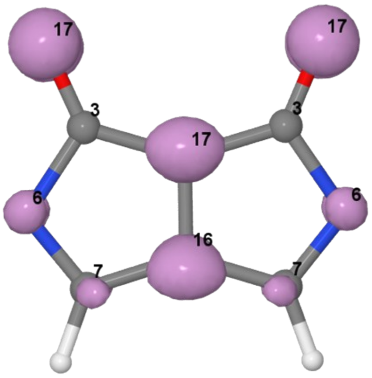
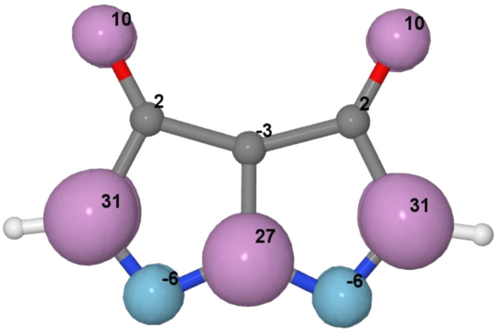


1,6_N (2,4)



1,6_N(2,5)



1,6_N(3,4)

References

1. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1994.
2. C. F. Matta, N. Castillo, R. J. J. Boyd, *Chem. Phys.,* 2006, **125**, 204103.
3. Matta *et al*. found this nice agreement despite the slightly different equilibrium geometries retrieved by HF and KS-DFT approaches, the dissimilar meaning of integrated kinetic energies for the two model cases and the different physical nature of HF and KS orbitals, with the former being defined in the mean field approximation and the latter including, instead, part of the Coulomb electron correlation effects. As a matter of fact, differences in integrated kinetic energies, which are the only relevant quantities when relative energy stabilities are discussed as in Matta *et al*. paper as well as in the present context, appear to be as quite robust quantities. This view is strengthened by considering that Matta *et al*. found the same nice agreement for those few cases where Møller Plesset MP2 energy differences were also compared with those obtained through Kohn-Sham DFT.