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Probing the Influence of Alkyne Substitution on the Electronic and Magnetic Properties of Diindeno[1,2-*b*;1′,2′-*i*]anthracenes

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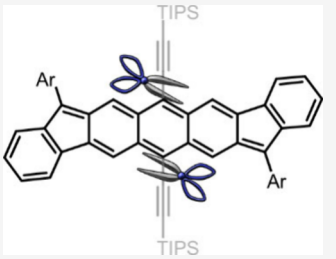
ABSTRACT: To further the ability to manipulate the properties of open-shell molecules, logical and incremental modifications to molecular structure are key steps that provide fine-tuning of established diradicaloid scaffolds. We report the synthesis of an electronically "pure" diradicaloid based on a 2,6-anthroquinoidal core where the once necessary ethynyl "wings" are removed. Through the simplification of the overall electronic structure, the singlet−triplet energy gap increases by 0.3−0.4 kcal mol^{-1} in the reported diradicaloids while avoiding significant disruption to their optoelectronic properties.



Open-shell polycyclic conjugated hydrocarbons are molecules that have unpaired π-electrons in their ground-state electron configurations, and, in the case of diradicaloids, there are two unpaired electrons available for through-space and through-bond communication. These molecules are important for an intimate understanding of π-bonding and spin−spin interactions.[1−7] Narrow highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy gaps,[8,9] amphoteric redox behavior,[10,11] strong low energy absorption in the UV−vis region,[8,12] and usually strong magnetic coupling[13,14] are associated properties of this unique class of molecules, which contribute to the deep interest in developing these systems. Due to their properties, organic diradicaloids are thought to be suitable in nanoscale electronics,[15,16] spintronics,[17,18] nonlinear optics,[19,20] and singlet fission.[21,22] The first of these diradicaloids was Thiele's hydrocarbon,[23] followed quickly by Tschitschibabin's hydrocarbon[24] as an extension to the quinoidal conjugation, lending a proaromatic nature to these systems. Many diradicaloids have been synthesized and studied since, such as zethrenes,[25,26] bisphenalenyls,[27,28] anthenes,[29,30] extended quinodimethanes,[31,32] and diindenoacenes.[33−36] Stability in these systems is accomplished by the inclusion of bulky groups on the high-spin density carbon centers to slow decomposition, thus allowing for thorough study of stable, novel, open-shell scaffolds.

In 2016, we reported the synthesis and properties of diindenoanthracene **1** (DIAn, Figure 1), a diradical with excellent stability, a narrow HOMO/LUMO energy gap (E_{gap}), strong absorption within the red region of visible light and weak absorption into the near-infrared region due to a doubly excited state, and a singlet−triplet energy gap (ΔE_{ST}) that allows for a thermally accessible triplet excited state above room temperature.[35] From design principles learned with **1** and a desire to rationally tune ΔE_{ST}, a library of DIAn derivatives (**2**−**5**) was prepared featuring varied arene fusion to the anthracene core while maintaining the same 2,6-diradical orientation (Figure 1).[36] Through judicious adjustments of the electronic parameters dictating the diradical character (y_0) and ΔE_{ST}, a rational, stepwise fine-tuning of ΔE_{ST} resulted in an overall range of 1.6 kcal mol^{-1} for **1**−**5**. Despite this success, their syntheses required the presence of bulky (triisopropylsilyl)ethynyl (TIPSethynyl) groups to ensure correct Friedel−Crafts ring closure to complete the requisite core, as well as to impart added solubility. Fortuitously, a recent publication described the synthesis of an anthracene core without diethynyl substitution,[37] providing the means of simplifying the electronic structure of the quinoidal backbone of DIAn. The current study of "alkyne-free" DIAns **6** and **7** aims to answer the influence alkyne substitution has on molecule properties and whether there are significant consequences in omitting the alkynes.

The ability to study an electronically "pure" DIAn core requires an anthracene-based building block with advantageous substitution on the 2,3/6,7 positions. Granhøj et al. recently reported a synthetic route to bis-triflate **8**,[37] which can be subjected to Suzuki−Miyaura cross-coupling conditions with 4-methylphenylboronic acid to reach diester **9** (Scheme 1). The 2,3/6,7 substitution pattern of the esters and pendant tolyl groups negates the need of the directing effect from the TIPSethynyl groups present on the 9 and 10 positions in the original DIAn synthesis to avoid unproductive ring closure at the 1 and 5 positions.[35] Saponification of the diester to **10** followed by Friedel−Crafts acylation gave dione **11**. This ketone

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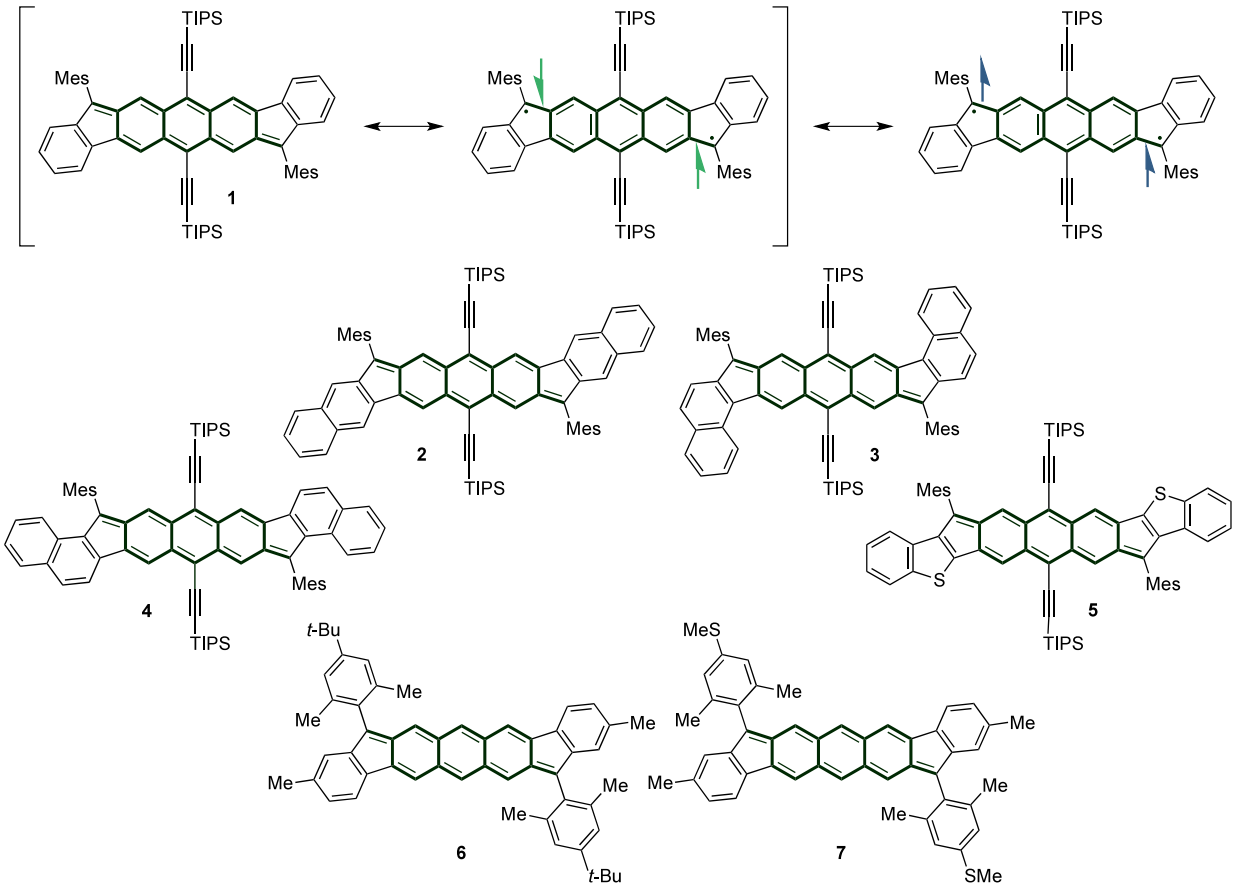
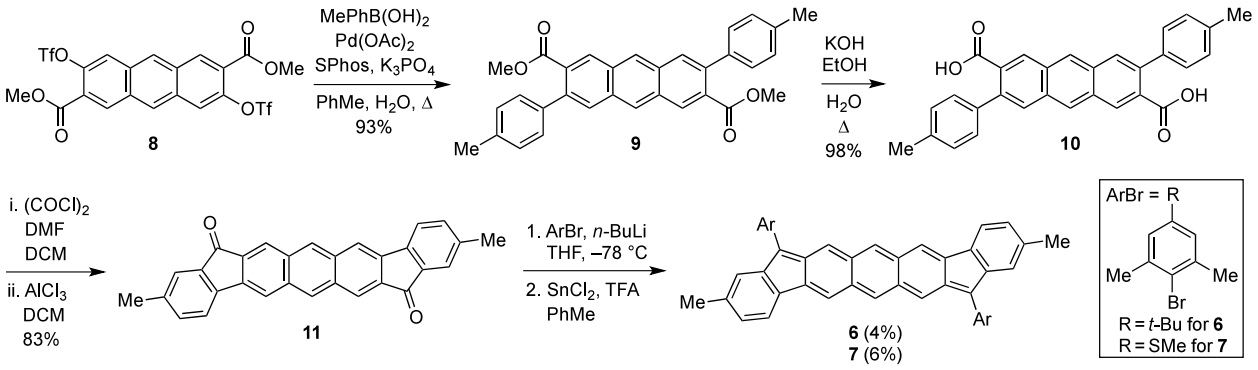


Figure 1. Structures of the known DIAn family **1**−**5** and new DIAn derivatives **6** and **7** lacking the alkyne groups. The common 2,6-anthroquinoidal/diyl relationship in all molecules is denoted by the bolded bonds.

Scheme 1. Synthesis of Diindeno[1,2-*b*:1′,2′-*i*]anthracenes 6 and 7



functionality permits the final two transformations: nucleophilic addition of the lithiate of 2-bromo-4-*t*-butyl-1,3-dimethylbenzene followed by trifluoroacetic acid-catalyzed $SnCl_2$ reduction of the diol intermediate to afford diradicaloid **6**. Similarly, use of 4-bromo-3,5-dimethylthioanisole[38] in the lithiate reaction results in the formation of DIAn derivative **7**. The low yields of **6** and **7** are due to material loss during the removal of residual Sn salts during purification, which we attribute to the significantly reduced solubility caused by the absence of the two TIPSethynyl groups.

The structural differences between **1**, **6**, and **7** allow us to rationalize changes in optoelectronic properties as a consequence of TIPSethynyl substitution, or lack thereof. As expected, the absorbance profiles in the UV−vis region for **6** and **7** resemble those of other acene-based quinoids and are very similar to that of **1** (Figure 2a). The λ_{max} values in the red region of the UV−vis spectra are at 659 and 661 nm for **6** and **7**, respectively, followed by second absorption deeper into the red (∼720 nm), compared to a single broad absorption for **1** (690 nm). It is reasonable to attribute both the broader absorption and the ∼30 nm red-shift to the two ethynyl groups in **1**, seeing as the spectra of both **6** and **7** illustrate multiple defined absorbance features in the same lower energy region. In addition, common to diradicaloids is the weak shoulder band (∼760 nm), indicative of a double-excitonic state.[12,36,39−41] This low-energy shoulder is present regardless of substitution and has a strikingly similar shape between all three DIAn

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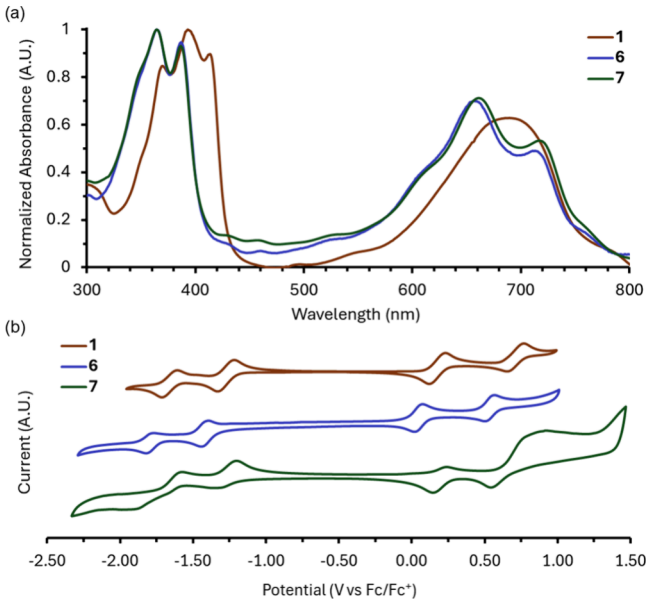

Figure 2. (a) Electronic absorption spectra for **1**, **6**, and **7** in CH_2Cl_2 at room temperature. (b) CV of **1**, **6**, and **7** in CH_2Cl_2 showing two quasi-reversible one-electron reductions and two quasi-reversible one-electron oxidations. Voltammograms are generated according to IUPAC plotting convention; the starting point for each voltammogram is 0.0 V, and scans proceed from oxidizing to reducing potentials.

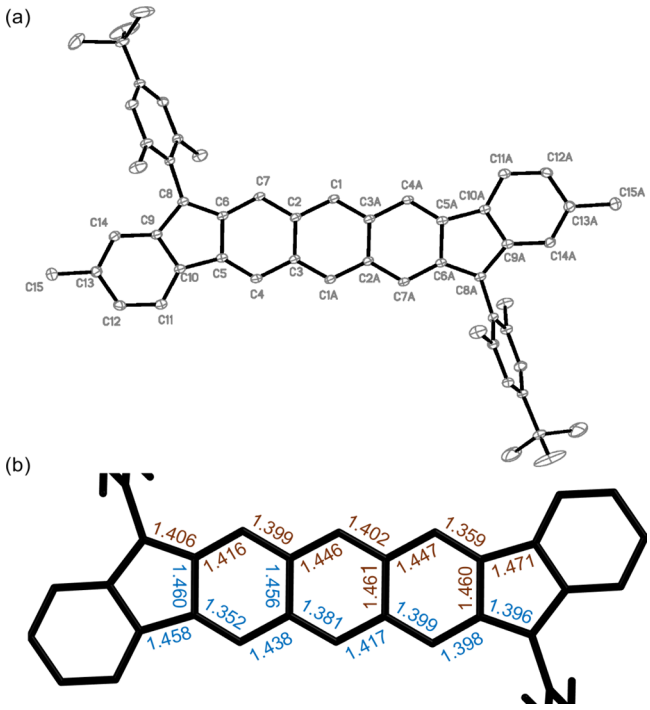

Figure 3. (a) Crystal structure of DIAn **6** drawn with 50% thermal ellipsoids; hydrogen atoms are omitted for clarity. (b) Comparison of selected bond lengths (Å) of **1** (brown)[35] and **6** (blue); pendant aryl groups have been truncated to show only the DIAn core.

derivatives, suggesting a nearly identical doubly excited electronic configuration within the polycyclic core.

Cyclic voltammetry (CV) of DIAns **6** and **7** exhibits two one-electron oxidations and reductions with symmetry between both processes that match parent DIAn **1** (Figure 2b). Notable differences between CV traces of **1** and **6** are their redox potentials. Quasi-reversible reductions occur at −0.93 and −1.31 V (vs SCE) without ethynyl substitution; however, analogous reductions are shifted upward to −0.81 and −1.20 V (vs SCE) with ethynyl substitution (see the Supporting Information for additional CV details). The oxidations of these systems also are shifted from 0.51 and 0.99 V in **6** to 0.63 and 1.17 V in **1**. HOMO energy levels are estimated as −5.19 and −5.32 eV for **6** and **1**, respectively, whereas LUMO energy levels are estimated as −3.72 and −3.87 eV. The electrochemically derived E_{gap} for DIAn **6** is 1.47 eV, which is very close to the reported E_{gap} of 1.45 eV for the bis-ethynyl substituted analogue **1**. In the case of **7**, the potentials for all four possible redox events are shifted slightly up from both **1** and **6**, making it more susceptible to electrochemical reduction, but also more resistant to oxidation (see Table S1 for full electrochemical data of **7**), yet it too has an E_{gap} of 1.47 eV. The equivalent energy gap between **6** and **7** can be rationalized by poor overlap between the orthogonal, bulky pendent aryl groups and the quinoidal core, rendering any electronic influence of the electron-rich sulfur atom in **7** on the gap itself negligible. There is very little change to the E_{gap} of DIAn diradicaloids despite substitution on the apical carbon of the five-membered rings and substitution on the central six-membered ring, analogous to related indeno[1,2-*b*]fluorenes featuring bulky substituents.[42]

Single-crystal X-ray diffraction (XRD) of crystals of **6** grown by vapor diffusion of heptane into a CH_2Cl_2 solution at room temperature successfully afforded its molecular structure (Figure 3a). Similar to **1**, analogue **6** is centrosymmetric, planar, and retains roughly 1D stacking with overlapping peripheral six-membered rings (Figure S3). Bond lengths within the quinoidal core of **6** alternate as was observed for **1**, which reflect the closed-shell structure well (Figure 3b). Within **6**, the bond distances vary between 1.352−1.460 Å and tend to be slightly shorter than those of DIAn **1**, indicating minimal changes in the ground-state structure between alkyne substituted and unsubstituted quinoidal cores. The bond distance between the apical carbon and the anthracene core (C6−C8), which can indicate contributions from both an open-shell and a closed-shell structure, is roughly the same (1.396 Å) as the values found in DIAn derivatives **1**−**4** (1.391−1.406 Å).[36] A discussion of the differences in the molecular packing of **1** and **6** (Figure S9) can be found in the Supporting Information.

Prior computational studies on simplified models of **1** and **6**/**7** have suggested that omission of the alkynyl substituents will have minimal effect on the diradical character index, y_0 (0.623 vs 0.615, respectively (PUHF/6-311G*)), yet will have an appreciable impact on ΔE_{ST} ((SF-NC)-TDDFT PBE50/6-311G*), raising it from −4.71 kcal mol^{-1} in **1** to −5.42 kcal mol^{-1} in **6**/**7**.[36] To this end, the magnetic properties of **6** and **7** were studied using superconducting quantum interference device (SQUID) magnetometry. While **6** and **7** do contain two additional methyl groups in the core, their presence should have very little influence on magnetic properties based on the computed odd-electron density map of **1**.[35] As expected, the two analogues have very similar SQUID magnetic responses (Figure 4) since the only difference is *t*-butyl- versus thiomethyl-substitution on the pendant phenyl rings. When fit to the Bleaney−Bowers equation,[43] the data better fit to a dimer model from which ΔE_{ST} values of −4.6 and −4.5 kcal mol^{-1} are obtained for **6** and **7**, respectively, numbers that are in fairly good agreement with the previously calculated ΔE_{ST} of −5.4 kcal mol^{-1}.[36] DIAns **6** and **7** exhibit a thermally accessible triplet

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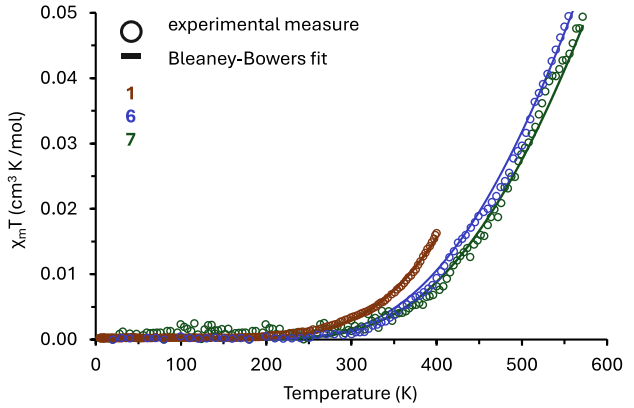

Figure 4. SQUID data of **1**, **6**, and **7** (○) and the corresponding Bleaney−Bowers fit (−).

excited state from a singlet ground state, which is consistent with the larger library of DIAn derivatives from our lab.[36] Comparing the ΔE_{ST} of **6** and **7** to that of **1** (−4.2 kcal mol^{-1}),[35] there is a difference of less than 0.4 kcal mol^{-1}, indicating a fine-tuning of the ΔE_{ST} in these anthracene-based diradicaloids.

In summary, we report the facile synthesis and study of DIAns **6** and **7** without ethynyl substitution. In depth characterization was completed with single-crystal XRD, UV−vis spectroscopy, CV, and magnetic measurements with computational support from previously reported theoretical values providing experimental corroboration to a long-standing curiosity toward the influence of bis-ethynyl substitution. Further fine-tuning of ΔE_{ST} extends the intrigue of this family of diradicaloids and parallels widespread interest of open-shell molecules in the realm of spintronics.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.4c01500.

Experimental procedures and spectral data for **6**−**11**, and additional UV−vis, X-ray, CV, and SQUID data (PDF)

Accession Codes

CCDC 2361007 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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