

Towards Polyradicals: A Planar and Fully π -Conjugated Organic Tetraradical(oid)



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Abstract

We provide a general strategy to stabilize the ground state of polyradical(oid)s and make higher spin states thermally accessible. As a proof of concept, we merged two planar fully π -conjugated diradical(oid)s to obtain a planar and cross-conjugated tetraradical(oid). Using multireference quantum chemistry methods, we show that the designed tetraradical(oid) is stabilized by aromaticity and delocalization in the π -system, and has 6 thermally accessible spin states within 1.72 kcal/mol. Analysis of the electronic structure of these states shows that the frontier π -system of the tetraradical(oid) consists of two weakly interacting subsystems: aromatic cycles and four unpaired electrons. Conjugation between unpaired electrons, which favors closed-shell structures, is mitigated by delocalization and aromaticity of the bridging groups leading to the synergistic cross-coupling between two diradical(oid) subunits to stabilize tetraradical(oid) electronic structure.

Introduction

The diradical(oid) 2,2'-(5,11-dihydroindolo[3,2-*b*]carbazole-3,9-diyl)dimalononitrile (*S*) and diradical(oid) 2,2'-((1,4-phenylenebis(ethyne-2,1-diyl))bis(4,1-phenylene))dimalononitrile (*L*) are merged to produce tetraradical(oid) 2,2'-(6,12-bis((4-(dicyanomethyl)phenyl)ethynyl)-5,11-dihydroindolo[3,2-*b*]carbazole-3,9-diyl)dimalononitrile (*LS*). [1] Both diradical(oid) substructures are singlet open-shell in the ground state according to Ovchinnikov's rule [2] and our calculations. *LS* is also predicted to have a singlet open-shell ground state, which has been verified by every calculation we performed. [1]

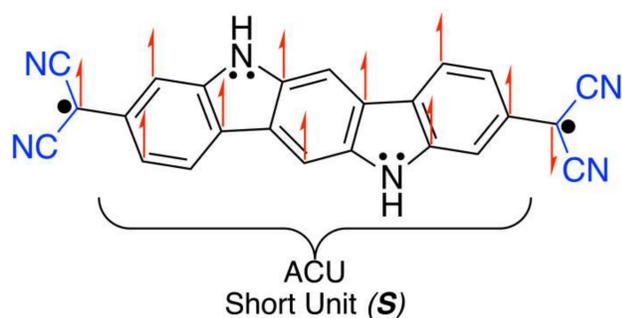


Figure 1: Ground state of diradical(oid) subunit *S* determined by Ovchinnikov's rule with antiferromagnetic coupling unit (ACU).

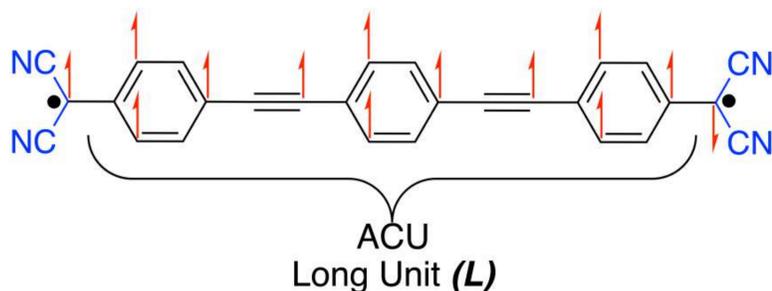


Figure 2: Ground state of diradical(oid) subunit *L* determined by Ovchinnikov's rule with antiferromagnetic coupling unit (ACU).

Main Objectives

- Design polyradicals with different properties by merging known diradical(oid) structures.
- Study electronic structure of the tetraradical(oid) *LS* shown in Figure 3 obtained by merging *L* and *S*.

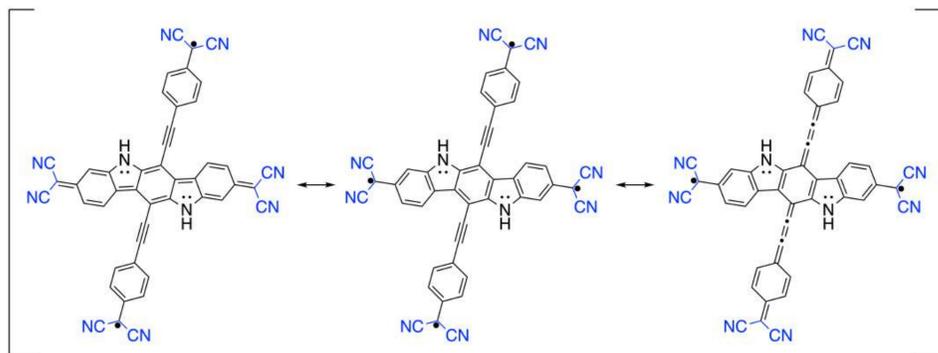


Figure 3: Resonance structures of the 2,2'-(6,12-bis((4-(dicyanomethyl)phenyl)ethynyl)-5,11-dihydroindolo[3,2-*b*]carbazole-3,9-diyl)dimalononitrile *LS*. 2,2'-(5,11-dihydroindolo[3,2-*b*]carbazole-3,9-diyl)dimalononitrile (in the figure, horizontal chain) will be referred to as *S* and 2,2'-((1,4-phenylenebis(ethyne-2,1-diyl))bis(4,1-phenylene))dimalononitrile (in the figure, vertical chain) will be referred to as *L*.

Methods

Geometry for each structure, *L*, *S* and *LS*, was optimized with Slater-type all-electron triple- ζ basis set (TZP) with BLYP exchange-correlation functional within unrestricted Kohn-Sham (UKS) Density Functional Theory (DFT), resulting in planar structures whether the starting geometries are planar or not.

For a tetraradical(oid), a qualitatively correct wave function could be obtained by Complete Active Space SCF (CASSCF) initiated using unrestricted Hartree-Fock natural orbitals guess. To explore the wavefunction of *LS* in detail and calculate exchange-coupling constants between radical centers by corresponding Heisenberg-Dirac-van Vleck model Hamiltonian and effective Hamiltonian (Bloch method), CAS Configuration Interaction (CASCI) calculations with (4,4) and (16,16) active spaces were performed.

Results

Symbolic assignment for frontier orbitals that characterize spin states of the tetraradical(oid) *LS* is given in Figure 4 and states in low-energy spectrum determined from CASSCF(16,16) is given in Table 1. A scheme of relative strengths of exchange-coupling constants and Anisotropy of Induced Current Density (ACID) plot for a tetraradical singlet state is given in Figure 5.

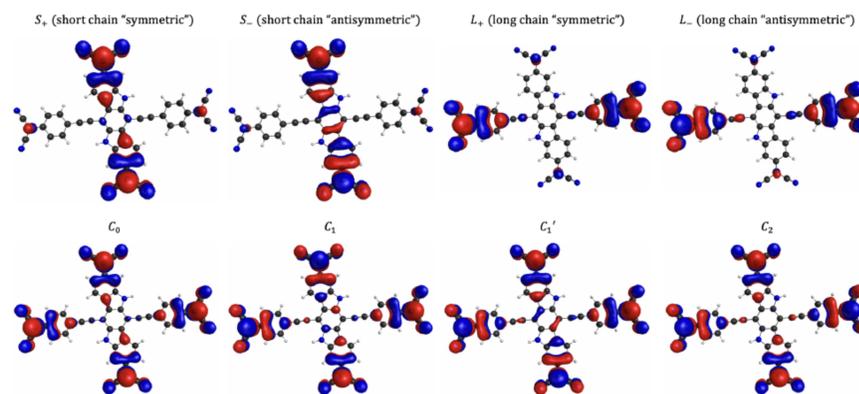


Figure 4: Symbolic assignments to Singly Occupied Natural Orbitals that appear for frontier orbitals in the CASSCF and CASCI solutions. Orbitals are shown as isosurfaces with value 0.015.

Table 1: CASSCF(16,16) results with energy gaps from ground state (G. S.). Under columns HONO - 1 ... LUNO + 1 are CASSCF NOs identities from Figure 4 and their occupation numbers.

State	Symmetry	HONO - 1	HONO	LUNO	LUNO + 1	ΔE from G. S. (cm ⁻¹)
<i>S</i> ₀	<i>A</i> _g	<i>S</i> ₊ 1.221	<i>L</i> ₊ 1.043	<i>L</i> ₋ 0.955	<i>S</i> ₋ 0.781	0.00
<i>T</i> ₀	<i>B</i> _u	<i>S</i> ₊ 1.222	<i>L</i> ₋ 1.000	<i>L</i> ₊ 0.998	<i>S</i> ₋ 0.780	56.76
<i>T</i> ₁	<i>B</i> _u	<i>L</i> ₊ 1.058	<i>S</i> ₊ 0.997	<i>S</i> ₋ 0.995	<i>L</i> ₋ 0.948	532.93
<i>S</i> ₁	<i>A</i> _g	<i>C</i> ₀ 1.059	<i>C</i> ₁ 1.011	<i>C</i> _{1'} 0.977	<i>C</i> ₂ 0.951	534.77
<i>T</i> ₂	<i>A</i> _g	<i>C</i> ₀ 1.043	<i>C</i> ₁ 1.021	<i>C</i> ₁ 0.975	<i>C</i> ₂ 0.959	549.13
<i>Q</i> ₀	<i>A</i> _g	<i>C</i> ₀ 1.002	<i>C</i> ₂ 0.999	<i>L</i> ₋ 0.999	<i>S</i> ₋ 0.997	602.74

$$J_{\bullet\bullet} > J_{\bullet\circ} > J_{\circ\bullet} > J_{\circ\circ} \neq 0$$

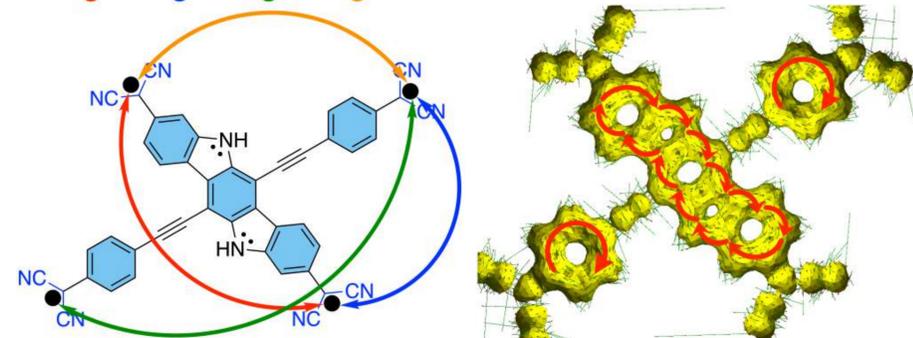


Figure 5: Scheme of strength of exchange-coupling interactions between radical centers in the tetraradical(oid) *LS* (left) and an ACID plot for a singlet state of *LS* calculated with PBE0/cc-pVDZ level of theory shown as isosurface with value of 0.030 (right).

Conclusions

- The conceptual union (\cup) of diradical(oid)s *L* and *S* creates tetraradical(oid) *LS*.
- *LS* has 6 accessible spin states within a maximum range of 603 cm⁻¹ (1.72 kcal/mol).
- Tetraradical(oid) is stabilized by "global aromaticity" of indolo[3,2-*b*]carbazole and aromaticity of phenyls.

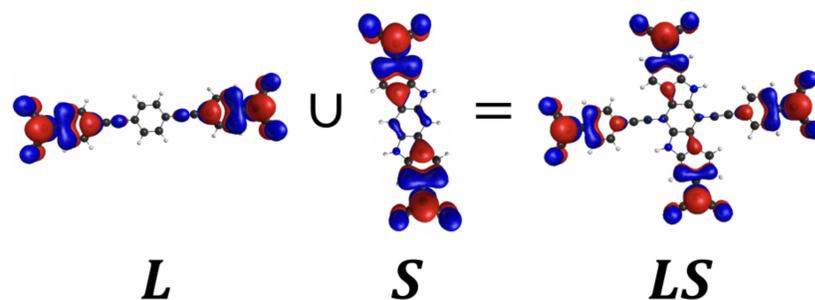


Figure 6: A conceptual union of two diradical(oid)s creates cross-conjugated tetraradical(oid).

Acknowledgements

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