ORGANIC LETTERS

2009
Vol. 11, No. 22
5222−5225

Alkynylated Aceno[2,1,3]thiadiazoles

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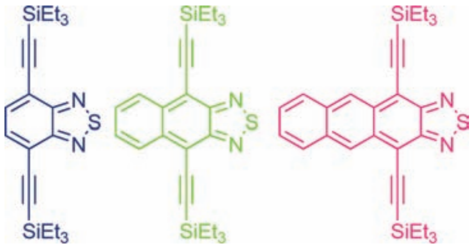
Received September 17, 2009

ABSTRACT



Enlarged acenothiadiazoles, which are easily prepared, display attractive optical and electrochemical properties. The annulation of thiadiazole to anthracene gives a stable material with optical properties similar to those of substituted pentacenes.

Synthesis and property evaluation of acenes and their derivatives has experienced a significant revival of interest as they have great potential in organic electronics.[1−5] If one looks carefully, however, there is an almost infinite number of structurally attractive, larger aromatic systems that have never been prepared. Such acene types are fascinating from a fundamental point of view with respect to their optical and electronic properties and might hold some promise in organic electronics applications. Here, we introduce hitherto unknown larger thiadiazole-fused acene[6] materials[7−10] with dramatically size-dependent optical properties. We demonstrate that a thiadiazoles unit is effective in lowering the HOMO−LUMO gap in molecules **1**−**3**, by approximately as much as two benzene rings. We have also evaluated the electrochemical and solid-state packing properties of derivatives of **3**.

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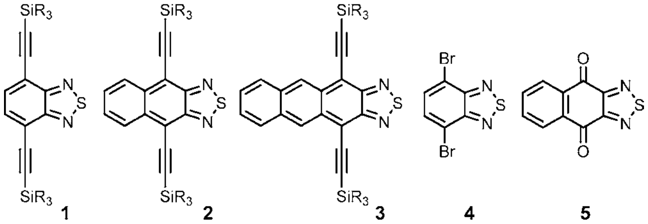
10.1021/ol902156x CCC: $40.75

The synthesis of **1a**−**c** is achieved by Sonogashira alkynylation of **4**,[11] while **2a**−**c** are obtained from **5** in yields ranging from 11−87% in a procedure adapted from ref 12 (see Supporting Information).

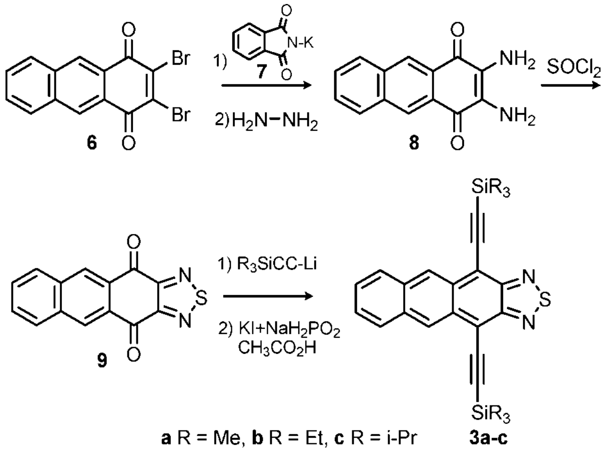


1 **2** **3** **4** **5**

a R = Me; **b** R = Et; **c** R = *iso*-Pr

As derivatives of **3** are unknown, we started from **6**, which was synthesized according to a modification of the procedure of Bedworth et al.[13] Reaction of **6** with potassium phthalimide (**7**), followed by treatment with hydrazine, afforded the diaminoquinone **8** in 40% yield (Scheme 1). Dissolution of **8** in refluxing thionyl chloride formed the thiadiazole ring to give **9** (91%), which was then treated with suitable alkynyllithium reagents.

Scheme 1. Synthesis of **3a**−**c**



After hydrolysis, the corresponding diols were directly reduced by sodium hypophosphite and potassium iodide in acetic acid to afford **3a**−**c** in 9−92% yield after column chromatography over silica gel (hexane/dichloromethane 10:1−3:1). The compounds form blue-black crystalline powders displaying a metallic luster.[14]

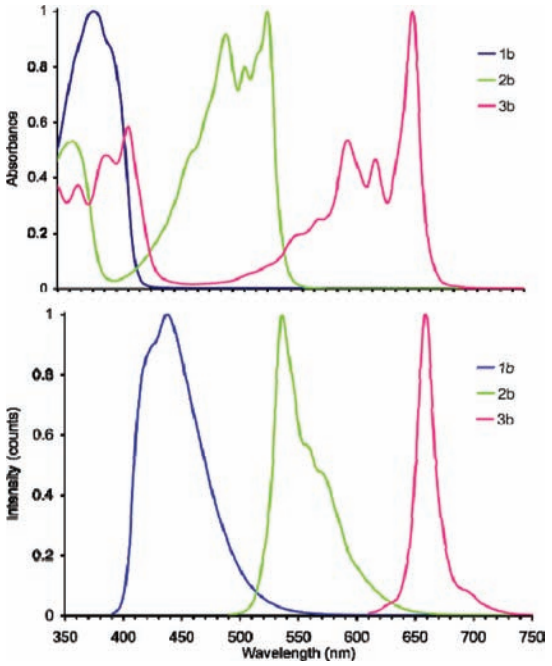


Figure 1. Normalized absorption (top) and emission spectra (bottom) of **1b**−**3b** in hexanes.

The UV−vis and emission spectra (Figure 1) of **1b**−**3b** in hexane solution provide insight into the electronic structure of the molecules. Compound **1b** has a broad absorption with a maximum at 382 nm with a comparably broad emission peaking at 439 nm. In the case of **2b**, an absorption spectrum with significant vibronic structure ($\lambda_{\max} = 530$ nm) and an emission peaking at 538 nm is observed.[15]

In the case of **3b**, the absorption is also structured with the peak absorbance at 655 nm, while the emission is centered at 659 nm and strongly 0−0 peaked. As expected, the Stokes shifts for **2** and **3** are small, due to the rigidity of the molecules; however, the small spectral bandwidth and the occurrence of some vibronic structure in the emission spectra are unusual when compared to the spectra of

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(14) Synthesis of 4,11-Bis(triisopropylsilylethynyl)anthra[2,3-*c*]-[1,2,5]thiadiazole, **3c**. To an oven-dried Schlenk flask were added triisopropylsilylacetylene (2.10 mL, 9.36 mmol) and dry THF (10 mL), followed by 1.6 M *n*-butyllithium in hexane (4.69 mL, 7.49 mmol) at 0 °C. The solution was stirred at room temperature for 1 h, and then compound **9** (0.420 g, 1.58 mmol) was added to the solution. The mixture was stirred at ambient temperature for 12 h and then quenched with wet ethyl ether. After evaporation of the solvent, the residue was filtered over silica gel using hexane/ethyl acetate (v/v, 5:1) to yield the corresponding diol. After the solvent was evaporated, the crude diol was, without further characterization, suspended in acetic acid (20 mL) with KI (1.30 g, 7.83 mmol) and NaH_2PO_2 (0.690 g, 7.84 mmol). The mixture was heated to reflux for 30 min. After the mixture was cooled to room temperature, H_2O (100 mL) was added and the aqueous solution was extracted with hexanes (3 × 100 mL). The combined organic layers were dried in vacuo. The solids were further purified by chromatography on silica gel using a hexane/CH_2Cl_2 (v/v, 10:1) solvent mixture. Compound **3c** (0.867 g, 92% yield, two steps) was isolated as dark-blue crystals. **3c:** mp = 172−174 °C; IR (KBr, cm^{-1}) 2941, 2863, 2122, 1526, 1462, 1373, 1069, 1013, 993, 879, 734, 672; ^{1}H NMR (δ in $CDCl_3$) 9.23 (s, 2H), 7.93 (dd, 2H, $^3J_{hh} = 6.5$ Hz, $^4J_{hh} = 3.5$ Hz), 7.42 (dd, 2H $^3J_{hh} = 6.5$ Hz, $^4J_{hh} = 3.5$ Hz), 1.32−1.31 (m, 42H); ^{13}C NMR (δ in $CDCl_3$) 152.9, 133.0, 132.6, 128.5, 126.8, 126.8, 112.3, 108.9, 102.6, 18.9, 11.5; accurate mass for $C_{36}H_{48}N_2SSi_2$ *m/e* = 596.30700 [M^+], calcd *m/e* = 596.30768.

diethynylacenes of analogous structure. The experimental transition energies closely follow the trends observed in the values of the HOMO−LUMO gap obtained from quantum-chemical DFT calculations (Table 1); the calculations also show that the HOMO energy is increased and the LUMO energy is decreased upon increasing the size of the acenothiadiazoles.

Table 1. Calculated and Measured HOMO−LUMO Gaps

compd	HOMO^a (eV)	LUMO^a (eV)	gap (10^3 cm^{-1}; eV) calcd	gap (10^3 cm^{-1}; eV) exp^b
1a	−5.90	−2.67	26.1; 3.23	24.4; 3.03 ^{c}
2a	−5.38	−2.98	19.4; 2.40	18.7; 2.31
3a	−5.03	−3.16	15.1; 1.87	15.2; 1.88

^{a} Obtained by SPARTAN 08/windows using the B3LYP method with the 6-31G**//6-31G** basis set. ^{b} Gap obtained from the λ_{max} of absorption. ^{c} Gap obtained from intersection of absorption and emission curves.

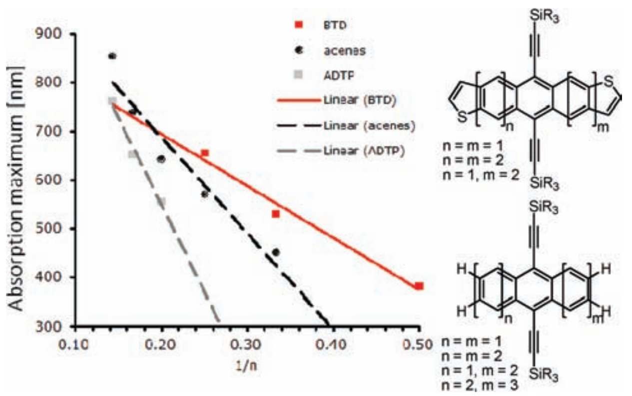

Figure 2. Absorption maxima versus 1/*n*, with *n* being the number of rings in a specific class of compounds. BTD: acenothiadiazoles.[1−3] Acenes: 9,10-bis(trimethylsilylethynyl)-anthracene, bis(trialkylsilylethynyl)tetracene, -pentacene, -hexacene, and -heptacene.[5,7] ADTP: bis(trialkylsilylethynyl)acenodithiophenes.[13]

Figure 2 shows the dependence of the absorption maxima, λ_{max}, of **1**−**3** on the number of rings in comparison to the dependencies seen for Anthony's dialkynylacenes[5,7] and dialkynylacenodithiophenes.[15] Naphthothiadiazole **2**, which contains a total of three rings, displays optical properties similar to those of the four-ring tetracenes and the five-ring acenodithiophenes, while **3** has an absorption maximum similar to that of a dialkynylated pentacene and the six-ring-based acenodithiophenes. The reason for the increased auxochromic effect of the annulated thiadiazole ring in comparison to a benzene or thiophene might be the enforced quinoidal character of **3**, resulting in an absence of resonance structures that one can draw for **3** that contain an aromatic sextet. A similar observation of red-shifted electronic transitions has been made by Wudl et al. in the case of the isoquinolones.[16]

The ease of oxidation and reduction of **3** was investigated using cyclic voltammetry of **3c** in dichloromethane/0.1 M $^{n}Bu_4NPF_6$; one reversible oxidation (+0.74 V vs ferrocene) and two reversible reductions (−1.18 V, −1.78 V) were observed. The electrochemical "band gap" of 1.92 eV (≡ 646 nm) is in surprisingly good agreement with the UV−vis data and with the HOMO−LUMO gap obtained from quantum chemical calculations. The reduction potential of **3c** is similar to that of the four-ring dialkynyldiazatetracenes (−1.2 V)[12] and close to those for perylene diimides (ca. −1.0 V), which are a well-established class of materials for n-channel field-effect transistors,[17] indicating the possibility of electron injection into **3**. On the other hand, a large barrier to hole injection from typical electrode materials is anticipated.

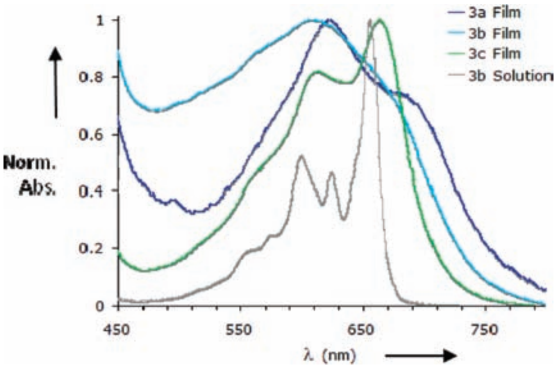

Figure 3. Normalized absorption spectrum of **3b** in hexanes and of **3a**−**c** in thin films.

The thin-film UV−vis spectra of **3a**−**c** are shown in Figure 3. Films of **3c** are optically clear. Therefore, we assume that they are amorphous. The spectrum of **3c** is somewhat broadened with its absorption maximum red-shifted by ca. 10 nm relative to its solution spectrum. The film spectrum of **3c** retains a similar vibronic envelope, suggesting relatively minor intermolecular interations in the solid state. Solutions of **3c** do not show aggregation effects even at high dye concentrations (see the Supporting Information). On the other hand, films of **3a** and **3b**, which are microcrystalline, exhibit spectra different from those seen in solution, being much broader with the strongest feature blue-shifted relative to the solution maximum and with a weaker low energy feature. In both cases, the spectra suggest significant intermolecular interaction of the π-systems in the solid state and the occurrence of J- and/or H-aggregates. Single-crystal X-ray analyses of **3a** and **3b** (Figures 4 and 5) reveal π-stacking columns with intrastack intermolecular distances of 3.4 Å; this type of

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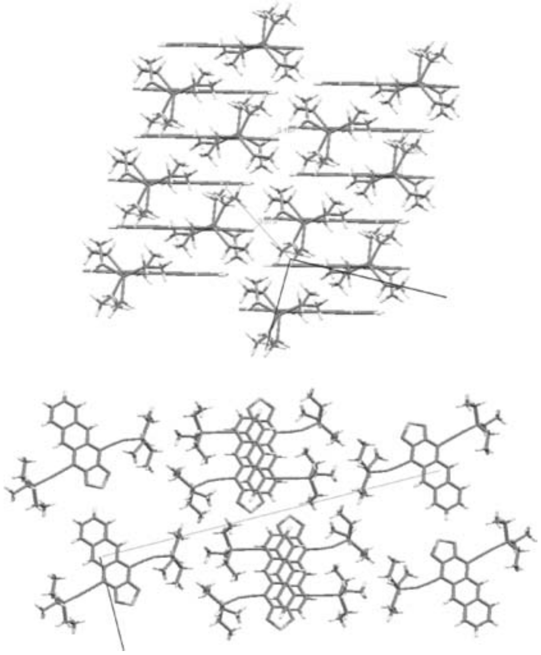

Figure 4. Packing of **3b**. The molecules pack in stacks that are connected by supramolecular S···N interactions in which the intrastack π-stacking distance in a single column is 3.4 Å.

intermolecular interaction is similar to that of H-aggregates and is consistent with blue-shifts of the most intense features in the UV−vis spectra. In the case of **3a**, the π-systems of adjacent columns are isolated, while in **3b** adjacent columns interact via S···N interactions. Noticeable is the absence of intercolumn $\pi-\pi$ interactions, a hallmark of the diethynylacenes[15] and -heteroacenes.[12]

In conclusion, we have prepared a series of acenothiadiazoles, of which the three largest members **3a**−**c** were hitherto unknown. In relation to their size, **1**−**3** display small band gaps; apparently, one can substitute two fused benzene rings for one thiadiazole ring and achieve the same effect with respect to lowering the HOMO−LUMO gap. We are currently investigating the formation and structure of thin films of **3a**−**c** on SiO_2 surfaces and the synthesis of larger congeners of **3**.

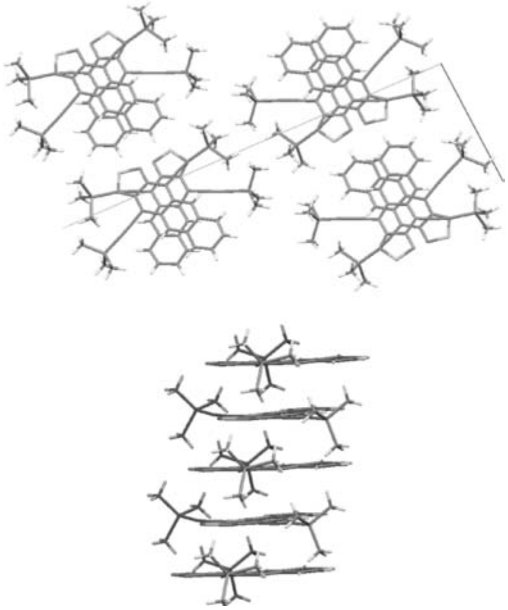

Figure 5. Packing of **3a**. Isolated columns form with an intrastack distance of 3.4 Å between the nearest neighbors.

Acknowledgment. We thank the National Science Foundation for generous funding (NSF-CHE 0548423 U.H.F.B., A.L.A., N.J.B., S.M.B.; DMR-0120967 S.R.M., S.B.).

Supporting Information Available: Experimental procedures, spectral data of all new compounds, and crystal structure data of **3a** and **3b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OL902156X