Are organic molecules able to break the Hund's rule?

Correlation
E(S₁)<E(T₁)

Exchange

E(S₁)>E(T₁)
Correlation vs. exchange competition drives the singlet–triplet excited-state inversion in non-alternant hydrocarbons


In this work, we focus on the understanding of the driving force behind the S\textsubscript{1}–T\textsubscript{1} excited-state energy inversion (which would thus violate Hund’s rule, making the S\textsubscript{1} state lower in energy than the T\textsubscript{1} state) of two non-benzenoid non-alternant hydrocarbons, composed of odd-membered rings. The molecules considered here have identical chemical composition but different atomic configuration in space. The delicate interplay between structural and electronic factors that might induce inversion and its energy extension, only by a few meV, is systematically investigated here by state-of-the-art calculations. Qualitative and quantitative accurate predictions are obtained employing post-HF methods, thanks to the balanced and careful inclusion of electron correlation effects. The obtained results might guide and rationalize new searches for molecules violating Hund’s rule, concomitantly demonstrating the importance of key contributions from the theoretical method of choice.

1. Introduction

The molecules dicycloheptac[cdgh]pentalene (1) and dicyclopenta-[ef,kl]heptalene (2) are non-benzenoid non-alternant hydrocarbons, see Fig. 1, historically predicted as candidates violating Hund’s rule in their lowest singlet (S\textsubscript{1}) and triplet (T\textsubscript{1}) excited states.\textsuperscript{1,2} Thus, hypothetically situating S\textsubscript{1} lower in energy with respect to T\textsubscript{1}, contrarily to most of the known conjugated systems.\textsuperscript{3} The simplest combination of cycloheptatriene (a 7-membered ring) and cyclopentadiene (a 5-membered ring) indeed constitutes the azulene molecule, which can thus be viewed as the building block of compounds 1 and 2. However, it has been experimentally confirmed by photodetachment photoelectron spectroscopy that azulene does not violate Hund’s rule.\textsuperscript{4} On the other hand, the violation of Hund’s rule has been very recently predicted from theoretical calculations\textsuperscript{5} only for compound 1 and not for 2, but experiments to corroborate this finding are still missing, as far as we know, which has prompted us to systematically investigate in detail these systems given their structural similarity. Interestingly, the violation of Hund’s rule for excited states of compounds 1 and/or 2 would arise without the need to introduce heteroatoms into their structure, as opposed to the recently synthesized heptazine derivatives for which a negative $\Delta E_{ST}$ was demonstrated.\textsuperscript{6} The latter study first screened a large set (around $35 \times 10^3$) of compounds to identify viable candidates for this excited-state energy inversion, to then narrow down the set of candidates to only 3% of the original number. They finally selected a pair of molecules to be synthesized and experimentally analyzed by temperature-dependent transient photoluminescence spectroscopy, constituting a clear advance from an experimental point of view and showing how challenging and costly can be the whole process to optimize molecules expected to behave in this way.

Actually, the different calculations so far performed on nitrogen and/or boron-doped materials not only anticipated this effect long ago for heterodoped compounds, but also allowed the understanding of the physical effects driving this excited-state inversion.\textsuperscript{7–16} Invigorated by this set of
2. Computational details

The geometries of azulene and compounds 1 and 2 are fully optimized (with no symmetry restrictions) at the oB97XD/def2-TZVP level of theory.\textsuperscript{25} We calculate the vertical excitation singlet ($S_1 \leftrightarrow S_0$) and triplet ($T_1 \leftrightarrow S_0$) energies, resulting in the energy difference $\Delta E_{S_1T_1} = E(S_1) - E(T_1)$, employing a variety of wavefunction methods. First, configuration interactions (CI) with single (S) and partially introduced double (D) substitutions, or CIS and CIS(D),\textsuperscript{26} respectively, as well as the spin-component-scaled (SCS-) version of the latter, SCS-CIS(D),\textsuperscript{27} will be applied, followed by a second-order approximate Coupled Cluster singles and doubles method CC2\textsuperscript{28,29} and second-order Algebraic Diagrammatic Construction ADC(2)\textsuperscript{30} together with their corresponding SCS-based versions, named SCS-CC2 and SCS-ADC(2), respectively. The latter corrects excitation energies by introducing different opposite-spin ($C_{sp}=6/5$) and same-spin ($C_{sp}=1/3$) coefficients, which are obtained after a reparameterization against some training sets.\textsuperscript{31}

The restricted active space (RAS) method is selected here to obtain reference results due to its excellent trade-off between accuracy and computational cost for any spin-dependent multi-state calculation.\textsuperscript{32-34} First, a Configuration Interaction (RAS-CI)\textsuperscript{15-17} is obtained through the hole-particle formalism. A Spin-Flip (RAS-SF\textsuperscript{38–40}) flavor is next applied, using a triplet state as a high-spin reference and incorporating by default mostly the non-dynamical (long-range) correlation energy. Then, an additional exchange–correlation energy functional is coupled (RAS-CI-srDFT or simply RAS-srDFT in the following) to incorporate some of the missing dynamic (short-range) correlation energy.\textsuperscript{41} As the active space of $n$ electrons in $m$ orbitals needed for any of these RAS-based calculations, denoted here simply as $[n,m]$, we will use minimalistic $[2,2]$, moderate $[4,4]$ and $[6,6]$, and large $[8,8]$ and $[10,10]$ active spaces in all cases to understand the influence of the correlation energy added by increasing the active space size. All of these results are compared with the equation-of-motion coupled-cluster single and doubles method, or EOM-CCSD,\textsuperscript{42} which has recently been shown to be a very accurate method for electronic excitations too.\textsuperscript{43}

Time-dependent density functional theory (TD-DFT) will also be applied complementarily due to its wide use for excited-state calculations. To isolate the dependence of the TD-DFT results with respect to the functional form, we keep the parameter-free PBE exchange ($E_x[p]$) and correlation ($E_c[p]$) functionals fixed, and systematically vary the weight ($c_x$) of the EXact-eXchange (EXX) term to form the corresponding hybrid expression as:

$$E_{\text{EXX}}[\rho] = c_x E_x[\rho] + E_c[\rho] = c_x E_{\text{EXX}} + (1 - c_x) E_x[\rho] + E_c[\rho],$$

with $c_x = 0$ (PBE\textsuperscript{44}), $c_x = 1/10$ (PBE0\textsuperscript{45}), $c_x = 1/4$ (PBE0\textsuperscript{46}), $c_x = 1/3$ (PBE0-1/3\textsuperscript{47}), and $c_x = 1/2$ (PBEHH\textsuperscript{48}). For completeness, we will also assess the long-range corrected LC-PBE functional\textsuperscript{49} (with
the range-separation parameter \( \omega = 0.47 \text{ bohr}^{-1} \) and LC-\( \omega \)PBE functional\(^{30,31} \) [with the range-separation parameter \( \omega = 0.40 \text{ bohr}^{-1} \)]. A further step, from hybrid to Double–Hybrid (DH) functionals, can be done by merging second-order Perturbation Theory (PT2) and the correlation functional,

\[
E_{\text{corr}}[\rho] = E_{\text{xc}}[\rho] + c_E E^{\text{PT2}}_E + (1 - c_E) E_{\text{xc}}[\rho],
\]

with \( c_E \) being the weight given to that contribution with the following specifications: \( c_E = 1/2 \) and \( c_E = 1/8 \) (PBE0-DH\(^{52} \)), \( c_E = 3^{-1/3} \) and \( c_E = 1/3 \) (PBE-QIDH\(^{53} \)), and \( c_E = 2^{-1/3} \) and \( c_E = 1/2 \) (PBE-2\(^{54} \)). We also explore the use of the modern \( r^2 \)SCAN parameter-free exchange–correlation functional\(^{55} \) for the latter expressions, that is \( r^2 \)SCAN0-DH, \( r^2 \)SCAN-QIDH, and \( r^2 \)SCAN0-2, respectively.\(^{56} \)

The cost-effective 6-31G(d) basis set will be employed for all the excited-state calculations, with the ESI† (see Fig. S1) showing the negligible effect beyond the 6-31G(d) basis set, compared with the larger aug-cc-pVDZ or the def2-TZVP ones, at e.g. the RAS-SF level. Nucleus-independent Chemical Shifts (NICS) were evaluated for each of the rings at the \( \text{HF/6-31G(d)} \) level\(^{57} \) using the gauge-independent atomic orbital (GIAO) method.\(^{57} \) The TD-DFT, CIS and (SCS-)CIS calculations are done with the ORCA 5.0 package,\(^{58} \) (SCS-)CC2 and (SCS)-ADC(2) with the TURBOMOLE 7.4 package,\(^{59} \) while NICS, RAS[r,n]-CI, RAS[r,n]-SF, RAS[r,n]-srDFT, and EOM-CCSD calculations employed the Q-CHEM 6.0 package.\(^{60} \)

3. Results and discussion

3.1 General remarks

In the following, we explore the performance of a variety of wavefunction and TD-DFT approaches in the computation of singlet and triplet excitation energies for molecules 1 and 2. Moreover, we use the accuracy of the different methods in the calculation of singlet and triplet excitation energies to rationalize the physical effects controlling the singlet–triplet gap, concretely, in 1 and 2, also serving as a general reminder of the necessary requirements to observe their inversion.

Ground state optimized structures of 1 and 2 correspond to the \( D_{2h} \) symmetry point group. The lowest-lying singlet (S\(_1\)) and triplet (T\(_1\)) excited states of the two non-alternant hydrocarbons are (almost) exclusively composed by a HOMO to LUMO electronic excitation (i.e., from the highest occupied molecular orbital or HOMO to the lowest unoccupied molecular orbital or LUMO), regardless of the employed computational method. Interestingly, despite that the frontier molecular orbitals of 1 and 2 have different symmetries (see Fig. 2), S\(_1\) and T\(_1\) in both cases belong to the \( B_{1g} \) irreducible representation. Therefore, the optical transition to \( S_1 \) at the Franck–Condor region is symmetry forbidden, i.e., would display a zero oscillator strength.

EOM-CCSD/6-311G(d) results reveal that the computed vertical energies to \( S_1 \) and \( T_1 \) for 1 are 2.053 and 2.078 eV, respectively, hence suggesting a singlet–triplet inversion of \( \approx 25 \text{ meV} \), in good agreement with previous calculations\(^5 \) at the EOM-CCSD/aug-cc-pVDZ level (\( \Delta E_{ST} = -14 \text{ meV} \)). On the other hand, in 2, the excited singlet lies slightly above the lowest triplet (\( \Delta E_{ST} = 23 \text{ meV} \)), with transition energies obtained at 1.991 and 1.968 eV, respectively, thus indicating a different state ordering for 1 and 2.

3.2 The role of orbital localization, exchange, and aromaticity

The origin of the small singlet–triplet gap in these \( \pi \)-conjugated molecules (\( \Delta E_{ST} < 100 \text{ meV} \)) emerges from the small exchange energy, which relates to the properties of the two frontier orbitals (mostly) describing the \( S_1 \leftarrow S_0 \) and \( T_1 \leftarrow T_0 \) electronic transitions. Note that HOMO and LUMO of both biazulenes exhibit a disjoint-like nature (Fig. 2), thus resulting in a small spatial overlap, which is known to promote low \( \Delta E_{ST} \) values.\(^{61} \) Actually, we have calculated Tozer’s A index,\(^{62} \) a measure of spatial overlap for a given excitation ranging between 0 (no overlap) and 1 (full overlap), at the HF/6-311G* level, to find values of \( A = 0.466 \) and \( A = 0.566 \) for 1 and 2, respectively, thus indicating a smaller overlap for compound 1 than for compound 2, as well as for azulene for which \( A = 0.589 \).

This situation resembles the electronic structure of disjoint non-Kekulé diradicals, in which both semioccupied orbitals are represented over different sets of atoms. Then, by decreasing the electronic repulsion, the triplet is less favored over the singlet; i.e., the gap between both states narrows.\(^{63} \) Indeed, in a simplified two-electrons in two-orbitals (2e2o) model, i.e., CAS-CI(2,2), \( S_1 \) and \( T_1 \) states correspond (entirely) to the spin adapted single electron occupation of HOMO and LUMO for compounds 1 and 2. For disjoint orbitals, as those HOMO and LUMO found in 1 and 2, the small exchange integral \( K = \int \phi_i(\mathbf{r})\phi_j(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|^{-1}\phi_j(\mathbf{r})\phi_i(\mathbf{r})d\mathbf{r}d\mathbf{r}' \) between the HOMO (\( \phi_i \equiv \phi_{\text{HOMO}} \)) and the LUMO (\( \phi_j \equiv \phi_{\text{LUMO}} \)) gives rise to low exchange energy and thus to low \( \Delta E_{ST} \) gap, since \( \Delta E^{2e2o}_{ST} = 2K \), computed as 323 and 370 meV for 1 and 2, respectively.

The description of \( S_1 \) and \( T_1 \) in 1 and 2 by the simple CIS method nearly corresponds to the 2e2o model (HOMO to LUMO amplitudes greater than 0.98 for both cases). CIS overestimates both excitation energies (see Table 1 and Fig. 3),
Table 1  Vertical excitation energies to $S_1$ and $T_1$ (in eV) and associated $\Delta E_{ST}$ energy difference (in meV) calculated with different methods and the 6-311G(d) basis set

<table>
<thead>
<tr>
<th>Method</th>
<th>$S_1 \rightarrow S_0$</th>
<th>$T_1 \rightarrow S_0$</th>
<th>$\Delta E_{ST}$</th>
<th>$S_1 \rightarrow S_0$</th>
<th>$T_1 \rightarrow S_0$</th>
<th>$\Delta E_{ST}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS</td>
<td>2.684</td>
<td>2.376</td>
<td>308</td>
<td>2.576</td>
<td>2.177</td>
<td>399</td>
</tr>
<tr>
<td>PBE</td>
<td>1.985</td>
<td>1.701</td>
<td>284</td>
<td>1.942</td>
<td>1.732</td>
<td>210</td>
</tr>
<tr>
<td>PBE</td>
<td>1.989</td>
<td>1.711</td>
<td>278</td>
<td>1.941</td>
<td>1.732</td>
<td>209</td>
</tr>
<tr>
<td>PBEH</td>
<td>2.050</td>
<td>1.867</td>
<td>183</td>
<td>1.994</td>
<td>1.761</td>
<td>233</td>
</tr>
<tr>
<td>PBE0</td>
<td>2.139</td>
<td>1.924</td>
<td>215</td>
<td>2.070</td>
<td>1.798</td>
<td>272</td>
</tr>
<tr>
<td>PBE0-1/3</td>
<td>2.186</td>
<td>1.953</td>
<td>233</td>
<td>2.110</td>
<td>1.816</td>
<td>294</td>
</tr>
<tr>
<td>PBEHH</td>
<td>2.279</td>
<td>1.996</td>
<td>283</td>
<td>2.190</td>
<td>1.847</td>
<td>343</td>
</tr>
<tr>
<td>LC-PBE</td>
<td>2.305</td>
<td>2.061</td>
<td>244</td>
<td>2.266</td>
<td>1.943</td>
<td>323</td>
</tr>
<tr>
<td>LC-oPBE</td>
<td>2.252</td>
<td>2.019</td>
<td>233</td>
<td>2.221</td>
<td>1.903</td>
<td>318</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>2.171</td>
<td>1.962</td>
<td>209</td>
<td>2.087</td>
<td>1.808</td>
<td>279</td>
</tr>
<tr>
<td>oB97X-D</td>
<td>2.190</td>
<td>1.995</td>
<td>195</td>
<td>2.110</td>
<td>1.842</td>
<td>268</td>
</tr>
<tr>
<td>PBE0-DH</td>
<td>2.136</td>
<td>1.970</td>
<td>166</td>
<td>2.075</td>
<td>1.849</td>
<td>226</td>
</tr>
<tr>
<td>rSCAN0-DH</td>
<td>2.198</td>
<td>2.134</td>
<td>64</td>
<td>2.125</td>
<td>2.044</td>
<td>81</td>
</tr>
<tr>
<td>PBE-QDGH</td>
<td>2.072</td>
<td>2.138</td>
<td>–66</td>
<td>2.027</td>
<td>2.039</td>
<td>–12</td>
</tr>
<tr>
<td>rSCAN0-QDGH</td>
<td>2.101</td>
<td>2.145</td>
<td>–44</td>
<td>2.048</td>
<td>2.035</td>
<td>13</td>
</tr>
<tr>
<td>PBE0-2</td>
<td>2.010</td>
<td>2.137</td>
<td>–127</td>
<td>1.977</td>
<td>2.049</td>
<td>–72</td>
</tr>
<tr>
<td>rSCAN0-2</td>
<td>2.025</td>
<td>2.134</td>
<td>–109</td>
<td>1.988</td>
<td>2.038</td>
<td>–50</td>
</tr>
</tbody>
</table>

- Taken from ref. 5.

especially for $S_1$, which might be attributed to the lack of electron correlation. In fact, CIS can be seen as a mean-field approach for excited states, similar to HF for the electronic ground state. The CIS singlet–triplet energy gap can be approximately related to the exchange interaction, $\Delta E_{ST} \approx 2K$, because CIS includes configuration interaction effects beyond the 2e2o scheme. Since $K > 0$, CIS always locates $S_1$ above $T_1$, with a 308 meV gap for 1 and higher (399 meV) for 2.

Taking into account previous studies, the strength of the exchange interaction in both systems seems sufficiently weak to be influenced by correlation effects and revert the sign of $\Delta E_{ST}$, as obtained from EOM-CCSD calculations on 1. Actually, the $\Delta E_{ST}$ values recently computed for cyclazine and heptazine at the CIS level, two molecules to violate Hund’s rule, are 340 and 400 meV, respectively, i.e., of the same order as those obtained for molecules 1 and 2. On the other hand, despite the disjoint-like character of the HOMO and LUMO in azulene (Fig. 2), it shows a considerably larger 2K value (624 meV at the CIS level), which might thus preclude the inversion of its $S_1$ and $T_1$ energies. Complementarily, sophisticated DFT/MRCI calculations predicted a $\Delta E_{ST}$ value for azulene of 69 meV, small but positive, in agreement with the arguments exposed here.

Note that the orbital localization, aimed at minimizing the exchange integral, is a consequence of symmetry, which in some instances is triggered by aromaticity. We use the Nucleus-Independent Chemical Shifts (NICS) to describe the aromaticity of ground state of azulene, and compounds 1 and 2. The NICS values (see Fig. 3) indicate the local aromaticity of all the 5- and 7-membered rings of the compounds under study. Moreover, the values for molecules 1 and 2 fully reflect their $D_{2h}$ nuclear symmetry. Comparing azulene with compounds 1 and 2, the 7-membered ring is always less aromatic than the 5-membered ring, in agreement with previous results. Local aromaticities of cycloheptatriene and cyclopentadiene are understood as the consequence of electron sharing, so they both fulfill the $(4n+2)$-electron Hückel rule for aromaticity. Nevertheless, the lowest $\pi^*$ excited states (those $S_1$ and $T_1$ here) in most cases follow the Baird’s rule, being classified as aromatic/antiaromatic those cycles with $(4n+2)$-electrons. We thus highlight that the localization of the orbitals involved in the $S_1$ and $T_1$ excited state transition is a prerequisite but not a sufficient condition for the excited-state inversion and that aromaticity (in view of Baird’s rule for excited states) cannot be used by itself as a criterion for rationalizing or predicting the excited-state energy inversion without further and deeper investigation. Additionally, NICS calculations performed at the DFT level with different exchange–correlation functionals (i.e., CAM-B3LYP, LC-oPBE, oB97X-D, PBE0, PBE and PBEh) do not show any clear correlation between state aromaticity and computed $S_1/T_1$ gaps (see the ESI†). On the other hand, although it would be interesting to explore differences in excited singlet and triplet aromaticities with correlated wavefunctions, e.g. CASSCF, these calculations are beyond the scope of the present study.
3.3 The critical role of the correlation energy

The results discussed above clearly indicate that weak exchange interaction, although required, it is not a sufficient condition to invert the energy ordering of $S_1$ and $T_1$. Hence, it seems necessary to consider electron correlation effects beyond the mean-field (CIS) solution. For this, we turn our attention to the impact of electron correlation in the computation of singlet–triplet energies within TD-DFT in various flavors and a manifold of wavefunction-based methods.

### 3.3.1 TD-DFT calculations

Next, TD-DFT calculations are assessed, considering a set of functionals all based on the PBE expression. More precisely, we explore the performance of PBEx (an exchange-only functional), PBE exchange–correlation functional, and four hybrid functionals with a linear increase in $c_x$: PBEh, PBE0, PBE0-1/3, and PBEHH. The results gathered in Table 1 (Fig. 4) show that the PBE-derived functionals correct the systematic overestimation of the CIS singlet and triplet excitation energies, with the values for these excitation energies increasing with the amount of exact exchange or $c_x$. Interestingly, there is a negligible effect from the PBE correlation functional, with nearly identical PBEx and PBE excitation energies. But, despite the correction of the excitation energies, hybrid functionals have also a small impact on singlet–triplet relative energies, which remain notably larger with respect to the reference EOM-CCSD values (Fig. 5). These results agree with the inability of standard TD-DFT approaches to invert the energy of the $S_1$ and $T_1$ states, as they have been previously demonstrated in many related studies.\(^8\textsuperscript{,}12\textsuperscript{–}16\) Moreover, the computed $\Delta E_{ST}$ values for 1 and 2 increase with $c_x$, a variation typically found in other conjugated molecules. All TD-DFT calculations done here for azulene also strongly overestimate $\Delta E_{ST}$ by 400–500 meV with respect to reference results, irrespective of the functional choice (see the ESI). Excitation energies with long-range corrected functionals (i.e., CAM-B3LYP and oB97XD) are close to those with large HF exchange, e.g., PBE0-1/3 and PBEHH, always leading to large $\Delta E_{ST}$ values.

Next, we analyze the performance of double-hybrid functionals for excited-state calculations.\(^6\textsuperscript{8}\textsuperscript{,}6\textsuperscript{9}\) In this sense, we would like to remark that excitation energies with these methods, $\Omega^{DH}$, are obtained in a two-step procedure as: $\Omega^{DH} = \Omega + c_D\Delta(D)$, with $c_D$ being the weight given in eqn (2) to the perturbative term, which translates to a $(D)$-like correction to excited states\(^7\textsuperscript{0}\) of any type. Additionally, their recent application to N-doped organic molecules showing the equivalent excited-state inversion has confirmed their accuracy in the computation of small $S_1/T_1$ energy gaps.\(^14\) In general, the DH excitation energies for both biazulenes are slightly larger than
the EOM-CCSD values (Table 1 and Fig. 4), with $\Delta E_{ST}$ approaching the reference energy gaps (especially for larger $c_v$ values) and linearly decreasing with the $c_v$ coefficient. Hence, indicating the importance of wavefunction-like second-order perturbative corrections in order to capture the differential correlation effects between the excited singlet and triplet states. Interestingly, the $\Delta E_{ST}$ value for compound 1 always remains lower than that for compound 2, although PBE0-DH (PBE-QIDH and PBE0-2) both predicted to be positive (negative).

The use of the r$^2$SCAN exchange–correlation functional instead of PBE attenuates the values in all cases, bringing them closer to the reference results, with r$^2$SCAN-QIDH providing $\Delta E_{ST}$ values of $-44$ and $13$ meV for compounds 1 and 2, respectively, in close agreement with the reference results. Note that the newest r$^2$SCAN correlation functional recovers more exact constraints than the PBE original one, and it is thus expected to behave more accurately once a pair of $(c_s, c_v)$ values is determined.\footnote{By analyzing now the contribution of the $c_v \Delta(D)$ correction for the successful r$^2$SCAN-QIDH model, this amounts to $-314$ and $-224$ meV ($-251$ and $-159$ meV) for the $S_1$ and $T_1$ excited states of 1 (2), respectively, indicating a slightly more pronounced impact of the second-order perturbative-like correlation correction for the former molecule but always larger for $S_1$ than for $T_1$ in both cases.}

\subsection{Post-Hartree–Fock methods.}

Given the importance of second-order perturbative correlation effects observed with the TD-DFT results with double-hybrid functionals, we now investigate the role of higher excitations (beyond singles in CIS) in the calculation of $\Delta E_{ST}$ for the two studied biazulenes through the lens of wavefunction methods. In general, the singlet–triplet energy difference computed with post-HF methods can be split into mean-field and correlation contributions. We associate the former to the CIS gap, mostly emerging from exchange interaction ($\Delta E_{ST}^{\text{CIS}} \approx 2K > 0$) and the remaining to the differential correlation effects:

$$\Delta E_{ST} = \Delta E_{ST}^{\text{CIS}} + \Delta E_{ST}^{\text{corr}}$$

A first estimate of the importance of correlation effects to correct mean-field (CIS) $S_1$ and $T_1$ excitation energies is given by the CIS(D) and SCS-CIS(D) single-reference methods (see Table 1 and Fig. 4), which introduces double excitations although approximately. Both methods considerably stabilize excitation energies of compounds 1 and 2, particularly for the $S_1$ state, leading to a marked inversion of the excited-state energies (Fig. 5). In other words, they provide too negative (overestimated, vide infra) $\Delta E_{ST} < 0$ values. Note that previous theoretical results at the CISD/T level, done with a minimal basis set, also predicted the excited-state inversion for both compounds.\footnote{Additionally, all of these methods predict a negative $\Delta E_{ST}$ value for compound 2, ranging between $-64$ and $-124$ meV. Strikingly, at all of these levels of theory, a negative $\Delta E_{ST}$ energy difference is also predicted for azulene, contrary to experimental (49 meV) and other theoretical results (69 meV) for this molecule.\footnote{Note that even the very costly CC3 method (results available in ref. 73) predicts a negative $\Delta E_{ST}$ value of $-40$ meV, with the 6-31G+(d) basis set, for azulene. Our own EOM-CCSD calculations, done here as a sanity check, predict a lower triplet state with a 51 meV gap instead, in close agreement with the experimental estimate of 49 meV (see the ESI†).}}

We have also applied (SCS-)CC2 and (SCS-)ADC(2) methods to this challenging energy difference (see Table 1 and Fig. 4), since they have shown to be very accurate in the evaluation of excitation energies of related compounds.\footnote{To rationalize the results obtained by the SCS-CC2 method, we first note that when moving from CC2 ($C_{OS} = C_{SS} = 1.0$) to SCS-CC2 ($C_{OS} = 6/5$ and $C_{SS} = 1/3$), $T_1$ is destabilized by 49 meV,}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_5.png}
\caption{Singlet–triplet energy gaps (in meV) for 1 (a) and 2 (b) computed with different methods with the 6-311G(d) basis set. Horizontal dashed lines indicate the EOM-CCSD (reference) values.}
\end{figure}
92 meV and 51 meV for compounds 1, 2, and azulene, respectively, essentially due to the lowering of the same-spin interaction associated with a decrease of the exchange interaction, while \( S_1 \) undergoes a stabilization of \(-10\) meV and \(-46\) meV for compound 1 and azulene, respectively, and a destabilization of 36 meV for compound 2. This leads to the wider negative gap predicted by including the SCS scheme for the three compounds, suggesting that the original values chosen for \( C_{\text{OS}} \) and \( C_{\text{SS}} \) are, in fact, not the optimal ones for these compounds. In light of this, we computed the excitation energies and the \( \Delta E_{\text{ST}} \) values of the three compounds by systematically changing these two parameters (grid of 0.05) to meet the values obtained at the EOM-CCSD level (see the ESI†). For this modified SCS-CC2 (mSCS-CC2), the \( \Delta E_{\text{ST}} \) value is \(-24\) meV (24 meV) for compound 1 (2), with fine-tuned parameters \( C_{\text{OS}} = 0.75 \) and \( C_{\text{SS}} = 0.40 \) \((C_{\text{OS}} = 0.80\) and \( C_{\text{SS}} = 0.50\)). Not surprisingly, the \( S_1 \) excitation energy is more sensitive to \( C_{\text{OS}} \) (and thus to the coulomb correlation effect) than \( T_1 \) (see Fig. S5 for 1 and 2, ESI†) due to the dominant opposite-spin configurations of its wavefunction. Hence, reducing \( C_{\text{OS}} \) leads to a large reduction in the \( S_1-T_1 \) gap. For consistency, we would like to remark that: (i) mSCS-CC2 provided an excited state nature consistent with all other methods employed in this work, e.g., both \( S_1 \) and \( T_1 \) are dominated by a HOMO-to-LUMO transition; (ii) the same procedure is also extended to azulene, for which a \( \Delta E_{\text{ST}} \) value of 47 meV is found for \( C_{\text{OS}} = 0.90 \) and \( C_{\text{SS}} = 0.10 \). This demonstrates that the pristine CC2 \((C_{\text{OS}} = 1.0)\) and SCS-CC2 \((C_{\text{OS}} = 1.2)\) clearly overestimates the role of the coulomb correlation and a tuning of the parameters deems appropriate here.

### 3.3.3 RAS-based calculations

Finally, we evaluate singlet and triplet excitation energies with CI wavefunctions constructed with a restricted active space, RAS-CI, RAS-SF and RAS-srDFT, by considering a fully-correlated RAS2 space with 10 electrons in 10 \( \pi \)-orbitals and expanding the excitation

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**Fig. 6** Evolution of the excitation energies for 1 (top) and 2 (bottom) at all the RAS-based levels of theory as a function of the active space size.

**Fig. 7** (a) Singlet–triplet energy gaps (in meV) for 1 (blue) and 2 (orange) computed with RAS\([n,n]\)-CI as a function of \( n \). 2\( K \) energies are indicated with dashed lines. (b) % non HOMO-to-LUMO contributions to the \( S_1 \) (full circles) and \( T_1 \) (empty circles) of 1 (blue) and 2 (orange). Values at \( n = 0 \) correspond to the 2e2o model.
operator to include hole and particle excitations beyond the RAS2 orbital space. RAS1 and RAS3 orbital spaces include the entire set of occupied and virtual orbitals beyond RAS2. In order to rationalize the correlation effects in tuning the S\(_1\) and T\(_1\) energies, we first inspect the (ground state) open-shell character of compounds 1 and 2. For this, we quantify the number of unpaired electrons (\(N_U\)) obtained from the natural occupation numbers (\(n_i\)) of the electronic ground-state wavefunction computed at the RAS-SF level, according to the Head-Gordon formula:74

\[
N_U = \sum_i \min(n_i, 2 - n_i).
\]

Both compounds exhibited relatively small \(N_U\) values, 0.76 for 1 and 0.68 for 2, considerably lower than the \(N_U = 1.42\) value displayed by cyclazine also obtained at the RAS-SF level,\(^7\) but still higher than the values for typical emitters that are not prone to excited-state inversion (e.g. the PXZ-TRZ molecule\(^75\) has \(N_U = 0.06\)). The \(N_U\) values of the excited singlet and triplet states for the two studied biazulenes are slightly higher that 2, which indicates that they mostly correspond to configurations with two unpaired electrons with minor contributions from higher \(n\)-tuple excitations. These terms, i.e., double, triple, etc. excited configurations, are those providing for electron correlation effects neutralizing the exchange interaction (\(\Delta E_{ST}\) in eqn (3))

These results are in agreement with the HOMO-to-LUMO configuration being the main term describing the S\(_1\) and T\(_1\) states in both compounds.

Excited state energies computed at the RAS-CI, RAS-SF and RAS-srDFT levels are presented in Fig. 6 as a function of the active space size, with Table 1 including the results with the largest [10,10] one. The RAS\([n,n]\)-CI results for compound 1 clearly show the importance of the active space size to consistently decrease both S\(_1\) \(\rightarrow\) S\(_0\) and T\(_1\) \(\rightarrow\) S\(_0\) excitation energies, thus progressively approaching the EOM-CCSD values, and concomitantly passing from a positive to a negative value for \(\Delta E_{ST}\). A similar trend is found for compound 2, but always keeping a positive sign for \(\Delta E_{ST}\) in agreement with EOM-CCSD results too. The application of the RAS[10,10]-srDFT method yielded very accurate results, confirming the key role played by a large and balanced introduction of correlation effects, with a close agreement with EOM-CCSD reference results: a negative \(\Delta E_{ST}\) value (singlet–triplet inversion is predicted) for compound 1 (−21 meV) together with a slightly positive \(\Delta E_{ST}\) value for compound 2 (23 meV). Looking again (see Table 1 and Fig. 6) at the individual excitation energies S\(_1\) \(\rightarrow\) S\(_0\) and T\(_1\) \(\rightarrow\) S\(_0\), we can confirm that this accuracy in the calculation of \(\Delta E_{ST}\) for both systems does not come from any error cancellation, since RAS[10,10]-srDFT values for both compounds and for both excitation energies differ by less than 0.1 eV compared with reference EOM-CCSD results.

3.3.4 Understanding the origin of the S\(_1\)/T\(_1\) differential correlation. In order to understand in more detail the source of the electron correlation reducing the S\(_1\)/T\(_1\) gap, we compute singlet and triplet excitation energies at the RAS-CI (RHF reference) level with various RAS2 orbital spaces, that is, RAS\([n,n]\)-CI with \(n = 2, 4, 6, 8,\) and 10. In Fig. 7, we represent \(\Delta E_{ST}\) as a function of \(n\). As \(n\) increases, i.e., more electron

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**Fig. 8** Main doubly excited configurations contributing to the S\(_1\) and T\(_1\) states of molecules 1 (left) and 2 (right) computed at the RAS[10,10]-CI/6-311G(d) level. Single vertical lines indicate singly occupied orbitals.
correlation is included, the singlet–triplet gap decreases towards the EOM-CCSD reference values, since the differential correlation ($\Delta E_{\text{ST}}$) becomes more negative and compensates for the exchange interaction ($\Delta K$) as obtained by the 2e2o model. The $n$-dependent $\Delta E_{\text{ST}}$ profiles followed for molecules 1 and 2 are rather similar, but the larger exchange in 2 prevents correlation effects to induce singlet–triplet inversion as done for 1.

The increase of the $\Delta E_{\text{ST}} < 0$ magnitude shrinking the singlet–triplet gap can be related to the differential mixing of electronic configurations beyond the 2e2o model (HOMO-to-LUMO terms), which increases with $n$ (Fig. 7). Moreover, the contribution of these additional terms is larger in $S_1$ than in $T_1$, which might explain the fact that correlation effects have a larger impact in the excitation of the singlet than the triplet state. Larger active orbital spaces increase the possibility to mix in additional electron correlations, which further reduce the $S_1$ energy with respect to $T_1$.

These extra contributions mostly correspond to double excitations with respect to the HF determinant and can be classified into two types: (i) configurations with two unpaired electrons obtained as double excitations from or to a single orbital, and (ii) double excitations resulting in four unpaired electrons. In fact, the configurations beyond 2e2o with the largest weight in the excited singlet and triplet states of 1 and 2 exhibit four unpaired electrons and can be seen as single excitation with respect to the HOMO-to-LUMO term (Fig. 8).

It is important to notice that closed-shell-like configurations, e.g., two-electron HOMO-to-LUMO excitation, belong to the totally symmetric irreducible representation ($A_g$) and are thus symmetry forbidden in $B_{1g}$ excited states, i.e., $S_1$ and $T_1$. We also identify triple excitations contributing to the wavefunctions of the excited singlet and triplet states, but with a considerably lower weight.

4. Conclusions

We have systematically investigated the physical reasons driving the (lowest-energy) singlet ($S_1$) and triplet ($T_1$) excited-state energy inversion of a biazulene hydrocarbon (1), which constitutes another example of Hund’s rule violation, placing the $S_1$ lower in energy than the $T_1$ excited state, that is, leading to a negative energy difference $\Delta E_{\text{ST}} < 0$. To better understand the reasons for that, we have designed and investigated another biazulene compound (2), chemically identical to 1 just differing in the spatial arrangement of atoms, for which that inversion is not calculated. Therefore, the inversion happens only for molecule 1 as a consequence of a delicate trade-off between exchange and correlation contributions to those $S_1$ and $T_1$ excited states. We found that RAS[10,10]-srDFT calculations led to results closely agreeing with reference EOM-CCSD values but, most importantly, have also allowed us to carefully disentangle and understand the reasons for having a $\Delta E_{\text{ST}} < 0$ value for 1: a delicate balance between a larger weight of double excitations for $S_1$ than $T_1$ (correlation effects) together with a relatively small exchange energy. The situation for molecule 2 differs in the sense that these double excitations are slightly attenuated with respect to 1, but also due to the fact that the exchange energy was slightly larger, thus representing a not-so-ideal starting point for the excited-state energy inversion.

Not surprisingly, the majority of the rest of the methods considered in this work fail to cope with the aforementioned exchange and correlation balance, leading to qualitative and/or quantitative wrong results for either one or the two molecules, with the notable exception of TD-DFT calculations performed with the recently proposed r²SCAN-QIDH double-hybrid functional, thus representing these apparently simple molecules a real challenge for excited-state calculations. Overall, the conscious and systematic use of quantum-chemical methods is key to rationalize these complex phenomena arising from meV excited-state energy differences, thus revealing all their potential to tackle any challenging situation.

Data availability statement

The data that support the findings of this study are available in the ESI† of this article or available upon request.

Conflicts of interest

There are no conflicts to declare.

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