Computational Investigation of Azaacene Diradicals and their Dimerization Reaction

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Open-shell molecules, such as diradicals and diradicaloids, exhibit interesting magnetic and electronic properties, making them attractive systems for both application and basic research. Areas of possible application include organic electronics, nonlinear optics and spintronics. From a quantum chemical perspective, they present a particular challenge since singlet diradicals cannot be correctly described by single-reference methods.

It was previously found that in isomeric quinoidal azaacenes the relative orientation of the sulfur atoms determines the diradical character. In this work, dicyanomethylene substituted benzodithienophenazines *o*-1 and *p*-1 (Figure 1a) are investigated regarding their diradical character, ground state multiplicity and optical properties using density functional theory (DFT) and (Spin-flip) time-dependent DFT (TDDFT). Furthermore, the unusual dimerization of the ortho-derivative forming four σ-bonds and resulting in a covalent azaacene cage is investigated using the semi-empirical tight binding method GFB2-xTB. The diradical character y_0 of *o*-1 and *p*-1 is determined to be 0.98 and 0.01 respectively. Spin-flip TDDFT calculations furthermore show that *o*-1 has an open-shell singlet ground state with a singlet-triplet gap of 0.01 eV, while *p*-1 has a closed-shell singlet ground state and a singlet-triplet gap of 1.30 eV. Investigation of the dimerization reaction suggests the consecutive formation of two sets of two σ-bonds as a plausible reaction mechanism (Figure 1b).

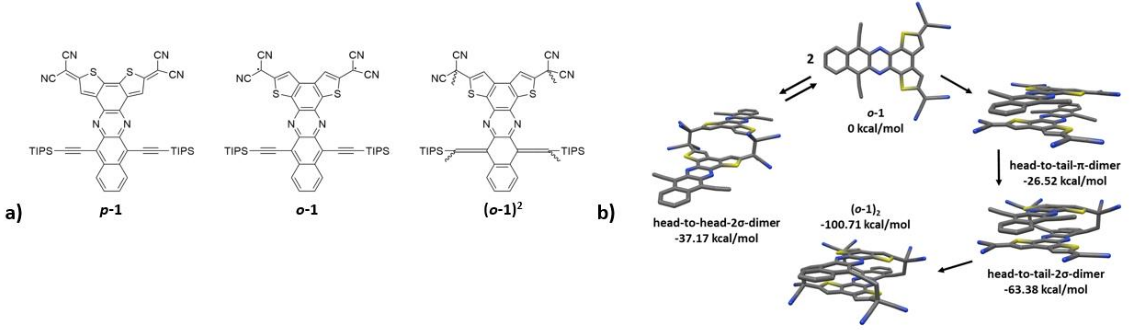

Figure 1. a) Chemical structures of dicyanomethylene substituted benzothienophenazines *p*-1, *o*-1 and dimerization product (*o*-1)^2. b) Structures and relative energies of *o*-1, (*o*-1)^2 and possible intermediates of the dimerization process (obtained using the GFN2-xTB method).

References

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