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SHORT-LIVED INTERMEDIATES DERIVED FROM *SYM*-TRIAZINES: STRUCTURE, THERMODYNAMIC PROPERTIES AND REACTIVITY

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Sym-triazines show extended π-electron delocalization ranging over adjacent substituents in positions 2, 4 and 6. *Sym*-Triazines are widely used as systemic herbicides (inhibit photosynthesis), and as dyes (their planarity being determinant to their dying properties). Melamine {1,3,5-Triazine-2,4,6-triamine} has potential as a supramolecular synthon, due to both its ease to establish extended hydrogen bond networks. We have previously studied different aspects of *sym*-triazines chemistry.[1–3]

We report on the neutral and singly charged radical species derived from *sym*-triazine (**1**): 2,4-diamino-(1,3,5)-triazine (**2**), atrazine {N-ethyl-N'-isopropyl-6-chloro-1,3,5-triazine} (**3**), atraton {N-ethyl-N'-isopropyl-6-methoxy-1,3,5-triazine} (**4**) and ametryne {N-ethyl-N'-isopropyl-6-methylthio-1,3,5-triazine} (**5**). From laser flash photolysis and pulse radiolysis experiments, we report on the spectra of radical cations and radical anions, and of the lowest triplet state, their ionization threshold, the reduction potential for the radical cation ($E^{o}(T^{\bullet+}/T)$), and radical anion ($E^{o}(T/T^{\bullet-})$), the pKa of the radical anion, as well as kinetic information and linear free energy relationships showing inductive and steric effects for one-e^- oxidation and one-e^- reduction. From DFT, we report optimised geometries of neutral and singly charged radicals, and show that the triazine ring and exo -NR_2 groups in (**1**)–(**5**) tend to be planar in radical cations, whilst for radical anions only (**5**) shows an important conformational change in the exo groups. We also report computed vertical and adiabatic ionization potentials (VIP, AIP) and electron affinities (EA) for (**1**)–(**5**). Reduction potentials of the radical cations ($E0(T^{\bullet+}/T)$), and radical anions ($E0(T/T^{\bullet-})$) have been computed, as well as pKa's for the radical anions.

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