

## Design, Synthesis, and Characterization of a Persistent Nonacene Derivative

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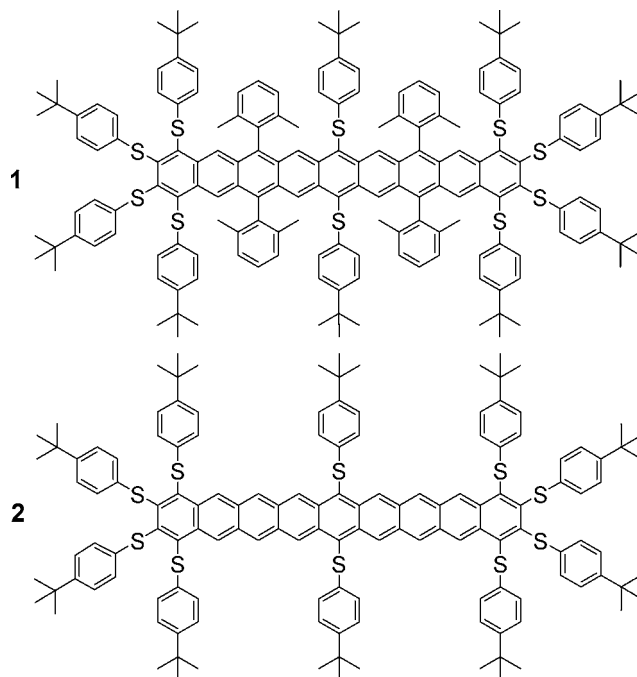
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Acenes<sup>1</sup> are an important class of organic compounds. The smallest acene, anthracene, is a stable molecule and well-known synthetic building block. Tetracene and pentacene, the next two largest acenes, are organic semiconductors that have been utilized in organic field-effect transistors (OFETs),<sup>2</sup> organic light-emitting diodes (OLEDs),<sup>3</sup> and organic photovoltaics (OPVs).<sup>4</sup> Although they are considered to be among the best organic semiconductors because of their high charge-carrier mobilities,<sup>5</sup> tetracene, pentacene, and their derivatives are susceptible to photodegradation, especially in solution.<sup>6</sup> Larger acenes such as hexacene, heptacene, octacene, and nonacene are inherently more interesting species. They have smaller band gaps and potentially higher charge-carrier mobilities, but they are also far more prone to oxidative degradation, a characteristic that limits their opportunities of use in OFET, OLED, OPV, and other electronic applications. Parent hexacene and heptacene have been isolated only in rigid polymeric matrices, where they show lifetimes of approximately 12 and 4 h, respectively.<sup>7</sup> One triisopropylsilyl ethynyl (TIPS)-substituted hexacene<sup>8</sup> and two TIPS-substituted heptacenes<sup>8,9</sup> have been reported. Parent octacene and nonacene are predicted to have open-shell, singlet-diradical,  $\pi$ -conjugated ground states,<sup>10</sup> but neither they nor any of their derivatives have been isolated.

Recently, we completed a substituent-effect study for a large series of pentacene derivatives<sup>11</sup> in which it was revealed that steric effects, electronic effects, and the positional location of substituents are all important factors in determining the photooxidative resistance and HOMO–LUMO gap. The most impressive effects were observed with alkylthio and arylthio substituents, which were more successful than the TIPS substituent at enhancing the photooxidative resistance when placed at the 6 and 13 positions (i.e., on the center ring) of pentacene. We subsequently exploited arylthio substituent effects to produce an unusually persistent heptacene derivative.<sup>12</sup> Buoyed by these successes, we began developing a strategy for the design of an oxidatively resistant nonacene derivative. The strategy would necessarily have to mitigate the high reactivity expected for an open-shell singlet-diradical species. We now report the successful design, synthesis, and characterization of the first persistent nonacene derivative, **1**, as well as a less persistent nonacene derivative, **2**.

Bendikov and co-workers<sup>10</sup> described heptacene and larger acenes as singlet diradicals using unrestricted density functional theory (DFT) methods [e.g., UB3LYP/6-31G(d)]. We corroborated this prediction at a higher level of theory (i.e., UB3LYP/6-311+G\*\*//B3LYP/6-31G\*) that in its restricted form was shown to be useful for describing the electronic properties of pentacene derivatives.<sup>11</sup> As noted by Bendikov, the total spin,  $\langle S^2 \rangle$ , associated with large acenes increases down the series hexacene, heptacene, octacene, nonacene, and decacene, as does the difference in energy between the open-shell singlet (preferred) and either the triplet or closed-shell species. We surmised that the total spin should be directly related to the rate of oxidation and inversely related to half-

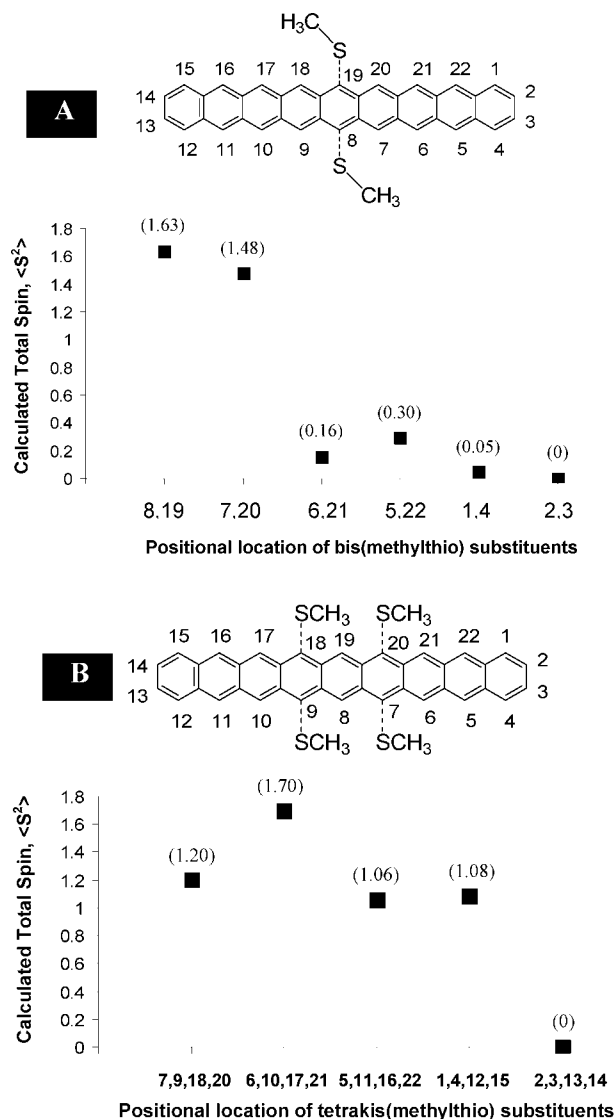


life. That is, a stepwise diradical addition of either triplet oxygen, <sup>3</sup>O<sub>2</sub>, or singlet oxygen, <sup>1</sup>O<sub>2</sub>, should become more facile with increasing total spin of the acene. In fact, UB3LYP/6-31G\* calculations have suggested that a stepwise, diradical mechanism of oxidation may already be significant for pentacene.<sup>13</sup>

We established substituent effects on total spins and HOMO–LUMO gaps by subjecting several nonacene derivatives to unre-

**Table 1.** HOMO, LUMO, and SOMO Orbitals and Energies, Associated Gaps, and Total Spin,  $\langle S^2 \rangle$ , for Nonacene and Three Phenylthio-Substituted Derivatives Calculated at the UB3LYP/6-311+G\*\*//B3LYP/6-31G\* Level of Theory

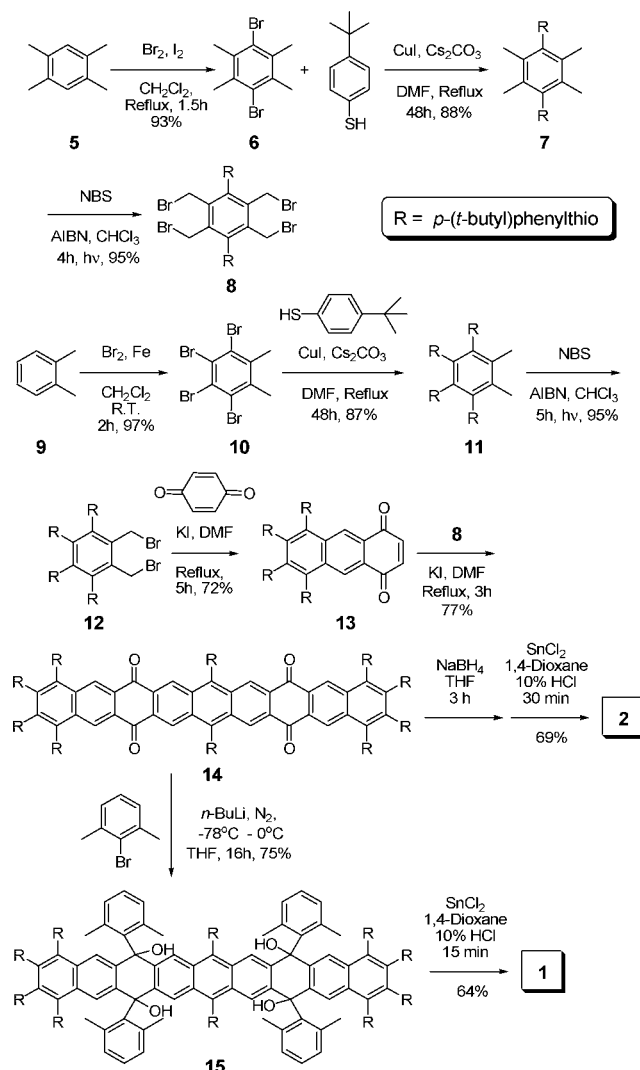
Nonacene	HOMO/ SOMO (eV)	LUMO/ SOMO (eV)	Gap (eV)	$\langle S^2 \rangle$
	-4.69	-3.08	1.61	1.20
	-4.85	-3.21	1.64	1.57
	-4.59	-3.55	1.04	0
	-4.70	-3.70	1.0	0



**Figure 1.** Calculated (UB3LYP/6-311+G\*\*//B3LYP/6-31G\*) total spin,  $\langle S^2 \rangle$ , as a function of positional location of (A) bis(methylthio) and (B) tetrakis(methylthio) substituents.

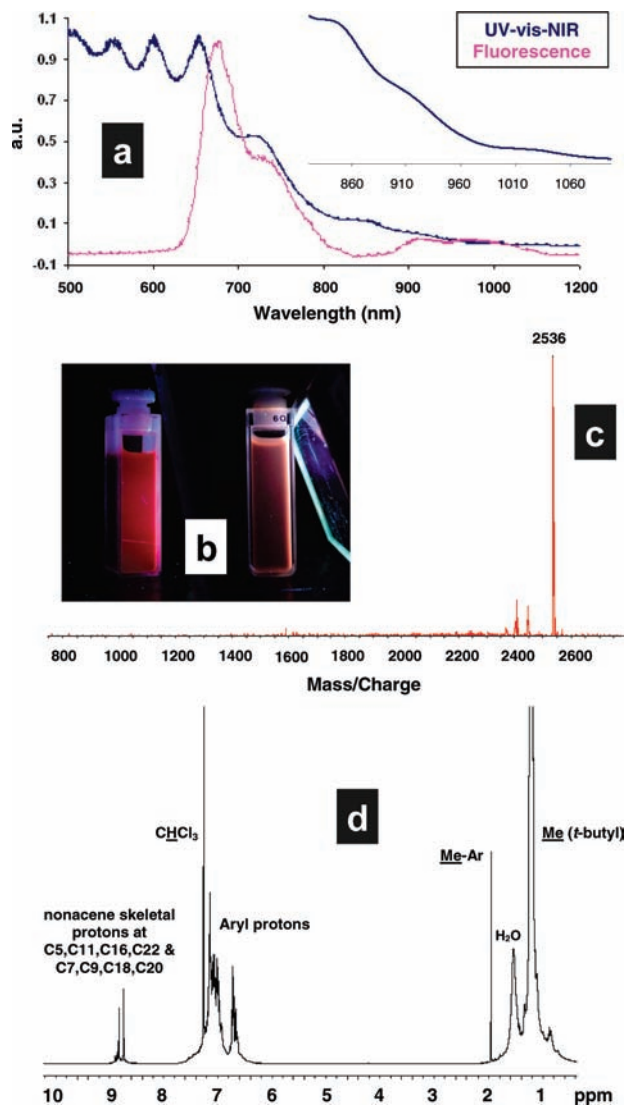
stricted DFT calculations (Table 1). Unsubstituted nonacene has a calculated  $\langle S^2 \rangle$  of 1.20 and a HOMO–LUMO gap of 1.61 eV. The placement of arylthio substituents at the 8 and 19 positions of nonacene (i.e., on the center ring) increases the total spin of the system ( $\langle S^2 \rangle = 1.57$ ) while minimally impacting the HOMO–LUMO gap. However, arylthio substituents placed on the terminal rings of the nonacene skeleton are calculated to eliminate total spin (i.e.,  $\langle S^2 \rangle = 0$ ) while lowering the HOMO–LUMO gap to  $\sim 1$  eV. In order to further evaluate organothio substituent effects on the total spin, we calculated  $\langle S^2 \rangle$  for several bis(methylthio) and tetrakis(methylthio) isomers as a function of positional location (Figure 1). As before, the results indicate diminished total spin when the methylthio groups are placed on the terminal rings. A slight preference exists for 2,3-bis(methylthio)nonacene ( $\langle S^2 \rangle = 0$ ) over 1,4-bis(methylthio)nonacene ( $\langle S^2 \rangle = 0.05$ ), while a much larger preference exists for 2,3,13,14-tetrakis(methylthio)nonacene ( $\langle S^2 \rangle = 0$ ) over 1,4,12,15-tetrakis(methylthio)nonacene ( $\langle S^2 \rangle = 1.08$ ). We have begun to study the effects of other substituents (e.g., methoxy, aryl, halogen, cyano) on the total spin as a function of positional location. Preliminarily, it appears that the most profound effects are unique to alkylthio and arylthio substituents.

**Scheme 1.** Synthesis of 1,2,3,4,8,12,13,14,15,19-Deca(4'-*t*-butylphenylthio)-6,10,17,21-tetra(2',6'-dimethylphenyl)nonacene (**1**) and 1,2,3,4,8,12,13,14,15,19-Deca(4'-*t*-butylphenylthio)nonacene (**2**)



With a closed-shell electronic configuration, nonacene derivatives bearing alkylthio or arylthio groups at the 1, 2, 3, 4, 12, 13, 14, and 15 positions should be susceptible to the same substituent effects as previously reported for closed-shell pentacene derivatives.<sup>11</sup> Consequently, the placement of arylthio or alkylthio substituents on both the center ring and the terminal rings of nonacene was predicted to be a particularly advantageous design that could yield a persistent nonacene derivative. The additional placement of *o*-dimethylphenyl substituents at the 6 and 21 and 10 and 17 positions of nonacene was predicted to further retard oxidation across the noncentral rings, as recently demonstrated for a persistent heptacene derivative.<sup>12</sup>

With the aforementioned design elements in mind, we synthesized nonacene derivatives **1** and **2** as illustrated in Scheme 1. A key step involved the reaction of 6,7,8,9-tetra(4'-*t*-butylphenylthio)-1,4-anthracene quinone **13** with bis-*o*-quinodimethane precursor **8** to produce a nonacene skeleton in the form of nonacene diquinone **14**. Nonacenes **1** and **2** were initially formed as solids with a black color akin to that of carbon nanotubes. Upon dissolution, they formed black solutions (not suspensions). With oxidation, the solids and solutions faded to brown-black and eventually golden-brown. Nonacene derivative **2** persisted for several minutes in solution but



**Figure 2.** Solution-phase characterizations of the first persistent nonacene derivative, **1**. (a) UV-vis-NIR (blue) and fluorescence (pink) spectra of freshly prepared **1**. (b) Solutions of **1** in  $\text{CH}_2\text{Cl}_2$  exposed to long-wavelength UV light (left) before oxidation (blood-red fluorescence) and (right) after oxidation (pale-pink fluorescence). (c) Laser-desorption mass spectrum of **1**. (d)  $^1\text{H}$  NMR spectrum of **1**.

not long enough for thorough characterization by solution-phase methods. Nonacene derivative **1**, on the other hand, was sufficiently persistent to be characterized by a suite of solution-phase techniques, including  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, UV-vis-NIR, and fluorescence spectroscopies (Figure 2). The  $^1\text{H}$  NMR spectrum of **1** includes two singlets at 8.83 and 8.74 ppm corresponding to two sets of equivalent X protons at C5, C11, C16, and C22 and C7, C9, C18, and C20 of the nonacene skeleton, respectively. In the  $^{13}\text{C}$  NMR spectrum, 32 of 33 expected signals were observed, with one instance of coincidental overlap involving quaternary carbons from inequivalent sets of *t*-butyl groups. The laser-desorption mass spectrum shows a strong molecular ion cluster centered at  $m/z$  2536. On the basis of the onset of the longest-wavelength absorption, the optical HOMO-LUMO gap for nonacene derivative **1** was calculated to be 1.12 eV, which is slightly larger than the predicted value (Table 1) but still the smallest experimentally measured HOMO-LUMO gap for an acene.

Interestingly, nonacene derivative **1** shows an intense blood-red fluorescence (Figure 2b), a characteristic that can serve as a fast and effective diagnostic tool for the detection of other nonacene derivatives during their syntheses. Thus, upon dissolution of freshly prepared nonacene derivative **1** in  $\text{CDCl}_3$ , an intense, persistent blood-red fluorescence was observed. In contrast, dissolution of freshly prepared nonacene derivative **2** showed blood-red fluorescence only for several minutes. In this case, the color faded to pale-pink and, after several weeks, to yellow. These color changes indicate successive oxidations of **2**. When stored as a solid in the dark, nonacene derivative **1** persisted for at least six weeks, after which time small amounts of oxidation products were observed by NMR spectroscopy. When protected from light, solutions of **1** persisted for at least 24 h. When directly exposed to light and air, solutions of **1** persisted for approximately 2 h.

Finally, we note that the results given in Table 1 and Figure 1 warrant a detailed computational study of the total spin and HOMO-LUMO gaps as a function of substituent type, number of substituents, and positional locations of substituents for octacene, nonacene, and larger acenes prepared in silico. Such a study will help to identify additional worthy synthetic targets. The prospect of preparing very large, persistent acenes with closed-shell ground states and vanishingly small HOMO-LUMO gaps is an intellectually tantalizing and increasingly realistic goal.

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**Supporting Information Available:** Detailed synthetic procedures and spectroscopic data for nonacene derivatives **1** and **2** and their precursors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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