

Excited-state Hund's Rule Violations in Bridged [10]- and [14]Annulene Perimeters

J. Terence Blaskovits^{||}, Clémence Corminboeuf,^{*} and Marc H. Garner^{§*}

Laboratory for Computational Molecular Design, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

E-mail: clemence.corminboeuf@epfl.ch; marc.garner@epfl.ch

Abstract

Molecules with Hund's rule violations between low-lying singlet and triplet states may enable a new generation of fluorescent emitters. However, only a few classes of molecules are known with this property at the current time. Here, we use a high-throughput screening algorithm of the FORMED database to uncover a class of compounds where the first excited state violates Hund's rule. We examine this class of bridged [10]- and [14]annulene perimeters with saturated bridges, and relate them to known conjugated polycyclic systems with Hund's rule violations. Despite the structural similarities with the related class of non-alternant polycyclic hydrocarbons, the mechanism is different in these bridged annulene perimeters. Here, two molecular orbital configurations contribute to each excited state. Consequently, a Hund's rule violation can only be unambiguously assigned based on the symmetry of the lowest excited singlet and triplet states. With several examples of synthetically realistic molecules, the class of bridged [10]- and [14]annulenes thus provides a structural link between the known non-alternant and alternant (azaphenylene) classes of molecules violating Hund's rule, and may open avenues for design of molecules with inverted singlet-triplet gaps.

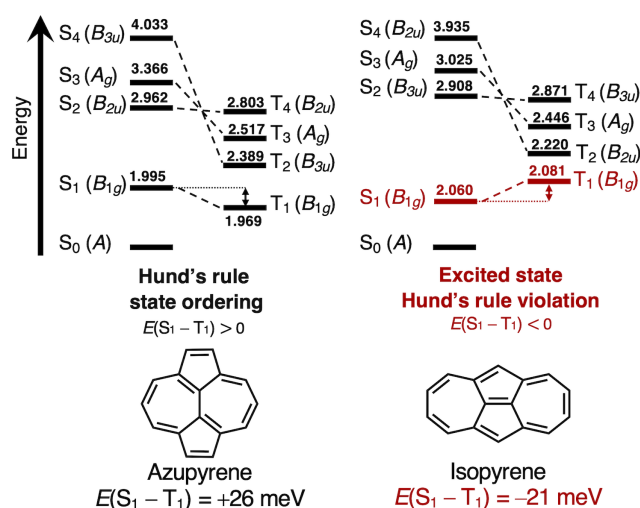


Figure 1: Excited-state diagram of azupyrene and isopyrene computed at EOM-CCSD/cc-pvdz// ω B97X-D/def2-TZVP level. Left) The first four excited states of isopyrene follow Hund's rule. Right) The B_{1g} states of isopyrene violate Hund's rule resulting in an inverted singlet-triplet gap.

Introduction

The vast majority of closed-shell organic molecules obey Hund's rule, which predicts that each triplet state will be of lower energy than the singlet state with the same electron configuration.¹ Hund's rule thus provides a state ordering where the singlet and triplet manifolds are paired as illustrated with the non-alternant hydrocarbon azupyrene in Figure 1a. Molecules that violate this rule are rare

and of fundamental interest. While violations in open-shell ground-state configurations attracted much early attention,^{2–4} excited-state violations in closed-shell molecules have recently seen a revival due to their potential use for design of molecular emitters.^{5–18} In such molecules, there are low-lying singlet states that have lower energy than the equivalent triplet state, for example in isopyrene where $E(S_1-T_1)$ is negative,^{19,20} as shown in Figure 1b. Ideally, it is the gap between the lowest excited singlet (S_1) and triplet (T_1) states that is inverted, which is the case in isopyrene. However, it is often the case that the singlet and triplet manifolds do not follow the same order, for example the B_{2u} and B_{3u} states in azupyrene and isopyrene (Figure 1). Consequently, there are often lower energy triplet states with a different electron configuration than the S_1 state.^{20–22}

The mechanism responsible for Hund’s rule violations is still being explored. It is clear that the molecular orbitals (MOs) involved in the excitation, typically the highest occupied and lowest unoccupied MO (HOMO and LUMO), must have minimal overlap. A symmetric molecular core is essential for achieving this, which is seen in the azaphenalene class.^{10,11} Similarly, we have recently explored a class of non-alternant hydrocarbons with high-symmetry pentalenic or heptalenic cores that are achieved through aromatic stabilization, *e.g.* isopyrene, or by appropriate substituent patterns.^{19–25} It is imperative to build a fundamental understanding of the structural and electronic mechanisms responsible for excited-state Hund’s rule violations by further exploring molecules with inverted singlet-triplet gaps.

Here, we continue the search for new types of compounds with excited-state Hund’s rule violations by significantly expanding our previous high-throughput screening approach.²⁰ Given how rare Hund’s rule violations are, this task turns out to be an effort of finding a few needles in a haystack. From the FORMED database,²⁶ we uncover two bridged [14]annulenes. With these two molecules as base structures, we go on to expand a class of bridged annulene perimeter systems with excited-state Hund’s rule vio-

lations.

Methods

To identify potential excited-state Hund’s rule violations, we screen vertical excitation energies in the Fragment-Oriented Materials Design (FORMED) dataset, which is publically available.^{26,27} This database consists of nearly 117,000 curated experimentally-reported organic crystal structures and their associated optical properties computed with Tamm-Dancoff-approximated time-dependent density functional theory (TDA-TDDFT) using ω B97X-D/6-31G(d) on geometries optimized using the GFN2-xTB semiempirical method, Figure 2, top box.^{26–28}

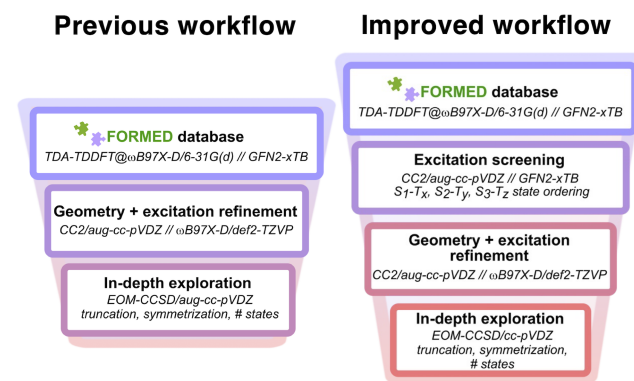


Figure 2: Schematic of the screening workflow from our previous communication,²⁰ and the improved screening workflow used in this study.

TDA-TDDFT-based methods cannot account for double excitation character, which is essential for predicting Hund’s rule violations.^{5–7,29–31} Indeed, there are many outliers when we compare the first two steps of our previous dataset,²⁰ that is, the initial TDA-TDDFT-based ω B97X-D/6-31G(d) on GFN2-xTB geometries on one hand, and the second-order approximate coupled-cluster level (CC2/aug-cc-pVDZ) with structures optimized at the ω B97X-D/def2-TZVP level on the other (Figure S1a).³² We identified the second step in our previous screening workflow as a bottleneck (Figure 2, left).²⁰

In this work, we implemented an extra step of refinement to improve the flow and efficiency

of the screening process. We find that the GFN2-xTB-optimized structures produce only small errors in excitation energies relative to the DFT-optimized structures (Figure S1b).²⁶ Although the resource scaling of CC2 can be challenging, it is efficient for studying vertical excitation energies in molecules of 20-40 atoms. As illustrated in the improved workflow in Figure 2, we therefore screen excitation energies at the CC2/aug-cc-pVDZ//GFN2-xTB level prior to further structural refinement at the DFT level. In this way, we optimize fewer structures with DFT in the following step, which was a bottleneck in the initial screening workflow.

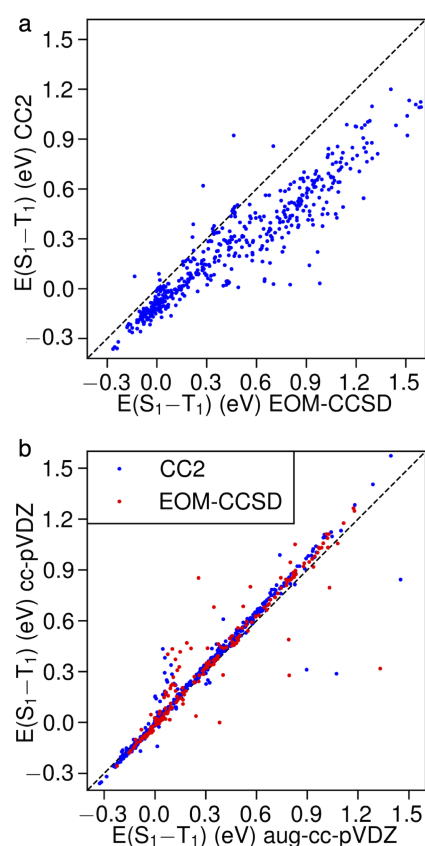


Figure 3: a) Benchmark of singlet-triplet gaps computed at the CC2/cc-pVDZ and EOM-CCSD/cc-pVDZ levels. b) Benchmark of singlet-triplet gaps computed with cc-pVDZ and aug-cc-pVDZ using CC2 or EOM-CCSD methods.

Starting from the over 115,000 molecules in the FORMED database and excluding the molecules we had already screened in our previous study,²⁰ we evaluate 4070 molecules at the CC2/aug-cc-pVDZ//GFN2-xTB level based on

their size and their $E(S_1-T_1)$ computed at the ω B97X-D/6-31G(d)//GFN2-xTB using the improved workflow. All optimizations were carried out using Gaussian16,³³ while CC2 computations used Turbomole 7.1.³⁴ We select molecules with $E(S_1-T_x) < 0.01$ eV for in-depth exploration (T_x being the triplet state with same electron configuration as S_1). Finally, we compute the excitation energies for leading candidates at the equations-of-motion coupled-cluster level (EOM-CCSD) as implemented in the QChem 5.1 package.^{35,36}

We used CC2 as the workhorse in the screening process as it is more computationally efficient than EOM-CCSD. Based on the data in this and our previous studies,²⁰⁻²² CC2 provides an excellent compromise between accuracy and efficiency for the initial screening steps because it systematically underestimates the singlet-triplet gaps (Figure 2b). This way, we avoid false negatives while the false positives will be removed at the final step that is carried out at the EOM-CCSD level (Figure 2).

We have previously reported that the cc-pVDZ basis set appears to provide sufficient accuracy in the azaphenalenenes and non-alternant hydrocarbons classes, which are constituted of near-planar conjugated molecules. As we do not have this knowledge when screening for unknown molecular classes, we employ the aug-cc-pVDZ basis set for the initial screening steps. Some, particularly non-planar, molecules may require diffuse basis functions, as is evident in Figure 3b. For larger molecules ($\geq \sim 30$ atoms) it is not feasible to use this basis set with the EOM-CCSD method, and we instead use cc-pVDZ. The size of most compounds in the bridged annulene class limits the possibility of using the aug-cc-pVDZ basis set. Although we only have limited data at the EOM-CCSD level (Table S1), when considered along with the CC2 data, it suggests that the cc-pVDZ basis set provides reasonable accuracy across this class of molecules. State energies, orbitals and eigenvalues reported in the manuscript are all based on the EOM-CCSD/cc-pVDZ method unless otherwise noted.

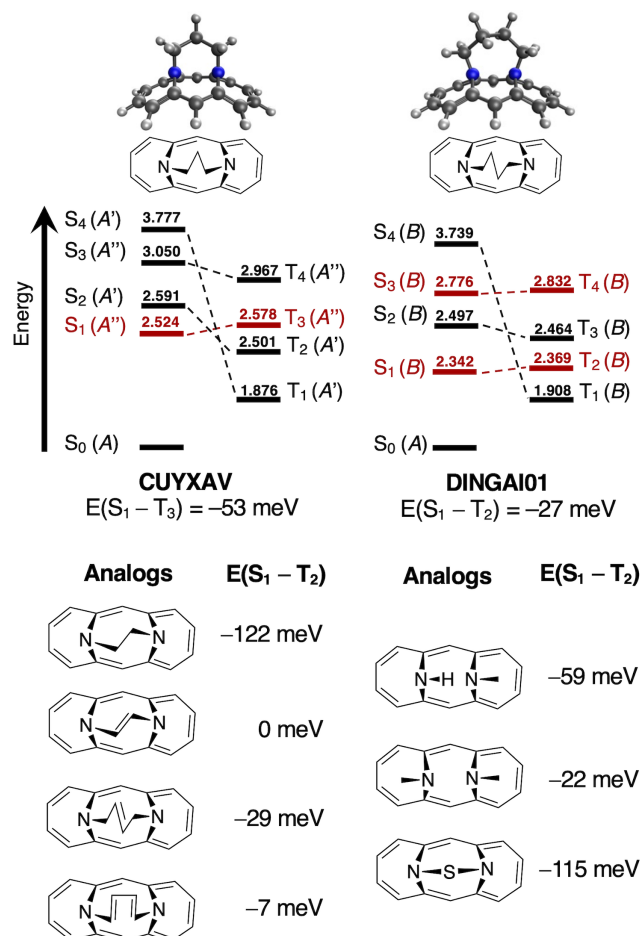


Figure 4: Excited-state gaps that are Hund's rule violations in CUYXAV, DINGAI01 and some of their analogs.

Results

Through the extensive screening protocols outlined in Figure 2, we identify two molecules with Hund's rule violations, CUYXAV and DINGAI01,^{37,38} which both have a structure based on an anthracene-like [14]annulenic perimeter with two linked saturated bridges. In a recent publication, DINGAI01 was also uncovered as a potential case of singlet-triplet inversion by Padula and co-workers via a neural network-based screening algorithm.³⁹ However, at the EOM-CCSD/cc-pVDZ level, the Hund's rule violation is between the S_1 and T_3 in the case of CUYXAV, and S_1 and T_2 in DINGAI01 as illustrated in Figure 4.

The content of the FORMED database is limited to crystal structures in the Cambridge Structural Database. We therefore proceed by

expanding the class by computing a series of analogs of CUYXAV and DINGAI01. Several of such analogs have already been explored synthetically.^{37,38,40,41} Many of these show similar Hund's rule violations as listed in Figure 4. We therefore conclude that CUYXAV and DINGAI01 are not special cases, but are examples of a broader class of bridged compounds with [14]annulene perimeters that can display excited-state Hund's rule violations.

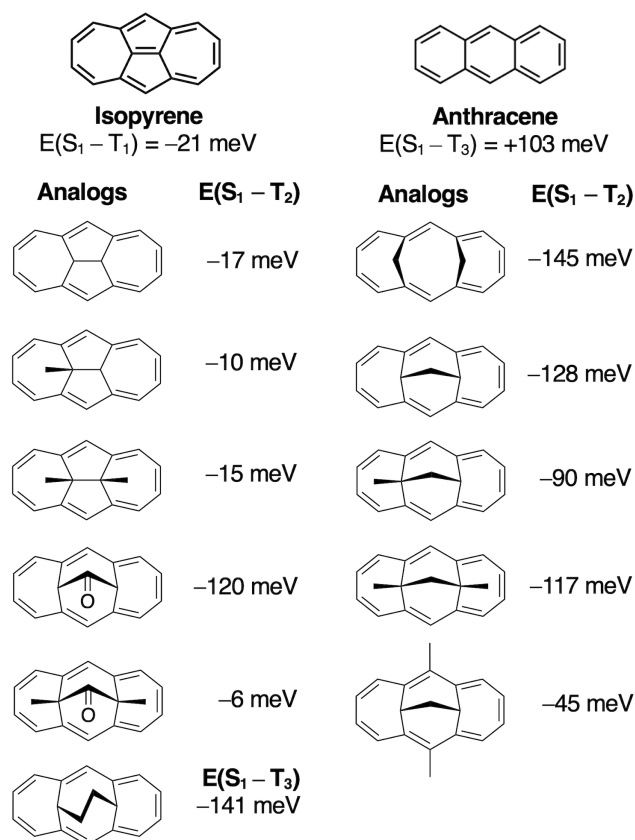


Figure 5: Excited-state gaps that are Hund's rule violations of isopyrene and anthracene and their bridged analogs.

Like CUYXAV and DINGAI01, isopyrene also has a [14]annulenic perimeter, albeit with a conjugated double-bond bridge. We therefore explore isopyrene and anthracene analogs with saturated bridges, of which some have been reported synthetically.⁴²⁻⁴⁶ Figure 5 lists several such compounds with excited-state Hund's rule violations between S_1 and T_2 , which have the same electron configuration (discussed below). All these molecules have small bond-length alternation and are symmetric (if the bridge allows it). The double-bond delocalization that

we have previously reported as essential for singlet-triplet inversion is thus also present in these molecules.^{21,22} This has been described in terms of the [14]annulenic perimeter being stabilized by aromaticity due to its having $4n+2$ π -electrons.^{47,48}

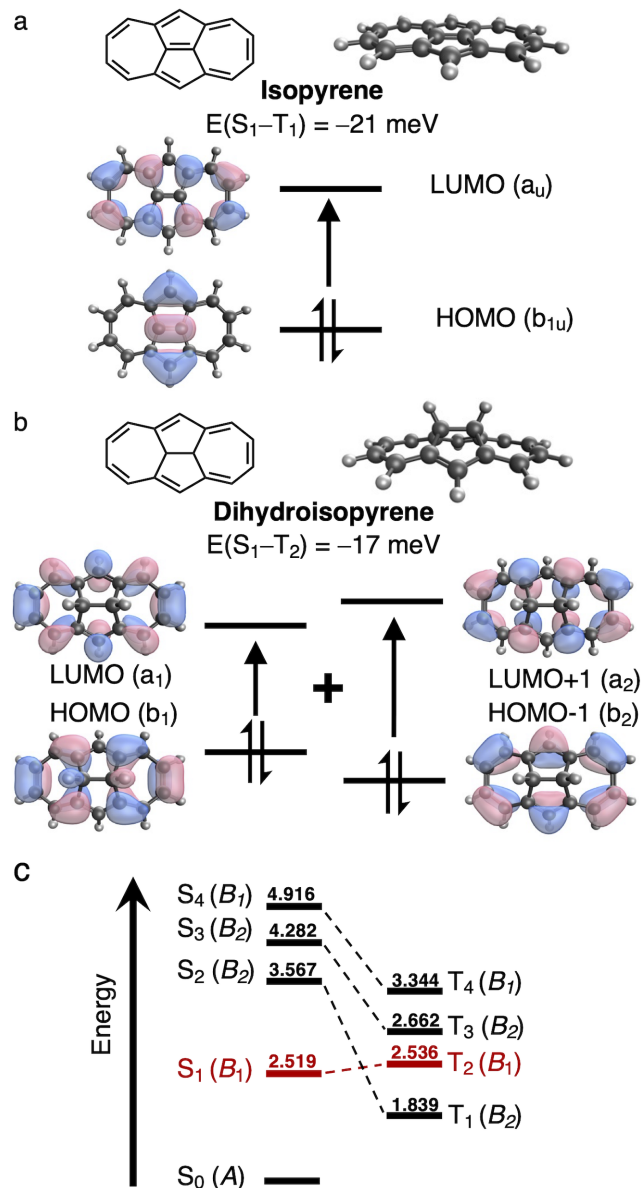


Figure 6: Frontier MOs involved in the primary configurations of the S_1 and T_1 transitions of isopyrene (a) and the S_1 and T_2 transitions of dihydroisopyrene (b), the latter being a superposition of the two configurations shown. c) Excited-state diagram of dihydroisopyrene.

The structural relation between isopyrene and the [14]annulenes is clear: the simplest bridged [14]annulene—dihydroisopyrene—consists of the same π -conjugated perimeter as isopyrene

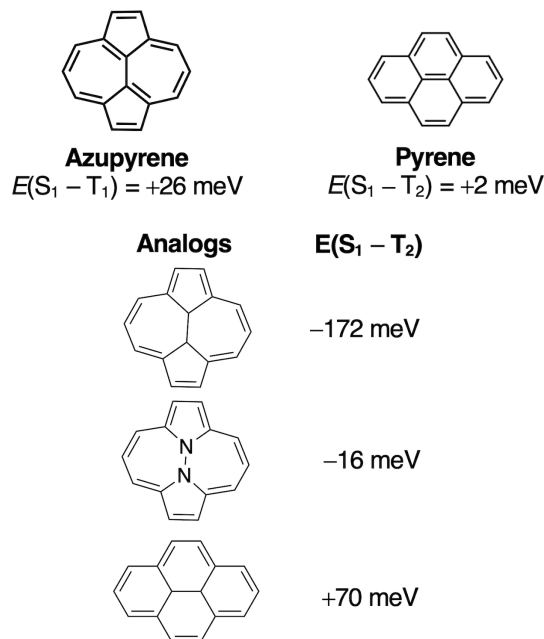


Figure 7: Excited-state gaps of azupyrene, pyrene and their bridged [14]annulene perimeter analogs.

but with a hydrogenated central double-bond (Figure 6). In isopyrene, the S_1 state is a regular $\pi - \pi^*$ transition which, as expected, is dominated by the HOMO to LUMO excitation as shown in Figure 6a.^{19,20} As seen in previously reported cases of Hund's rule violations, the HOMO and LUMO are non-overlapping.

In dihydroisopyrene, the S_1 state is an almost equally-weighted linear combination of the HOMO to LUMO and the HOMO-1 to LUMO+1 excitations. The HOMO is largely non-overlapping with the LUMO, and the HOMO-1 with the LUMO+1. However, the HOMO and LUMO+1 – as well as HOMO-1 and LUMO – are almost perfectly overlapping. Therefore the electron density may not change notably upon excitation. This appears to be the case in all the bridged annulene perimeters we explore here, as the S_1 state is described by a superposition of two single-excited configurations.

Despite not originating from a single electron configuration in the SCF-MO picture, the Hund's rule violations are well-defined because the involved triplet and singlet states are the lowest excited states within their irreducible representation. Furthermore, in most cases the

triplet and singlet states have similar linear combinations, making it easy to identify states with the same electron configuration. Natural transition orbitals (Figure S2) exhibit the same features as the frontier MOs. While these molecules already exhibit double-bond delocalization in the conjugated perimeter, we have tried to apply the substitution strategy described in our previous work.^{21,22} However, this does not work as intended because the nodal structure of the MOs in the linear combination differ; some examples are included in Table S1.

We further explore and expand this class by computing several azupyrene and pyrene analogs with saturated bridges, of which many have been synthesized.^{49–62} We only find a few of these to exhibit excited-state Hund’s rule violations. These are shown in Figure 7, while several substituted versions we have tested obey Hund’s rule and are listed Table S1. For example, while the diaza-azupyrene shown in Figure 7 is a Hund’s rule violation, the pyrene analog distorts and does not exhibit a Hund’s rule violation in its first excited singlet state (Figure 7, bottom).

[10]annulenic perimeters

Similar to the [14]annulenes, a number of [10]annulene perimeters have been reported based on naphthalene and azulene motifs.^{47,63–66} These have similar aromatic structures as their [10]annulene perimeters also contain $4n+2$ π -electrons.^{47,48} We find several bridged naphthalene analogs where the first excited state is a Hund’s rule violation (Figure 8). However, all azulene analogs we have tested obey Hund’s rule; for example, the azulene analog in which the bond shared by the 5- and 7-membered rings is replaced by a methylene moiety is shown in Figure 8.

Inspired by the synthetic literature, we also test a number of [10]annulenes based on the cyclopenta[*cd*]indene core, which is shown at the bottom of Figure 8.^{67,68} Several substituted analogs of this bridged [10]annulene perimeter exhibit excited-state Hund’s rule violations. As in the case of the [14]annulene perimeters, the [10]annulene perimeters are symmetric when

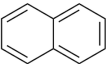
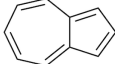
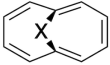
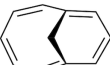

	Naphthalene	$E(S_1 - T_2) = +185$ meV
	Azulene	$E(S_1 - T_1) = +55$ meV
	Analog	$E(S_1 - T_3)$
	X=CH ₂	–65 meV
	X=CF ₂	–29 meV
	X=O	–52 meV
	X=NH	–28 meV
	X=NMe	–48 meV
		$E(S_1 - T_2)$
		+211 meV
		
	X=CH	+11 meV
	X=CMe	–4 meV
	X=COH	–46 meV
	X=COMe	–41 meV
	X=CNH ₂	–36 meV
	X=CNMe ₂	–51 meV
	X=N	+375 meV
	X=P	–41 meV

Figure 8: Excited-state gaps of naphthalene, azulene, and their bridged [10]annulene perimeter analogs.

possible based on the bridge, and the excited states are always described by a linear combination of two excitations (as in Figure 6, for example). The class of annulenic perimeters with excited-state Hund’s rule violations thus covers a range of both [10]- and [14]annulene motifs. The nature of the bridging atom connecting the rings (and its substituent) can have a strong impact on the energy gap between the S_1 and T_2 state energies, as highlighted in Figure 8.

[12]- and [16]annulenic perimeters

While [10]-, [14]- and larger $4n+2$ perimeters are formally Hückel aromatic, [12]- and [16]-annulenic perimeters also exist. These are formally antiaromatic and likely to distort, especially through bond length alternation.^{47,48,69,70} Consequently, we have not succeeded in finding species with negative singlet-triplet gaps.

The parent [12]annulene is a reactive species with a distorted structure and significant bond-length alternation.⁷¹ It is thus no surprise that it does not exhibit any Hund’s rule violations (Figure 9). The related [12]annulene-perimeter

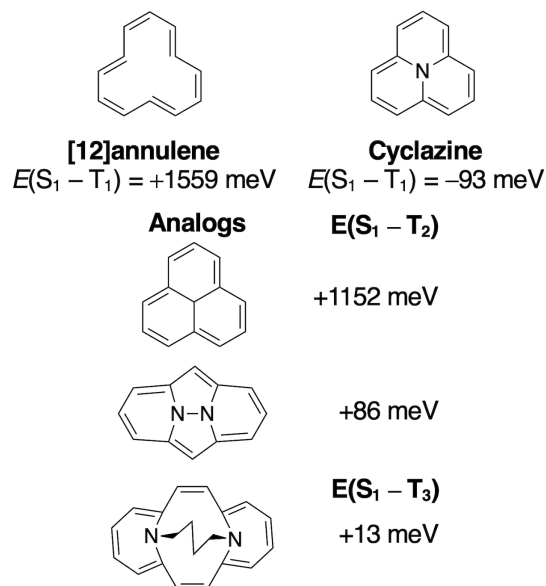


Figure 9: Excited-state gaps of [12]annulene, cyclazine, and their bridged [12]annulene and [16]annulene perimeter analogs.

cyclazine is a well-described case of singlet-triplet inversion.^{6,72} However, cyclazine is a symmetric molecule and the nitrogen in the middle adds two π -electrons. With a saturated bridge atom in the middle the perimeter is antiaromatic and we do not find such systems to exhibit Hund's rule violations. Inspired by cyclazine (and certain [14]annulene perimeters), we sample molecules with nitrogen heteroatoms or bridges but nonetheless we do not succeed in finding Hund's rule violations in [12]annulene perimeters beyond cyclazine.

A few bridged [16]annulene perimeters have been reported although the parent [16]annulene is unstable.^{73,74} The same challenge applies in the case of the [12]annulene perimeters. Most molecules we test have distorted structures with significant bond-length alternation. The best example we identified is the bridged [16]annulene perimeter shown at the bottom in Figure 9, where the first excited state is almost degenerate with the triplet of the same electron configuration.

While we have searched for variations of bridged annulenes in this work, we consider it likely that the class of molecules can be expanded into further subclasses. In particular, larger annulenic perimeters may exist,

and some have already been suggested as inverted gap systems.⁷⁵⁻⁷⁸ However, more bond-length alternation is to be expected in larger annulenic frames as the aromaticity in the perimeter weakens with increasing size, which may limit the potential for singlet-triplet inversion.⁷⁹ Considering the number of possible structural combinations there can be for [18]annulene perimeters, and how the increased molecular size will limit the possibility of using EOM-CCSD, we leave this exploration for future efforts.

Conclusions

Using a high-throughput screening algorithm on the FORMED database, we assessed the vertical excitation energies of 4070 molecules at the CC2/aug-cc-pVDZ level and uncovered two molecules with excited-state Hund's rule violations, of which one had also recently been reported by Padula and co-workers.³⁹ We explore these two molecules as part of a class of bridged annulene perimeters that we expand based on parent annulenes and previously synthesized annulene perimeters. We report many bridged [10]- and [14]annulene perimeters with excited-state Hund's rule violations at the EOM-CCSD/cc-pVDZ level, which have a great geometrical variety.

Conceptually, these annulenes are a bridge between the known alternant (cyclazine and derivatives) and non-alternant (e.g., isopyrene and pentalene derivatives) classes of Hund's rule violations, as they all possess double-bond delocalized π -conjugated perimeters. We discuss the structural traits of annulene perimeters in relation to their parent molecules, some of which themselves also exhibit Hund's rule violations. However, the mechanism of this class of annulene perimeters with a saturated bridge differs from known classes. Here, the excited state is always a linear combination of two excitations, typically involving transitions from the HOMO-1 and HOMO into the LUMO and LUMO+1, respectively. Nonetheless, the electron configuration (and thereby the Hund's rule violation) is straightforward to identify in

most cases as the singlet and triplet states are the lowest lying excited states within their irreducible representation.

This study exemplifies the importance of high-throughput screening as the initial step for identifying the first example of hitherto unknown molecular classes. Once the first member(s) of the class are known, it can be expanded through traditional exploration of chemical structures. Our work furthermore emphasizes some of the general challenges when screening for new types of molecules with rare properties, such as excited-state Hund's rule violations. When exploring molecular space it is essential to avoid false negatives, and to use methods that are as broadly applicable as possible as we cannot know beforehand what types of molecules will be uncovered.

Going forward, high-throughput screening will continue to be essential for discovering new types of inverted singlet-triplet gap molecules.^{7,80,81} Improved algorithms must be explored further to enable the screening of more molecules in an efficient manner. Recently reported examples of such includes screening using neural networks^{39,82} and by application of computationally cheaper simplified theoretical models.^{83,84} In this way bigger haystacks can be screened to find the needles needed to expand the chemical palette and provide further intuition in the design of molecules with inverted singlet-triplet gaps.

Acknowledgement The authors are grateful to the EPFL for financial support and the allocation of computational resources. M. H. G. is grateful for funding from the Carlsberg Foundation (CF21-0202).

Supporting Information Available: Additional figures and tables.

Present addresses:

|| Max-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

§ Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

References

- (1) Kutzelnigg, W. Friedrich Hund and Chemistry. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 572–586.
- (2) Dougherty, D. A. Spin Control in Organic Molecules. *Acc. Chem. Res.* **1991**, *24*, 88–94.
- (3) Borden, W. T.; Iwamura, H.; Berson, J. A. Violations of Hund's Rule in Non-Kekule Hydrocarbons: Theoretical Prediction and Experimental Verification. *Acc. Chem. Res.* **1994**, *27*, 109–116.
- (4) Hrovat, D. A.; Borden, W. T. Violations of Hund's rule in molecules — where to look for them and how to identify them. *J. Mol. Struct.* **1997**, *398-399*, 211–220.
- (5) Ehrmaier, J.; Rabe, E. J.; Pristash, S. R.; Corp, K. L.; Schlenker, C. W.; Sobolewski, A. L.; Domcke, W. Singlet-Triplet Inversion in Heptazine and in Polymeric Carbon Nitrides. *J. Phys. Chem. A* **2019**, *123*, 8099–8108.
- (6) de Silva, P. Inverted Singlet-Triplet Gaps and Their Relevance to Thermally Activated Delayed Fluorescence. *J. Phys. Chem. Lett.* **2019**, *10*, 5674–5679.
- (7) Pollice, R.; Friederich, P.; Lavigne, C.; dos Passos Gomes, G.; Aspuru-Guzik, A. Organic molecules with inverted gaps between first excited singlet and triplet states and appreciable fluorescence rates. *Matter* **2021**, *4*, 1654–1682.
- (8) Aizawa, N.; Pu, Y.-J.; Harabuchi, Y.; Nihonyanagi, A.; Ibuka, R.; Inuzuka, H.; Dhara, B.; Koyama, Y.; Nakayama, K.-i.; Maeda, S. et al. Delayed fluorescence from inverted singlet and triplet excited states. *Nature* **2022**, *609*, 502–506.
- (9) Sancho-García, J.-C. Engineered molecules solve fluorescence issues. *Nature* **2022**, *609*, 473–475.

- (10) Ricci, G.; Sancho-García, J.-C.; Olivier, Y. Establishing design strategies for emissive materials with an inverted singlet–triplet energy gap (INVEST): a computational perspective on how symmetry rules the interplay between triplet harvesting and light emission. *J. Mater. Chem. C* **2022**, *10*, 12680–12698.
- (11) Won, T.; Nakayama, K.-i.; Aizawa, N. Inverted singlet–triplet emitters for organic light-emitting diodes. *Chem, Phys. Rev.* **2023**, *4*, 021310.
- (12) Blasco, D.; Nasibullin, R. T.; Valiev, R. R.; Sundholm, D. Gold(i)-containing light-emitting molecules with an inverted singlet–triplet gap. *Chem. Sci.* **2023**, *14*, 3873–3880.
- (13) Actis, A.; Melchionna, M.; Filippini, G.; Fornasiero, P.; Prato, M.; Chiesa, M.; Salvadori, E. Singlet-triplet energy inversion in carbon nitride photocatalysts. *Angew, Chem. Int. Ed.* **2023**, *62*, e202313540.
- (14) Wang, X.; Wang, A.; Zhao, M.; Marom, N. Inverted Lowest Singlet and Triplet Excitation Energy Ordering of Graphitic Carbon Nitride Flakes. *J. Phys. Chem. Lett.* **2023**, *14*, 10910–10919.
- (15) Blasco, D.; Nasibullin, R. T.; Valiev, R. R.; Monge, M.; López-de Luzuriaga, J. M.; Sundholm, D. Experimental and computational studies of the optical properties of 2,5,8-tris(phenylthiolato)heptazine with an inverted singlet–triplet gap. *Phys. Chem. Chem. Phys.* **2024**, *26*, 5922–5931.
- (16) Kim, H.; Scholes, G. D.; Min, S. K. Extension of molecules with an inverted singlet–triplet gap with conjugated branches to alter the oscillator strength. *Phys. Chem. Chem. Phys.* **2024**, *26*, 5508–5516.
- (17) Kusakabe, Y.; Shizu, K.; Tanaka, H.; Tanaka, K.; Kaji, H. An inverted singlet-triplet excited state in a pentaazaphenylene derivative (5AP-N(C12)2). *Appl. Phys. Express* **2024**,
- (18) Wilson, K. D.; Styers, W. H.; Wood, S. A.; Woods, R. C.; McMahon, R. J.; Liu, Z.; Yang, Y.; Garand, E. Spectroscopic Quantification of the Inverted Singlet–Triplet Gap in Pentaazaphenylene. *J. Am. Chem. Soc.* **2024**,
- (19) Toyota, A. Violation of Hund’s rule in the lowest excited singlet-triplet pairs of dicyclohepta[cd,gh]pentalene and dicyclopenta[ef,ki]heptalene. *Theor. Chim. Acta* **1988**, *74*, 209–217.
- (20) Blaskovits, J. T.; Garner, M. H.; Corminboeuf, C. Symmetry-Induced Singlet-Triplet Inversions in Non-Alternant Hydrocarbons. *Angew. Chem. Int. Ed.* **2023**, *62*, e202218156.
- (21) Garner, M. H.; Blaskovits, J. T.; Corminboeuf, C. Double-bond delocalization in non-alternant hydrocarbons induces inverted singlet–triplet gaps. *Chem. Sci.* **2023**, *14*, 10458–10466.
- (22) Garner, M. H.; Blaskovits, J. T.; Corminboeuf, C. Enhanced inverted singlet–triplet gaps in azaphenalenenes and non-alternant hydrocarbons. *Chem. Commun.* **2024**, *60*, 2070–2073.
- (23) Koseki, S.; Nakajima, T.; Toyota, A. Violation of Hund’s multiplicity rule in the electronically excited states of conjugated hydrocarbons. *Can. J. Chem.* **1985**, *63*, 1572–1579.
- (24) Toyota, A.; Nakajima, T. Violation of Hund’s Multiplicity Rule in the Lowest Excited Singlet-Triplet Pairs of Cyclic Bicalicene and Its Higher Homologues. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1731–1734.
- (25) Sandoval-Salinas, M. E.; Ricci, G.; Pérez-Jiménez, A. J.; Casanova, D.; Olivier, Y.; Sancho-García, J. C. Correlation vs. exchange competition drives the singlet–triplet excited-state inversion in non-alternant hydrocarbons. *Phys. Chem. Chem. Phys.* **2023**, *25*, 26417–26428.

- (26) Blaskovits, J. T.; Laplaza, R.; Vela, S.; Corminboeuf, C. Data-Driven Discovery of Organic Electronic Materials Enabled by Hybrid Top-Down/Bottom-Up Design. *Adv. Mater.* **36**, 2305602.
- (27) Structures and data for all compounds in the FORMED dataset are provided in a Materials Cloud repository at <https://doi.org/10.24435/materialscloud:aa-2w>.
- (28) Bannwarth, C.; Ehlert, S.; Grimme, S. GFN2-xTB—An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15*, 1652–1671.
- (29) Ricci, G.; San-Fabián, E.; Olivier, Y.; Sancho-García, J. C. Singlet-Triplet Excited-State Inversion in Heptazine and Related Molecules: Assessment of TD-DFT and ab initio Methods. *ChemPhysChem* **2021**, *22*, 553–560.
- (30) Sobolewski, A. L.; Domcke, W. Are Heptazine-Based Organic Light-Emitting Diode Chromophores Thermally Activated Delayed Fluorescence or Inverted Singlet–Triplet Systems? *J. Phys. Chem. Lett.* **2021**, *12*, 6852–6860.
- (31) Loos, P.-F.; Lipparini, F.; Jacquemin, D. Heptazine, Cyclazine, and Related Compounds: Chemically-Accurate Estimates of the Inverted Singlet–Triplet Gap. *J. Phys. Chem. Lett.* **2023**, *14*, 11069–11075.
- (32) Christiansen, O.; Koch, H.; Jørgensen, P. The second-order approximate coupled cluster singles and doubles model CC2. *Chem. Phys. Lett.* **1995**, *243*, 409–418.
- (33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H. et al. Gaussian 16, Revision A.03. 2016; Gaussian Inc.: Wallingford, CT.
- (34) TURBOMOLE V7.4 2019, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- (35) Stanton, J. F.; Bartlett, R. J. The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties. *J. Chem. Phys.* **1993**, *98*, 7029–7039.
- (36) Epifanovsky, E.; Gilbert, A. T.; Feng, X.; Lee, J.; Mao, Y.; Mardirossian, N.; Pokhilko, P.; White, A. F.; Coons, M. P.; Dempwolff, A. L. et al. Software for the frontiers of quantum chemistry: An overview of developments in the Q-Chem 5 package. *J. Chem. Phys.* **2021**, *155*, 084801.
- (37) Destro, R.; Pilati, T.; Simonetta, M.; Vogel, E. Structural studies of syn-1,6:8,13-diimino[14]annulenes. 2. Molecules with connected bridges. *J. Am. Chem. Soc.* **1985**, *107*, 3192–3196.
- (38) Gerson, F.; Gescheidt, G.; Buser, U.; Vogel, E.; Lex, J.; Zehnder, M.; Riesen, A. The Radical Cation of N,N'-Tetramethylene-syn-1,6:8,13-diimino[14]annulene. An Experimental Study of the N–N Three-Electron σ Bond. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 902–904.
- (39) Barneschi, L.; Rotondi, L.; Padula, D. Molecular Geometry Impact on Deep Learning Predictions of Inverted Singlet–Triplet Gaps. *J. Phys. Chem. A* **2024**, *128*, 2417–2426.
- (40) Vogel, E.; Kuebart, F.; Marco, J. A.; Andree, R.; Guenther, H.; Aydin, R. syn-1,6:8,13-Diimino[14]annulene. *J. Am. Chem. Soc.* **1983**, *105*, 6982–6983.

- (41) Gerson, F.; Knöbel, J.; Lopez, J.; Vogel, E. The Radical Anions of *syn*-1,6:8,13-Bridged [14] Annulenes. A Compilation of Hyperfine Data. *Helv. Chim. Acta* **1985**, *68*, 371–376.
- (42) Vogel, E. Aromatic and nonaromatic 14π -electron systems. *Pure Appl. Chem.* **1971**, *28*, 355–378.
- (43) Kolc, J.; Michl, J.; Vogel, E. Excited states of bridged [14]annulenes with anthracene perimeter: absorption, polarized emission, linear dichroism, and magnetic circular dichroism. *J. Am. Chem. Soc.* **1976**, *98*, 3935–3948.
- (44) Vogel, E.; Schieb, T.; Schulz, W. H.; Schmidt, K.; Schmickler, H.; Lex, J. Bridged [14]Annulenes with a Phenanthrene-Perimeter: *anti*-1,6:7,12-Bismethano[14]annulene. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 723–725.
- (45) Vogel, E.; Püttmann, W.; Duchatsch, W.; Schieb, T.; Schmickler, H.; Lex, J. Bridged [14]Annulenes with a Phenanthrene-Perimeter: *syn*-1,6:7,12-Bismethano[14]annulene. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 720–723.
- (46) Mathey, P.; Lirette, F.; Fernández, I.; Renn, L.; Weitz, R. T.; Morin, J. Annulated Azuleno[2,1,8-*ija*]azulenes: Synthesis and Properties. *Angew. Chem. Int. Ed.* **2023**, *62*, e202216281.
- (47) Slayden, S. W.; Liebman, J. F. The Energetics of Aromatic Hydrocarbons: An Experimental Thermochemical Perspective. *Chem. Rev.* **2001**, *101*, 1541–1566.
- (48) Kleinpeter, E.; Koch, A. Cyclazines-Structure and Aromaticity or Antiaromaticity on the Magnetic Criterion. *Eur. J. Org. Chem.* **2022**, *2022*, e202101362.
- (49) Huber, W.; Lex, J.; Meul, T.; Müllen, K. *trans*-15,16-Dimethyl-1,4:8,11-ethanediylidene[14]annulene. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 391–393.
- (50) Huber, W.; Irmen, W.; Lex, J.; Müllen, K. Reductive transformations: 2. *Cis*- and *trans*-1,2-addition of electrophiles to dianionic π -systems. *Tetrahedron Lett.* **1982**, *23*, 3889–3892.
- (51) Flitsch, W.; Rutkowski, K. [10b, 10c]Diazapyraceheptylene. *Tetrahedron Lett.* **1985**, *26*, 5429–5432.
- (52) Neumann, G.; Muellen, K. Reductive alkylation of aceheptylene - a simple route to a series of novel π -perimeters. *J. Am. Chem. Soc.* **1986**, *108*, 4105–4110.
- (53) Alexander, J.; Baumgarten, M.; Klabunde, K.-U.; Müllen, K. Reductive transformations-14. Regioselective addition of carbanions to the “aromatic” pyrene isomer dicyclopenta(ef,kl)heptalene. *Tetrahedron Lett.* **1991**, *32*, 735–738.
- (54) Boekelheide, V.; Phillips, J. B. Aromatic Molecules Bearing Substituents within the Cavity of the π -Electron Cloud. Synthesis of *trans*-15,16-Dimethyldihydropyrene. *J. Am. Chem. Soc.* **1967**, *89*, 1695–1704.
- (55) Lai, Y. H. Synthesis and diatropicity of a phenanthrene annelated *trans*-dimethyldihydropyrene: a novel molecule to indicate the high π -bond order of the 9,10 bond of phenanthrene. *J. Am. Chem. Soc.* **1985**, *107*, 6678–6683.
- (56) Mitchell, R. H.; Chen, Y.; Iyer, V. S.; Lau, D. Y. K.; Baldrige, K. K.; Siegel, J. S. Bond Fixation in a [14]Annulene: Synthesis, Characterization, and ab Initio Computations of Furan Adducts of Dimethyldihydropyrene. *J. Am. Chem. Soc.* **1996**, *118*, 2907–2911.
- (57) Lai, Y.-H.; Jiang, J. Synthesis of 2-Aryl-10b,10c-dimethyl-10b,10c-dihydropyrenes and a Study of Their Conjugation Behavior: Linear Relationship between the Degree of Conjugation and the Electronic Nature of Substituents. *J. Org. Chem.* **1997**, *62*, 4412–4417.

- (58) Murphy, R. S.; Chen, Y.; Ward, T. R.; Mitchell, R. H.; Bohne, C. Photo-physical studies on the photochromism of trans-10b,10c-dimethyldihydropyrene. *Chem. Commun.* **1999**, 2097–2098.
- (59) Williams, R. V.; Armantrout, J. R.; Twamley, B.; Mitchell, R. H.; Ward, T. R.; Bandyopadhyay, S. A Theoretical and Experimental Scale of Aromaticity. The First Nucleus-Independent Chemical Shifts (NICS) Study of the Dimethyldihydropyrene Nucleus. *J. Am. Chem. Soc.* **2002**, *124*, 13495–13505.
- (60) Jiang, J.; Lai, Y.-H. Evidence for Homo-Conjugation between Two Revolving 14π -Electron Systems in 10b-Methyl-10c-[2-(10b,10c-dimethyl-10b,10c-dihydropyrenyl)]-10b,10c-dihydropyrene. *J. Am. Chem. Soc.* **2003**, *125*, 14296–14297.
- (61) Liesfeld, P.; Garmshausen, Y.; Budzak, S.; Becker, J.; Dallmann, A.; Jacquemin, D.; Hecht, S. Highly Cooperative Photo-switching in Dihydropyrene Dimers. *Angew. Chem. Int. Ed.* **2020**, *59*, 19352–19358.
- (62) Jana, P.; Koppayithodi, S.; Mahato, S.; Molla, S.; Bandyopadhyay, S. Stable Diradical on the Dimethyldihydropyrene Scaffold. *J. Phys. Chem. Lett.* **2023**, *14*, 7433–7439.
- (63) Dewey, H. J.; Deger, H.; Froelich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. Excited states of methano-bridged [10]-, [14]-, and [18]annulenes. Evidence for strong transannular interaction, and relation to homoaromaticity. *J. Am. Chem. Soc.* **1980**, *102*, 6412–6417.
- (64) Rautenstrauch, V.; Scholl, H.; Vogel, E. 11,11-Dihalogeno-1,6-methano-[10]annulenes as Dihalogenocarbene Transfer Agents. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 288–289.
- (65) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. Homoazulene. *J. Am. Chem. Soc.* **1981**, *103*, 5216–5220.
- (66) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. A Convenient Synthesis of “Homoazulene” (1,5-Methano[10]annulene). *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 274–275.
- (67) Gilchrist, T. L.; Tuddenham, D.; McCague, R.; Moody, C. J.; Rees, C. W. 7b-Methyl-7bH-cyclopent[cd]indene, an unsubstituted tricyclic aromatic [10]annulene. *J. Chem. Soc., Chem. Commun.* **1981**, 657–658.
- (68) McCague, R.; Moody, C. J.; Rees, C. W. Tricyclic [10]annulenes. Part 2. Synthesis of 7b-methyl-7bH-cyclopent[cd]indene. *J. Chem. Soc., Perkin Trans. 1* **1984**, 165–174.
- (69) Cyrański, M.; Havenith, R.; Dobrowolski, M.; Gray, B.; Krygowski, T.; Fowler, P.; Jenneskens, L. The Phenalenyl Motif: A Magnetic Chameleon. *Chem. Eur. J.* **2007**, *13*, 2201–2207.
- (70) Trujillo, C.; Sánchez-Sanz, G.; Alkorta, I.; Elguero, J. An insight on the aromatic changes in closed shell icosagen, tetrel, and pnictogen phenalenyl derivatives. *Struct. Chem.* **2017**, *28*, 345–355.
- (71) Kiesewetter, M. K.; Gard, M. N.; Reiter, R. C.; Stevenson, C. D. Reactions Involving Di-trans-[12]Annulenes. *J. Am. Chem. Soc.* **2006**, *128*, 15618–15624.
- (72) Leupin, W.; Wirz, J. *J. Am. Chem. Soc.* **1980**, *102*, 6068–6075.
- (73) Vogel, E.; Kürschner, U.; Schmickler, H.; Lex, J.; Wennerström, O.; Tanner, D.; Norinder, U.; Krüger, C. 1,6:9,14-bismethano[16]annulene - a new bridged [4n]annulene. *Tetrahedron Lett.* **1985**, *26*, 3087–3090.

- (74) Yamamoto, K.; Kuroda, S.; Shibutani, M.; Yoneyama, Y.; Ojima, J.; Fujita, S.; Ejiri, E.; Yanagihara, K. Synthesis and properties of methano-[12]-, -[18]-, -[20]-, -[22]-, -[24]-annulene and dimethano-[20]- and -[24]-annulene. *J. Chem. Soc., Perkin Trans. 1* **1988**, 395–400.
- (75) Sanz-Rodrigo, J.; Ricci, G.; Olivier, Y.; Sancho-García, J. C. Negative Singlet-Triplet Excitation Energy Gap in Triangle-Shaped Molecular Emitters for Efficient Triplet Harvesting. *J. Phys. Chem. A* **2021**, *125*, 513–522.
- (76) Pios, S.; Huang, X.; Sobolewski, A. L.; Domcke, W. Triangular boron carbon nitrides: an unexplored family of chromophores with unique properties for photocatalysis and optoelectronics. *Phys. Chem. Chem. Phys.* **2021**, *23*, 12968–12975.
- (77) Sobolewski, A. L.; Domcke, W. Excited-state singlet–triplet inversion in hexagonal aromatic and heteroaromatic compounds. *Phys. Chem. Chem. Phys.* **2023**, *25*, 21875–21882.
- (78) Duszka, M. W.; Rode, M. F.; Sobolewski, A. L. Computational Design of Boron-Free Triangular Molecules with Inverted Singlet-Triplet Energy Gap. 2024; <http://arxiv.org/abs/2404.15768>.
- (79) Wannere, C. S.; Sattelmeyer, K. W.; Schaefer III, H. F.; Schleyer, P. v. R. Aromaticity: The Alternating CC Bond Length Structures of [14]-, [18]-, and [22]Annulene. *Angew. Chem. Int. Ed.* **2004**, *43*, 4200–4206.
- (80) Omar, Ö. H.; Xie, X.; Troisi, A.; Padula, D. Identification of Unknown Inverted Singlet–Triplet Cores by High-Throughput Virtual Screening. *J. Am. Chem. Soc.* **2023**, *145*, 19790–19799.
- (81) Pollice, R.; Ding, B.; Aspuru-Guzik, A. Rational design of organic molecules with inverted gaps between the first excited singlet and triplet. *Matter* **2024**, *7*, 1161–1186.
- (82) Nigam, A.; Pollice, R.; Friederich, P.; Aspuru-Guzik, A. Artificial design of organic emitters via a genetic algorithm enhanced by a deep neural network. *Chem. Sci.* **2024**, *15*, 2618–2639.
- (83) Bedogni, M.; Giavazzi, D.; Di Maiolo, F.; Painelli, A. Shining Light on Inverted Singlet–Triplet Emitters. *J. Chem. Theory Comput.* **2024**, *20*, 902–913.
- (84) Jorner, K.; Pollice, R.; Lavigne, C.; Aspuru-Guzik, A. Ultrafast Computational Screening of Molecules with Inverted Singlet–Triplet Energy Gaps Using the Pariser–Parr–Pople Semiempirical Quantum Chemistry Method. *J. Phys. Chem. A* **2024**, *128*, 2445–2456.

TOC Graphic

