Organic Letters

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Letter

Enhancing the Antiaromaticity of *s*-Indacene through Naphthothiophene Fusion

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Cite This: *Org. Lett.* 2021, 23, 5012−5017

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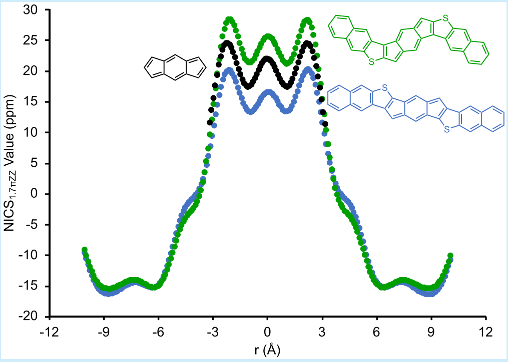
ABSTRACT: Addressing the instability of antiaromatic compounds often involves protection with bulky groups and/or fusion of aromatic rings, thus decreasing paratropicity. We report four naphthothiophene-fused *s*-indacene isomers, one of which is more antiaromatic than parent *s*-indacene. This surprising result is examined computationally through nucleus-independent chemical shift XY calculations and experimentally via nuclear magnetic resonance spectroscopy, X-ray crystallography, ultraviolet−visible spectrophotometry, and cyclic voltammetry, with the latter two indicating that this molecule possesses the lowest highest occupied molecular orbital−lowest unoccupied molecular orbital energy gap observed for heterocycle-fused *s*-indacene.



Aromaticity and antiaromaticity are foundational concepts in modern organic chemistry.[1,2] Although the definitions of aromaticity and antiaromaticity are debated,[3−5] they continue to be active areas of research.[6−12] Hückel's rule defines a planar, conjugated, cyclic system with 4*n* + 2 π elections as aromatic.[13] Later, Dewar and Breslow proposed the concept of antiaromaticity, as a planar, cyclic system with 4*n* π electrons;[14−16] however, neither rule clearly describes multi-ring systems.[17] Because there is no broadly applicable, physical measure of aromaticity or antiaromaticity, it is generally defined for polycyclic hydrocarbons using three criteria: structural, energetic, and magnetic. Applying only one criterion can lead to misclassification; however, when applied together, these criteria form a widely accepted basis of identification.[1,18]

An interesting test case that pushes the limits of this definition of aromaticity/antiaromaticity is *s*-indacene. *s*-Indacene (**1**; Figure 1) is a conjugated molecule consisting of a fused 5−6−5-membered ring system that has 12 π electrons, making it formally antiaromatic.[14,15] As a result, *s*-indacene is expected to be an unstable molecule with alternating bond lengths, leading to a C_{2h} symmetric structure and paratropic ring currents.[14,19,20] Most initial studies on this compound focused on its theoretical properties.[21,22] The parent molecule was later synthesized in the early 1960s, although it was too unstable to cleanly isolate.[23,24] Inclusion of bulky substituents allowed 1,3,5,7-tetra-*tert*-butyl-*s*-indacene (TTBI, **2**) to be fully characterized, but crystallographic analysis showed the molecule to have a D_{2h} delocalized structure.[25,26] Continued research has since led to debate on its classification as antiaromatic, aromatic, or non-aromatic within the criteria described above.[20,27,28]

The unusual combination of aromatic and antiaromatic characters means that *s*-indacene remains an interesting synthetic target, and therefore, other substitution patterns have been employed to make isolable, *s*-indacene-based compounds. Over the past decade, our group has generally focused on the indeno[1,2-*b*]fluorene ([1,2-*b*]IF) scaffold, which includes *s*-indacene at the core.[29−33] By fusing various carbocycles and/or heterocycles while simultaneously incorporating kinetically blocking functional groups, the highly antiaromatic *s*-indacene core can be isolated.[30,31] Unlike the derivatized *s*-indacene **2** along with additional early examples,[25,26,34,35] which have the delocalized D_{2h} geometry, the compounds we have prepared show pronounced bond length alternation in the *s*-indacene core, giving us the ability to access the C_{2h} symmetric conformation of *s*-indacene. One key study was the preparation of *syn*- and *anti*-indacenodibenzothiophene (*syn*- and *anti*-IDBT, **3** and **6**, respectively),[31] because we found that the fusion of benzothiophene units to parent *s*-indacene came close to the paratropicity of the C_{2h} structure of compound **1** itself. If it was possible for compound **3** to approximate the antiaromaticity of compound **1**, we set out to design and characterize molecules whose paratropicity would exceed that of compound **1**.

Received: May 3, 2021
Published: June 15, 2021

ACS Publications

https://doi.org/10.1021/acs.orglett.1c01514
Org. Lett. 2021, 23, 5012−5017

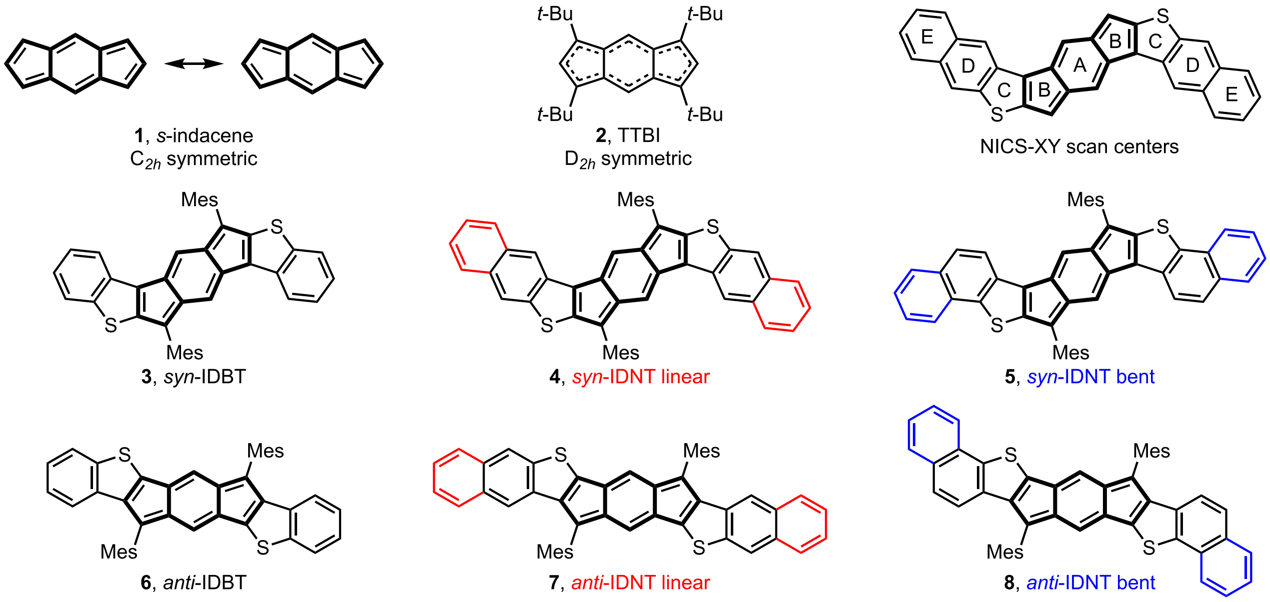


Figure 1. *s*-Indacene C_{2h} resonance structures (**1**), tetra-*tert*-butyl-*s*-indacene (**2**), indacenodibenzothiophene isomers (**3** and **6**), and four indacenodinaphthothiophene isomers (**4**, **5**, **7**, and **8**). The terms *syn* and *anti* refer to the orientation of the heteroatom with respect to the apical carbon of the five-membered ring. Mes = 2,4,6-trimethylphenyl.

Over the last six years, we have used nucleus-independent chemical shift (NICS)-XY scan calculations to guide many of our synthetic efforts, because these computations provide a clear, easy-to-understand visualization of ring currents (paratropic, diatropic, and atropic) within polycyclic molecules.[36] For a first attempt to enhance paratropicity, we explored the effects of naphthothiophene fusion on the *s*-indacene core. The additional ring now means that there are three different orientations of the naphthothiophene motif for each *syn*- and *anti*-indacenodinaphthothiophene (IDNT) isomer: one "linear" 2,3-fusion (e.g., **4**) and two "bent" 1,2-fusion (e.g., **5**; the other isomer is not shown[37]) of the naphthalene motif. All calculations were performed on simplified structures, where the mesityl substituents attached to the apical carbons of the five-membered rings have been replaced with hydrogen atoms, because these bulky groups have been shown to have little to no effect on the computed NICS values.[30]

The C_{2h} symmetric structure of *s*-indacene (**1**, black; Figure 2 and Figure S8 of the Supporting Information) serves as the benchmark for the NICS-XY scans, because it has strong paratropic ring currents and forms the core of our system. Gratifyingly, a comparison of linear *syn*-IDNT (**4**, green) to *syn*-IDBT (**3**, orange), the molecule that most approximates the paratropicity of compound **1**, reveals that extending the outer π system increases the antiaromaticity to the extent that compound **4** is more antiaromatic than *s*-indacene itself. Bent *syn*-IDNT (**5**, purple) is slightly below the NICS-XY scan of compound **3**, suggesting nearly comparable paratropicity. The *anti*-fused thiophene series shows less pronounced variation, with linear *anti*-IDNT (**7**, blue), bent *anti*-IDNT (**8**, gold), and *anti*-IDBT (**6**, red) having very similar NICS values. In all of the systems, we observe a strong paratropic ring current (from 17 to 28 ppm) over the center (the *s*-indacene moiety) moving to diatropic currents (from −14 to −17 ppm) over the outer benzene ring(s), with the tropicity of the thiophene rings (from −1 to −3 ppm) essentially extinguished. The NICS-XY scan calculations indicate that *syn*-IDNT isomer **4** is a desirable synthetic target for not only the fundamental interest of preparing a molecule more paratropic than compound **1** but also potential device applications. High antiaromaticity correlates with low highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) energy gaps, which can improve conductance both intermolecularly and intramolecularly.[38,39]

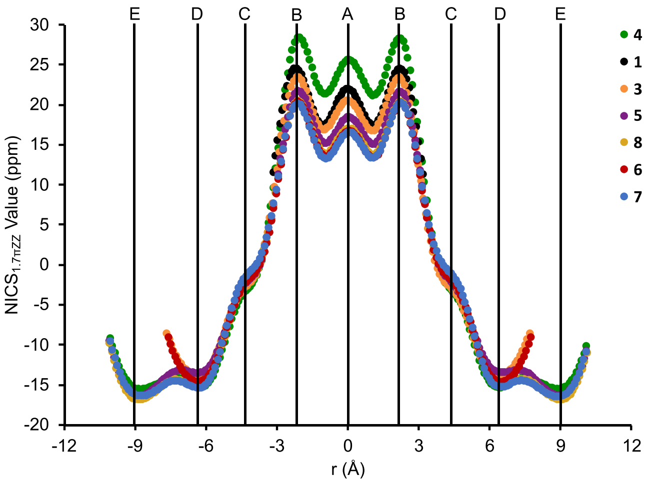
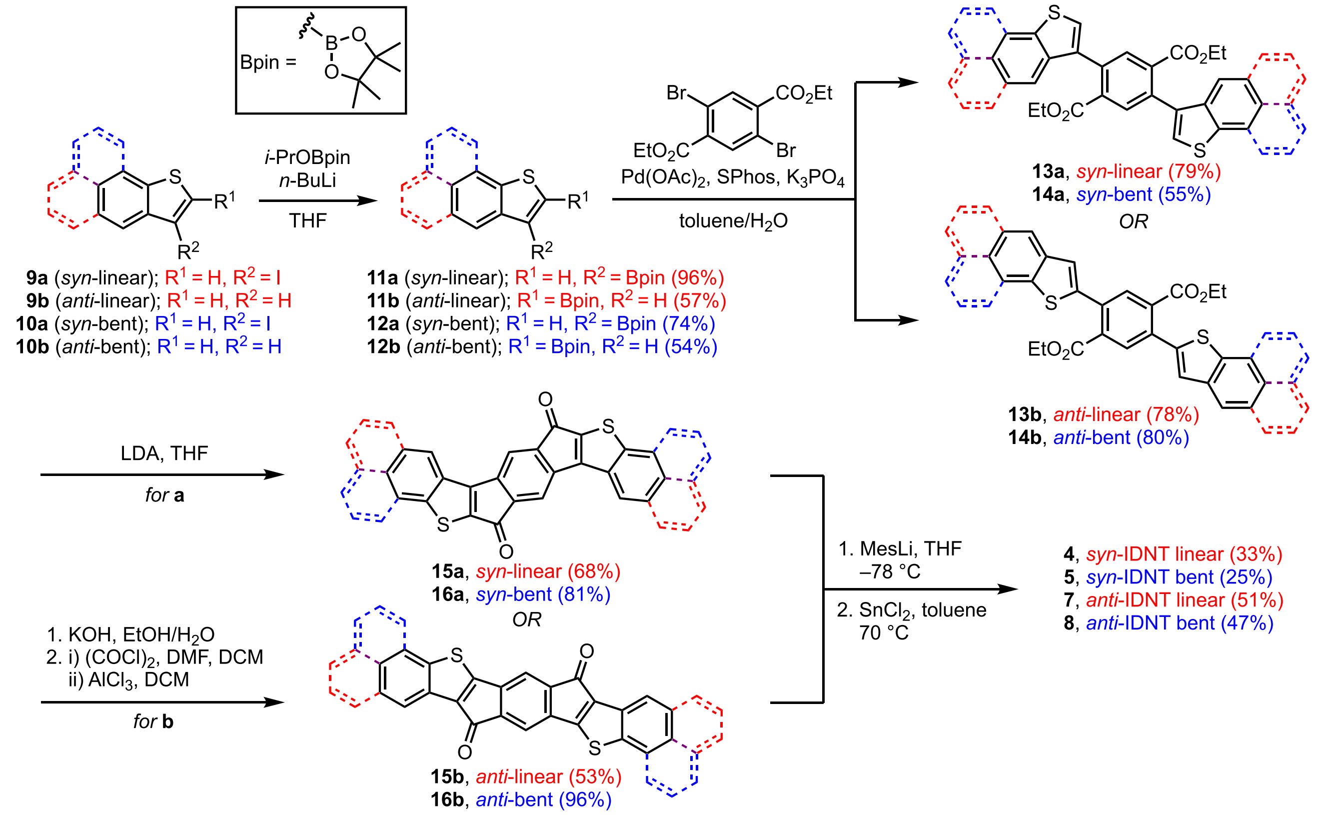


Figure 2. NICS-XY scans in descending order of paratropicity strength: **4** (green), **1** (black), **3** (orange), **5** (purple), **8** (gold), **6** (red), and **7** (blue).

Previous work from our lab found that increasing the 2,3-fusion bond order corresponds with an increase in antiaromaticity.[30] To continue examining this trend, we performed natural bond orbital (NBO) calculations on thiophene, benzothiophene, and naphthothiophene. The 2,3-fusion bond order increases across these three compounds from 1.64 in thiophene, 1.70 in benzothiophene, and 1.72 in the linear naphtho[2,3-*b*]thiophene. The increased fusion bond order forces the *s*-indacene core to have stronger bond length alternation, while thiophene acts as a thioether spacer separating aromatic naphthalene and antiaromatic *s*-indacene, Scheme 1. Synthesis of Linear and Bent *syn*- and *anti*-IDNT Isomers



as previously observed with IDBTs.[31] We recently uncovered the reasons for the stronger paratropicity in the *syn* isomer, which is due to a Clar sextet effect.[40] Finally, NICS-XY scans of thiophene and its benzo and naphtho analogues (Figure S7 of the Supporting Information) show that the diatropicity of the heterocycle is weakest in naphtho[2,3-*b*]thiophene, meaning its S atom can π donate into the *s*-indacene core more effectively, enhancing its paratropicity.[28] Taken together, this illustrates why the *syn*-linear fusion of naphthothiophene affords the most antiaromatic NICS values.

On the basis of the NICS-XY scans, we were most interested in preparing the linear *syn*- and *anti*-IDNT isomers (**4** and **7**), because they are calculated to be the most and least antiaromatic compounds, respectively. The boronic ester coupling partners (**11a** and **11b** and **12a** and **12b**; Scheme 1) for linear and bent IDNT isomers, respectively, were made from naphthothiophenes **9a** and **9b** and **10a** and **10b**, which, in turn, were prepared in five or six steps from the requisite bromonaphthols via a synthetic strategy adapted from the Tovar group (see the Supporting Information for the preparation of compounds **9** and **10**).[41] A Suzuki cross-coupling with diethyl 2,5-dibromoterephthalate yielded diester intermediates **13a**, **13b**, **14a**, and **14b**. Because of the competing reactivity of the naphthalene unit in Friedel−Crafts reactions, the *syn*-IDNT isomers were generated by an intramolecular ring closure accomplished by deprotonation of the R^1 hydrogen (**11a** and **12a**) with lithium diisopropylamide (LDA) to furnish diones **15a** and **16a**. Alternative ring closures were not necessary in the *anti*-IDNT isomers; therefore, in these cases, the cross-coupling was followed by saponification and Friedel−Crafts acylation to give diones **15b** and **16b**. Kinetically blocking mesityl groups were then added to each dione, followed by reductive dearomatization with $SnCl_2$ to provide the product IDNTs **4**, **5**, **7**, and **8** as either blue or purple solids.

The structures of the IDNT isomers were confirmed by ^1H nuclear magnetic resonance (NMR) spectroscopy. The proton on the center six-membered ring provides a convenient NMR handle with which to evaluate the paratropicity of the *s*-indacene core, because a more antiaromatic system will show an upfield shift. The core singlet appears for compound **4** at 5.99 ppm (Figure 3a) compared to a value of 6.09 ppm for compound **7**. These are shifted upfield from the IDBTs (*syn*-IDBT **3**, 6.06 ppm; *anti*-IDBT **6**, 6.11 ppm), respectively. Additionally, the resonances are farther downfield for compounds **5** (6.20 ppm) and **8** (6.16 ppm). These values are in general agreement with the NICS-XY scan trends shown above, where the linear *syn*-IDNT **4** is the most antiaromatic, followed by *syn*-IDBT **3**, and the remaining isomers appear at various levels.

Single crystals of compound **4** suitable for X-ray diffraction were obtained. The resultant crystal structure (Figure 3b) shows pronounced bond length alternation in the core of compound **4**, where the *s*-indacene bond lengths (Table 1) are 1.373 Å (a), 1.468 Å (b), 1.368 Å (c), 1.422 Å (d), 1.389 Å (e), and 1.438 Å (f). The previously prepared *syn*-IDBT **3**, which approximated the antiaromaticity of compound **1**, had core bond lengths of 1.391 Å (a), 1.457 Å (b), 1.371 Å (c), 1.421 Å (d), 1.407 Å (e), and 1.441 Å (f). A comparison of these two solid-state structures reveals that compound **4** possesses increased bond length alternation because the short bonds have decreased in length and the long bonds have generally increased in length (Table 1). Increased bond length alternation is an indication of enhanced paratropicity[30] and

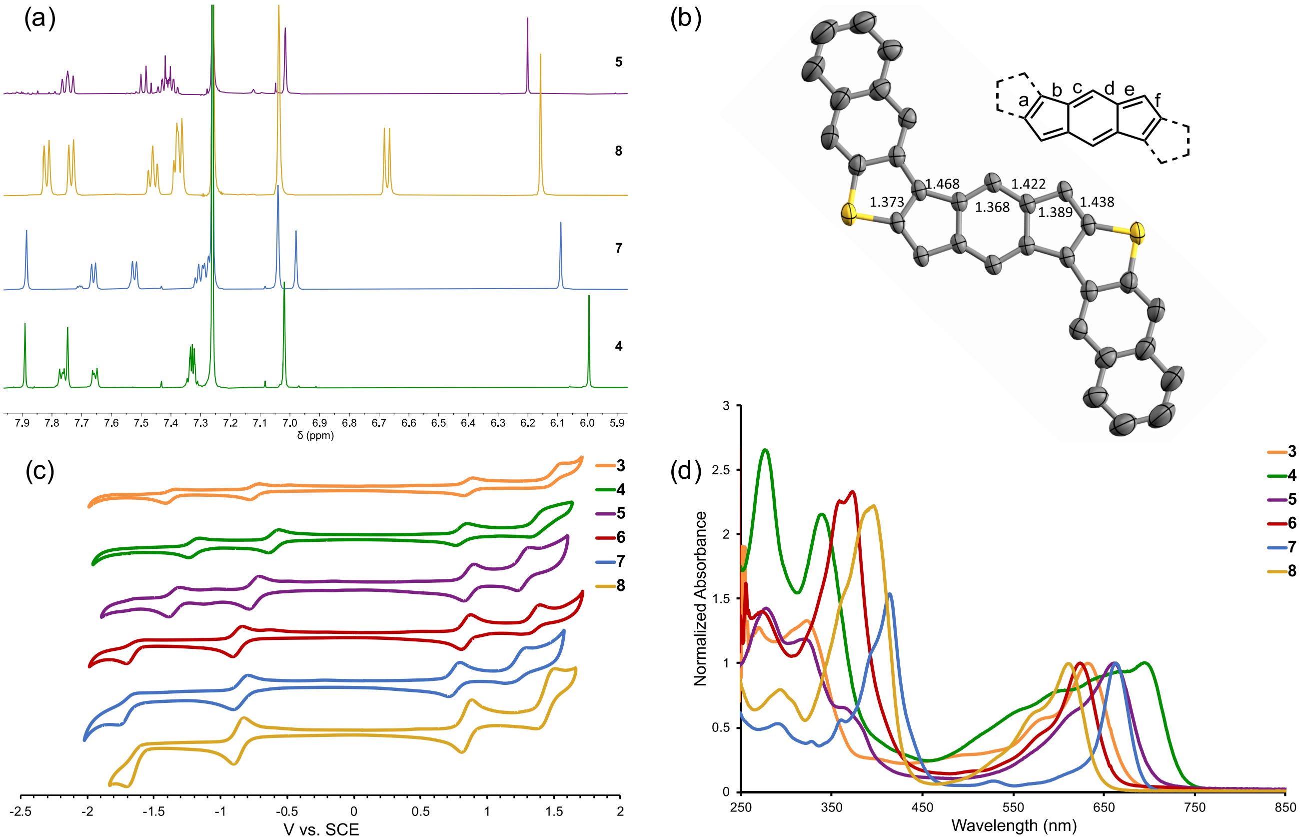


Figure 3. (a) Aromatic region of ^1H NMR spectra of compounds **4**, **5**, **7**, and **8** showing an upfield shift of core singlets, given in parts per million (ppm). (b) Core labeling scheme for Table 1 and *syn*-IDNT linear (**4**) crystal structure, with hydrogens and mesityl groups omitted for clarity. (c) Cyclic voltammograms of compounds **3**−**8**. (d) UV−vis absorption spectra of compounds **3**−**8**.

Table 1. Bond Length Comparison of the *s*-Indacene Core of Compounds 2−4[a]

bond	*syn*-IDBT **3**[b]	*syn*-IDNT **4**	TTBI **2c**[c]
a	1.391(2)	1.373(5)	1.408
b	1.457(2)	1.468(4)	1.434
c	1.371(2)	1.368(4)	1.395
d	1.421(2)	1.422(4)	1.394
e	1.407(2)	1.389(4)	1.406
f	1.441(2)	1.438(4)	1.438

[a] Bond lengths in angstroms (Å), and bond labels are shown in Figure 3b. [b] From ref 32. [c] From ref 26, with uncertainties not reported.

helps corroborate that the *s*-indacene core of *syn*-IDNT **4** is even more antiaromatic than previously synthesized *syn*-IDBT **3** and its parent **1**.

Antiaromatic compounds usually have much smaller HOMO−LUMO energy gaps than aromatic compounds, and we observe decreasing HOMO−LUMO energy gaps consistent with our increasingly antiaromatic systems. Cyclic voltammograms of the IDNTs as well as *syn*-IDBT and *anti*-IDBT are shown in Figure 3c, and the results are compiled in Table 2. All IDNTs have two reductions and two oxidations. The first reduction and oxidation are reversible for all IDNTs. The second reduction is reversible in compounds **4** and **5**, while compounds **7** and **8** display irreversible second reductions. Compounds **5** and **8** display a second reversible oxidation, which is irreversible in compounds **4** and **7**. E_{red1} values are between −0.60 and −0.86 V versus the saturated calomel electrode (SCE), and E_{ox1} values range from 0.75 to 0.86 V. The HOMO−LUMO energy gaps range from 1.41 eV (**4**) to 1.71 eV (**8**), which is in good agreement with computational values as well as the trend in antiaromaticity

Table 2. Electrochemical Values[a]

compound	E_{red2}	E_{red1}	E_{ox1}	E_{ox2}	E_{HOMO}	E_{LUMO}	E_{gap}
3[b]	−1.37	−0.75	0.86	1.57	−5.54	−3.93	1.61
6[b]	−1.72	−0.87	0.84	1.32	−5.52	−3.81	1.71
4	−1.20	−0.60	0.81		−5.49	−4.08	1.41
5	−1.35	−0.75	0.86	1.27	−5.54	−3.93	1.61
7	−1.77	−0.85	0.75	1.22	−5.43	−3.83	1.60
8	−1.71	−0.86	0.85	1.44	−5.53	−3.82	1.71

[a] All reduction/oxidation values are in volts (V), and E_{HOMO}, E_{LUMO}, and E_{gap} are in electronvolts (eV). [b] From ref 32.

described through the NICS-XY scans. Indeed, the value for compound **4** is, to date, the lowest HOMO−LUMO energy gap measured in one of our heterocycle-fused *s*-indacenes, which illustrates the high degree of antiaromaticity of this molecule.

Finally, a comparison of the ultraviolet−visible (UV−vis) spectra of the IDNTs shows that the isomers are generally red-shifted from the IDBTs (Figure 3d). Isomer **4** has a low energy absorption at 697 nm (ε = 10 500 L mol^{-1} cm^{-1}), which is the most red-shifted. This can be attributed to higher antiaromaticity as well as π extension. Additionally, compound **7** has a low energy absorption at 665 nm (ε = 23 200 L mol^{-1} cm^{-1}), which is almost the same as compound **5** at 661 nm (ε = 42 400 L mol^{-1} cm^{-1}). Isomer **8** has the least red-shifted absorption at 611 nm (31 600 L mol^{-1} cm^{-1}). Isomer **4** shows a broad shoulder on the UV−vis trace that is consistent with the calculated spectra and is attributed to a HOMO-2 to LUMO transition at 580 nm.

In conclusion, NICS-XY scan calculations predicted the enhanced antiaromaticity of four IDNT isomers and showed that extending the outer π system from benzothiophene to naphtho[2,3-*b*]thiophene increases the paratropicity within the *s*-indacene motif. The forecasted increase of paratropicity was corroborated by ^{1}H NMR spectroscopy, X-ray crystallography, cyclic voltammetry (CV), and UV−vis spectrophotometry, which showed that the linear *syn*-IDNT **4** is more antiaromatic than the C_{2h} symmetric *s*-indacene **1**. This continues the trend displayed by the benzothiophene-fused system **3**, where now compound **4** acts more like a C_{2h} symmetric *s*-indacene with naphthalenes fused onto thioether linkers. The other three IDNT isomers also possess strongly antiaromatic properties, consistent with the NICS-XY scan predictions. We continue to explore additional ways to enhance *s*-indacene paratropicity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01514.

^{1}H and ^{13}C NMR spectra for all new compounds, additional UV−vis, X-ray, and CV data, and computational details including the coordinates of optimized structures (PDF)

Accession Codes

CCDC 2076855 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.

■ ACKNOWLEDGMENTS

The authors thank the National Science Foundation (NSF, CHE-1954389) for support of this research. Mass spectrometry capabilities in the CAMCOR facility are supported by the NSF (CHE-1625529).

■ DEDICATION

In memoriam Klaus Hafner.

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(37) Isomers **5** and **8** are based on naphtho[1,2-*b*]thiophene, whereas the other two "bent" isomers are derived from naphtho[2,1-*b*]thiophene. Synthesis of these latter two bent IDNTs is ongoing.

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