Singlet-Triplet Inversions in Through-Bond Charge-Transfer States

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Abstract: Molecules where the lowest excited singlet state is lower in energy than the lowest triplet are highly promising for a number of organic materials applications as efficiency limitations stemming from spin statistics are overcome. All molecules known to possess such singlet-triplet inversions exhibit a pattern of spatially alternating but non-overlapping HOMO and LUMO orbitals, meaning the lowest excited states are of a local character. Here, we demonstrate that derivatives of the bicyclic hydrocarbon calicene exhibit Hund's rule violations in charge-transfer (CT) states between its rings. These CT states can be tuned with substituents, so that the first excited singlet and triplet state are energetically inverted. This provides a conceptual connection between the emerging fields of inverted gap molecules and existing molecular design rules for state-of-the art thermally-activated delayed fluorescence materials.

Molecules in which the first excited singlet state (S_1) is lower in energy than the lowest triplet state (T_1) are poised to make significant contributions to the field of organic electronic materials. Such a class of inverted singlet-triplet gap materials may overcome existing limitations stemming from spin statistics in, among other applications, organic light-emitting diodes (OLEDs), photocatalysts, and lasers.[1,2] Inverted gap molecules are a specific case of Hund's rule of maximum spin multiplicity being violated in the lowest excited states (red in Figure 1a).[3] This inversion was demonstrated in a heptazine-based OLED device by Aizawa *et al.*[4] However, violations of Hund's rule can exist among higher excited states (blue in Figure 1a), although such cases may not be optically useful. At this point, two types of compounds with inverted singlet-triplet gaps have been classified, namely azaphenalenes[4–18] and non-alternant polycyclic hydrocarbons[19–29] (Figure 1b).

All reported compounds with Hund's rule violations conform to a mechanism by which the frontier molecular orbital (MO) features are located on alternating atoms in a proximate but non-overlapping (disjoint) fashion (Figure 1b).[30] This includes azaphenalenes[7,8] and non-alternant pentalenic molecules,[19–21,23–25] as well as larger multiresonant emitters which have small positive singlet-triplet gaps.[31–33] We recently explored the Hund's rule violations in isopyrene, a pentalenic dimer of azulene, and *trans*-bicalicene, a dimer of calicene, see Figure 2a,b.[23] Azulene is well-studied for its charge-separated ground state, large dipole moment and anti-Kasha emission.[34–36] We and others recently reported substituted azulene derivatives that achieve excited-state Hund's rule violations.[25,28]

Calicene (triapentafulvalene) formally consists of cyclopentadiene (five-membered) and cyclopropylene (three-membered) rings linked by an exocyclic double bond.

As with azulene, the ground-state structure of calicene is aromatically stabilized owing to the push-pull effect between the rings (Figure 2a).[37–40] However, while azulene respects Hund's rule in its excited states,[25,34] calicene does not. In this letter, we explore the potential for controlling Hund's rule violations in calicene derivatives. Through analysis of the charge-transfer (CT) mechanism of its excited states, we show that the frontier MO energetics can be systematically tuned to achieve inversion of the S_1 and T_1 states.
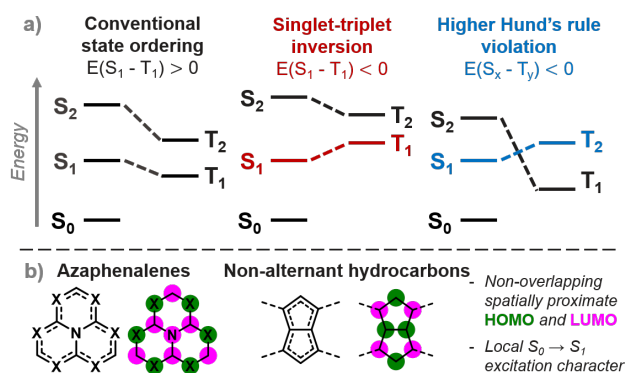
Figure 1. a) Schematic of three situations in the ordering of excited states: all considered states respect Hund's rule (black); Hund's rule is violated in the lowest excited singlet and triplet states (red); Hund's rule is violated in states other than the lowest excited states (blue). b) The ring motifs underpinning existing azaphenalenes and non-alternant hydrocarbons with negative singlet-triplet gaps.

We evaluate the excited state gaps by computing the vertical excitation energies using equations-of-motion coupled cluster with singles and doubles (EOM-CCSD)[41] and the cc-pVDZ basis. Structures are optimized in the ground state at the ωB97X-D/def2-TZVP level and are identified as energy minima with no imaginary frequencies (see Supporting Information for full computational details). EOM-CCSD provides a conservative assessment of excited-state singlet-triplet gaps in organic molecules,[42] and we compare with several other approximated CC methods with larger basis sets in Table S1 of the Supporting Information. Furthermore, our results for calicene are consistent with previously reported results at the CASPT2 level.[38]

Calicene exhibits a Hund's rule violation between the S_3 and T_4 states, which involve the same electron configuration and exhibit a robustly negative energy gap of $E(S_3-T_4)=-98$ meV at the EOM-CCSD/cc-pVDZ level (Figure 2d). A closer look at the orbitals of calicene reveals two quasi-degenerate highest occupied and lowest unoccupied MOs (HOMOs and LUMOs, Figure 2c). The first four singlet and triplet excited states of calicene are each described predominantly by a single-particle transition
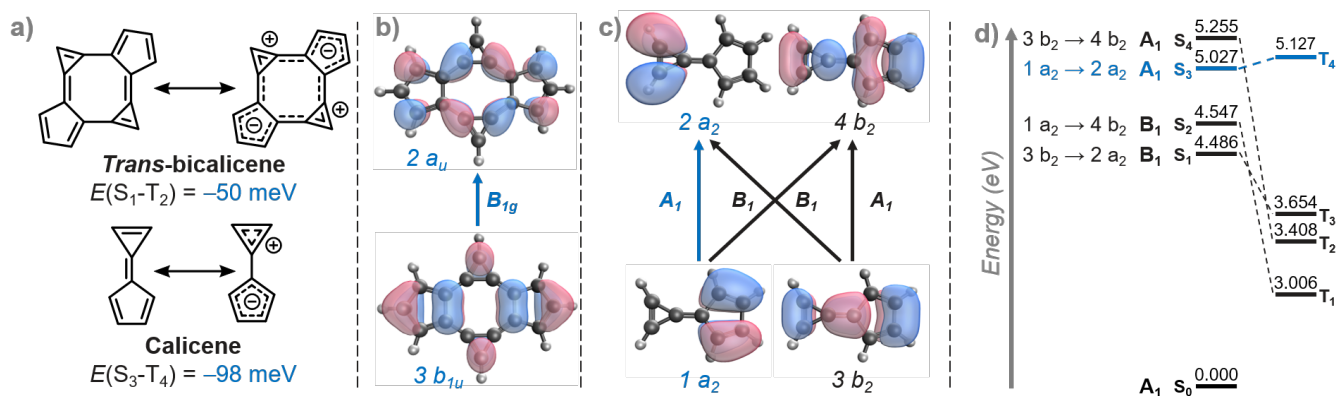
Figure 2. (a) The ground-state push-pull character and Hund´s rule inversions in *trans*-bicalicene and calicene. (b) The quasi-degenerates HOMOs (below) and LUMOs (above) of calicene and the configurations that dominate its first four singlet and triplet excited states. (c) The first four singlet and triplet vertical excited states of calicene. The transition and orbitals that correspond to the Hund´s rule violation are indicated in blue in (b) and (c).

between these four possible MO pairs (Fig 2c-d).

The S_3-T_4 state pair exhibiting the Hund´s rule violation involve a non-overlapping HOMO and LUMO of a_2 symmetry localized on the cyclopentadiene and cyclopropylene fragments, respectively (blue in Figure 2c-d). These states thus constitute a charge-transfer (CT) state with 95% CT character from the 5-membered to the 3-membered ring in S_3 (see Supporting Information).[43] This differs qualitatively from the Hund´s rule violation in *trans*-bicalicene, in which the contributing orbitals are both located on both the 3- and 5-membered rings in an alternating fashion (Figure 2b), leading to only 37% inter-ring CT character in S_1. The other three excited state pairs in calicene, which adhere to Hund's rule, involve two other π-type orbitals of b_2 symmetry (black in Figure 2c). These orbitals are delocalized over the entire molecule, and therefore exhibit significant overlap with each other and with the a_2 orbitals, leading to preservation of Hund´s rule in these three singlet-triplet state pairs.

While a violation of Hund's rule in the excited states is of theoretical interest, it is not optically relevant for the design of optoelectronic materials. Therefore, by stabilizing the LUMO localized on the cyclopropylene fragment and destabilizing the HOMO on the cyclopentadiene relative to the delocalized b_2 orbitals, we show that the energies of the singlet and triplet states violating Hund's rule can be lowered relative to the three other excited states.

Upon substituting the 3-membered ring with a strongly electron-withdrawing *pull* moiety (-CN, magenta in Figure 3), the a_2 LUMO energy is lowered by more than 3 eV, while smaller stabilizing effects are observed on the other orbitals. The Hund´s rule inversion is subsequently preserved but is lowered from S_3 to S_2 with $E(S_2-T_4)=-28$ meV, Figure 3.

Similarly, a large gap is introduced between the near-degenerate HOMOs by substituting at the 5-membered ring with a strong electron-donating *push* group (-NMe₂, green in Figure 3) and the violation is lowered from S_3 to S_2 with $E(S_2-T_4)=-16$ meV.

Finally, we apply both *push* and *pull* substituent strategies in tandem. This way, the gap between the occupied and unoccupied a_2-type orbitals is reduced considerably relative to the b_2 orbitals, and the resulting *push-pull* calicene becomes a true inverted-gap molecule with an inversion between the S_1 and T_1 states with $E(S_1-T_1)=-9$ meV;
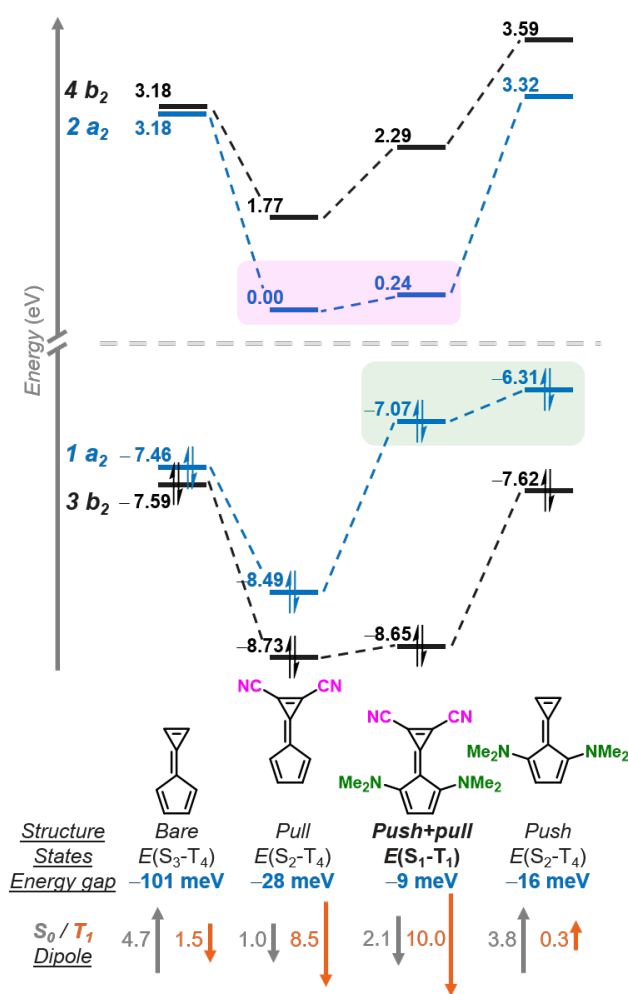
Figure 3. Partial orbital diagram of the two highest occupied and two lowest unoccupied molecular orbitals in calicene and derivatives substituted with electron-donating (push) and withdrawing (pull) groups. The a_2 orbitals dominating the excitations corresponding to the Hund's rule violation and the magnitude of the negative gap between these states are shown in blue. Magnitude and direction of the dipoles of the ground state and T_1 minima are shown in grey and orange, respectively. Energy axis not to scale.

further results in Table S2. Across all four compounds, the natural transition orbitals of the states violating Hund's rule closely resemble the a_2 orbitals shown in Figure 2c (see Figure S1).

Calicene is aromatic in the ground state and, due to its adaptive aromatic nature, exhibits a reversal of its dipole between the ground and lowest excited state.[23,39,40,44] The *push-pull* substitution pattern proposed here counteracts the dipolar aromatic resonance structure of calicene, leading to a reduction of ground-state aromaticity (Figure S2) and a reduction or reversal in the ground-state dipoles in the substituted compounds (grey in Figure 3). The substituted compounds do not exhibit dipole reversal, and the excited (T_1) state dipoles of the *pull* and *push-pull* compounds are much larger than in the bare compound (orange in Figure 3). Thus, it can be understood that the CT-type states become the lowest excited states by virtue of the substituents counteracting the intrinsic dipole of the calicene motif. As a result, the ground-state aromaticity of the substituted compounds is attenuated relative to to bare calicene. Furthermore, the *push-pull* derivative is mildly Baird aromatic in both rings in the T_1 state, unlike calicene[23,44] and the *push* and *pull* derivatives (Figure S2).

We explored functionalization of calicene at various positions and with different substituents to evaluate the scope of the Hund's rule violation. The a_2 occupied orbital has pronounced features on the carbon atoms of the 5-membered ring adjacent to the exocyclic double-bond (R_2 position in Figure 4), while the b_2 occupied orbital does not. By placing electron-donating groups at the R_2 position, the energy of the a_2 HOMO is raised selectively relative to the b_2 orbital. Substitution at the R_3 position, however, destabilizes both occupied orbitals and in fact can eliminate the Hund's rule violation (e.g. $E(S_4-T_4)=+65$ meV for -OH substitution, Figure 4). Substituting with donors at both available positions on the 5-membered ring preserves the Hund's rule violation, but changes the order of the state state pair to S_3-T_4. Once an acceptor and donor have been placed at the R_1 and R_2 positions, respectively, further functionalization at the R_3 position has no effect on either the magnitude or order of the violation. Reversal of the substituent strategy - by placing electron-donating groups on the 3-membered ring or electron-withdrawing groups on the 5-membered ring - also increases the state order of the Hund's rule violation or eliminates it entirely (Table S3).

A number of electron-withdrawing and -donating substituents were tested at the at the R_1 and R_2 positions, respectively. We find that the Hund's rule violations are robust with various substituents (Figure 4 and Table S3), but note that only the strongest donating and withdrawing groups which remain in the plane of the calicene rings are sufficient to maintain the inversion between the S_1 and T_1 states at the EOM-CCSD level. However, the specific order of the states in the triplet manifold is method-dependent; with the CC2 method we find that more inversions are potentially between the S_1 and T_1 states than the EOM-CCSD computations suggest.
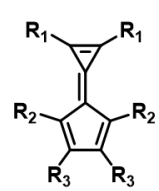
Electron-donating groups weaker than -NMe$_2$, such as -OH, -OMe, -NH$_2$, -Me and -NPH$_3$ (Figure 3) all exhibit inversions in the S_1 state when placed at the R_2 position, but the corresponding triplet of same configuration is not the T_1 state. The only other R_2 substituent we find which contributes to a negative S_1-T_1 gap at the EOM-CCSD level when used in conjunction with the -CN acceptor is the extremely strong alkylphosphazene (-NPMe$_3$) donor ($E(S_1-T_1)=-13$ meV, see Figure S3 for the full state diagram).

A review of the experimental literature reveals that many calicene derivatives have been synthesized, most commonly with alkyl, aryl and halide substituents.[45–48] We evaluated one synthesized derivative[48] which is small enough to be computed at the EOM-CCSD level and found that is has a Hund's rule inversion in the S2 state (4). While bare calicene has not been synthesized, reports of the synthesis of substituted derivatives containing strong electron-withdrawing groups[49,50] suggests that push-pull compounds such as those reported here may be feasible.

In the NMe$_2$-substituted push-pull compound discussed in Figure 3, the T_1-T_3 states are very close in energy to one another (T_2-T_1 < 0.01 eV, see Figure S3). The energetic proximity of multiple states of different (delocalized and CT) character to the lower S_1 state may provide efficient channels for reverse intersystem crossing.[51,52] By contrast, in the more strongly polarized NPMe$_3$-substituted compound, the CT-type T_1 state is 0.25 eV below the next lowest triplet (see Figure S3).

We further examine the excited state energies of these two compounds with S_1-T_1 inversions at their excited state minima (S_1, T_1, T_2 and T_3, see Figures S4-S5). In both compounds, the Hund's rule violation is preserved across all excited state minima considered. In particular, the Hund's rule violation persists in the S_1 and T_1 states at both the S_1 and T_1 minima, i.e., the inversion is still at S_1-T_1. It is therefore possible that the singlet-triplet inversion can help optimize the photophysical properties in this class of molecules.

Energy gap (*meV*)	R_1	R_2	R_3	
$E(S_2-T_4) = -24$	H	OH	H	*Position of*
$E(S_4-T_4) = +65$	H	H	OH	*electron donor*
$E(S_3-T_4) = -17$	H	OH	OH	
$E(S_1-T_3) = -17$	CN	OH	Me	
$E(S_1-T_3) = -17$	CN	OH	SH	*Outer position of*
$E(S_1-T_3) = -17$	CN	OH	F	*5-membered ring*
$E(S_1-T_3) = -19$	CN	OH	CF$_3$	
$E(S_1-T_3) = -21$	CN	Me	H	
$E(S_1-T_3) = -18$	CN	OMe	H	
$E(S_1-T_2) = -19$	CN	OH	H	*Strength of*
$E(S_1-T_2) = -16$	CN	NH$_2$	H	*electron donor*
$E(S_1-T_2) = -15$	CN	NPH$_3$	H	
$E(S_1-T_1) = -9$	**CN**	**NMe$_2$**	**H**	
$E(S_1-T_1) = -13$	**CN**	**NPMe$_3$**	**H**	
				Synthesized
$E(S_2-T_4) = -17$	Ph	Cl	Cl	*compound(a)*

Figure 4. Energy gaps between singlet and triplet excited states in some substituted calicenes. Full results are presented in Table S3. a = Synthesis reported by Bergmann and Agranat[48]

Triafulvene and pentafulvene consist of a three- and five-membered ring, respectively, and an exocyclic double bond (Figure S6). They can be seen as the parent compounds of calicene. Neither of these, nor the donor- and acceptor-substituted derivatives thereof, display a pair of non-overlapping orbitals. Consequently, none exhibits a Hund's rule violation in its low-lying excited states, highlighting that the push-pull mechanism inherent to calicene is a necessary requirement to achieve a CT-type inversion.

The next larger push-pull fulvalene is sesquifulvalene, in which the three-membered ring is replaced by a seven-membered ring (see Figure S6 for structure).[53] Analogous to calicene, the ground state possesses a dipolar

resonance structures and aromatic character.[44] However, despite exhibiting similar orbital features to calicene, no Hund´s rule violation exists among any of its excited states (Figure S7). This may be due to its lower intrinsic push-pull character; the dipole of sesquifulvalene is 3.3 D compared to 4.7 D for calicene.[44] We applied the strategy described for calicene above, where electron-donating and -withdrawing substituents were placed at the relevant orbital positions to minimize the orbital gap between the CT-type orbitals, but only one compound with a high-lying violation could be located (Table S4) at the EOM-CCSD/cc-pVDZ level.

CT-type inversion of the S_1 and T_1 state has been discussed previously different contexts.[54–56] Bonačić-Koutecký and Michl have observed that a highly twisted zwitterionic aminoborane (H_2B-NH_2, Figure S6) – corresponding to its relaxed S_1 geometry – yields a negative gap using configuration interaction.[54] These states are described by an electron transfer mechanism between the occupied nitrogen p-orbital lying at a $90°$ dihedral angle to the unoccupied boron p-orbital. The coupled-cluster-based methods we report here predict a small positive gap (50 meV) for aminoborane in its relaxed S_1 geometry (Table S5). However, with a small structural perturbation (methylation at both B and N), the orthogonal geometry is preserved in the S_1 state and the gap becomes negative at the EOM-CCSD/cc-pVDZ level (-9 meV, Table S5). By contrast, the calicene derivatives reported here are both organic and planar. Unlike CT states formed via couplings between orthogonal donor and acceptor fragments, the states violating Hund's rule here are not true dark states, but instead exhibit some oscillator strength (Table S2).

In summary, we have identified the first organic molecules to exhibit a negative singlet-triplet gap in a through-bond CT state. By substituting calicene, which exhibits a Hund's rule violation in upper excited states, the existing inversion is lowered to S_1 and T_1, a property which is preserved in the excited state geometries. This occurs by tuning the energies of the orbitals corresponding to these states' most significant configurations. The functionalization is shown to reverse the dipole and suppress both the ground-state aromaticity and excited state anti-aromaticity relative to bare calicene.

This result provides a conceptual link between two pre-existing design principles for organic light-emitting molecules. On one hand, a prevailing strategy for thermally-activated delayed fluorescence (TADF) emitters involves minimizing the (positive) singlet-triplet gap by tuning the spatial separation of HOMO and LUMO on distinct and often orthogonal fragments in donor-acceptor-type compounds. On the other hand, both multi-resonance TADF emitters[31–33] and the emerging family of inverted singlet-triplet gap molecules[1] rely on spatially proximate though non-overlapping frontier MOs which are found in specific alternant and non-alternant planar ring motifs. The compounds presented here simultaneously exhibit clear CT character emerging from a single conjugated donor-acceptor-type scaffold and a negative singlet-triplet gap without the alternating HOMO/LUMO orbital features. Such a combination of properties may be useful for applications requiring the harvesting of spin-pure electrons from a CT state, such as chirality-induced spin selectivity.[57]

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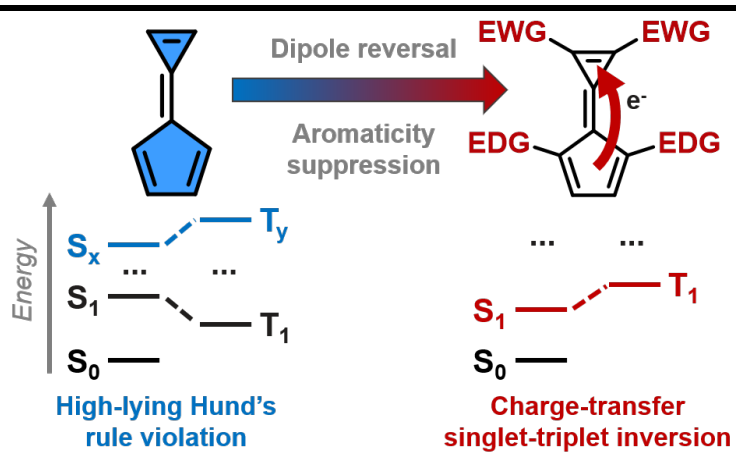
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