ORGANIC LETTERS

2010
Vol. 12, No. 9
2060−2063

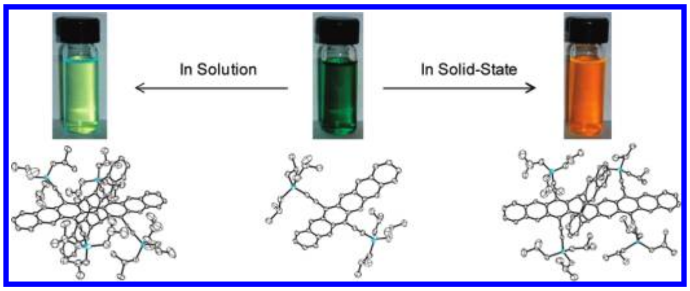
Synthesis and Stability of Soluble Hexacenes

Balaji Purushothaman, Sean R. Parkin, and John E. Anthony*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055
anthony@uky.edu

Received March 7, 2010

ABSTRACT



The synthesis of new silylethyne-substituted hexacene derivatives to investigate their solubility, stability, and π-stacking is reported. It was found that "butterfly" dimerization, rather than photooxidation, is the dominant decomposition pathway for these molecules and that stability can be enhanced by functionalization to prevent close contact between specific regions of the aromatic core. Dimerization regioselectivity can be altered by suitable engineering of the solid-state arrangement of the chromophores.

Electronic devices based on organic materials have been an area of intense research for the past few decades.[1] Among the organic materials used in these devices, acene-based semiconductors have been widely studied.[2] Pentacene, the largest sufficiently stable acene for device studies, has shown charge carrier mobility greater than 3 $cm^2\ V^{-1}\ s^{-1}$ and is regarded as a benchmark among organic semiconductors.[3] Acenes larger than pentacene have been of great interest due to their predicted lower reorganization energy,[4] potential higher charge carrier mobility,[5] and smaller band gap.[6] However, such an improvement in electronic properties is concomitant with decreasing stability and solubility in organic solvents, which in turn hampers the synthesis and application of these interesting molecules.[7] A thorough understanding of the reactivity of these materials will be required to design new functional compounds with stability and solubility sufficient for detailed device studies.

The decomposition pathways for acenes are typically assumed to proceed through photoinduced endoperoxide formation, with subsequent oxidation to the corresponding quinone,[8] or through a "butterfly" dimerization of the aromatic rings.[9] In pentacene, endoproxide formation is assumed to dominate in the solid state, whereas dimerization is the main decomposition pathway in solution.[9] Unsubstituted higher acenes such as hexacene and heptacene have only been synthesized successfully by photodecarbonylation of soluble diketone precursors in a polymer matrix, where such decomposition pathways can be retarded.[10]

Among the recent functionalization strategies employed for the synthesis of soluble and stable acene derivatives, the

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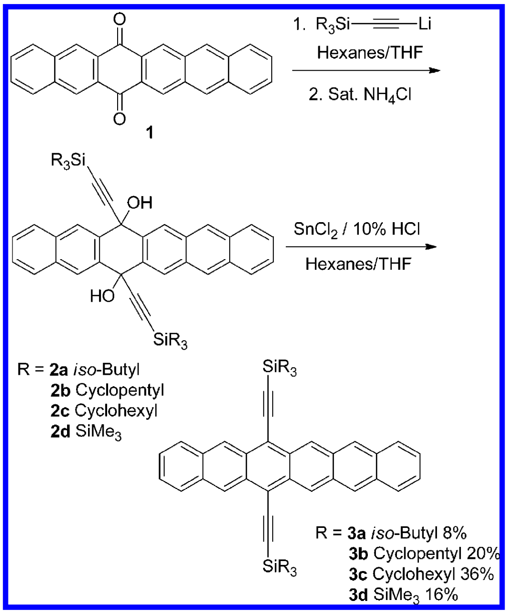
peri-functionalization approach utilizing trialkylsilylethynyl groups has been widely used to develop organic electronic materials.[11] The improved solubility, stability, and induced π-stacking of pentacene derivatives have paved the way for the synthesis of stable and soluble higher acenes.[12] However, in order to stabilize these highly reactive materials, significantly bulkier substituents had to be used to prevent Diels–Alder reaction between the alkyne substituent of one molecule and the reactive acene chromophore of another.[13] Hence bulky tri-*tert*-butylsiliylethynyl (TTBS) groups were used to stabilize hexacene, whereas for heptacene, a larger tris(trimethylsilyl)silylethynyl (TTMSS) substituent had to be employed. In a recent report, Wudl and co-workers have reported the synthesis of a stable tetraphenyl heptacene derivative using a tri-isopropylsilylethynyl substituent. The phenyl groups are effective in preventing the aromatic cores from reacting with each other or with the alkyne, and as a result the smaller alkyne substituent could be used.[14] Photoxidation of the aromatic core was reported to be the major decomposition process for this heptacene derivative.

Although TTBS hexacene exhibits reasonable stability in solution, the poor solubility in solvents such as toluene and chlorobenzene has prevented the measurement of its transport properties in organic thin film transistors (OTFTs). A major objective of the present work is to facilitate study of these materials by improving the solubility and π-stacking of these peri-functionalized hexacenes by changing the alkyl substituents on silicon. Concurrently, we planned to study the decomposition pathways of these molecules, both in solution and the solid state, to gain a better understanding of reactivity for the design of effective functionalization strategies.

For our studies, we surveyed a variety of branched alkyl- or cycloalkyl-substituted silyl acetylene substituents, such as tri-isobutylsilylethynyl (TIBS), tricyclopentylsilylethynyl (TCPS), tricyclohexylsilylethynyl (TCHS), and TTMSS. 6,15-Hexacenequinone (**1**) was converted to a series of diethynyl diols (**2**) by treatment with excess acetylide. The resulting diols were then converted to the desired hexacenes by treatment with a saturated solution of tin(II) chloride in 10% HCl. Purification of the crude hexacenes by silica gel chromatography followed by recrystallization gave dark green hexacene crystals in yields ranging from 8% to 36%, depending on the substituent. Compared to phenyl-substituted hexacenes,[10a] these materials exhibit significant persistence both in solution and the solid state. These materials showed higher solubility than the TTBS derivative, and all of them could be prepared as 1 wt % solutions in toluene.

Scheme 1. Synthesis of 6,15-Bis(trialkylsilylethynyl)hexacene



The dark green crystals of these compounds obtained from recrystallization were suitable for single-crystal X-ray diffraction analysis. Like TTBS hexacene,[12] TCPS hexacene (**3b**) exhibited a two-dimensional π-stacking motif with a close contact of 3.42 Å between the aromatic faces (Figure 1). By changing the substituent to the smaller TIBS group (**3a**) the π-stacking motif changed to a one-dimensional sandwich herringbone packing, and larger TCHS or TTMSS substituents (**3c**) or (**3d**) led to one-dimensional π-stacked arrangements with close contacts of 3.3 and 3.36 Å respectively (Figure 1). The change in packing motif with the size of the trialkylsilyl substituent is in accordance with the functionalization model developed for controlling π-stacking in pentacene.[11a] All of these hexacene derivatives exhibit significant bending of alkyne substituents ($\mathrm{C_{Ar}{-}C_{sp}{-}C_{sp}} \approx 176{-}178^\circ$ and $\mathrm{C_{sp}{-}C_{sp}{-}Si} \approx 169{-}179^\circ$) induced by crystal packing effects. However, the distortion is not as dramatic as seen with TTBS hexacene ($\mathrm{C_{Ar}{-}C_{sp}{-}C_{sp}} \approx 176^\circ$ and 173° and $\mathrm{C_{sp}{-}C_{sp}{-}Si} = 169^\circ$ and 174°) and is typical of alkynes having large substituents.[11a,12,13] Another important observation is the twisting of the acene core (torsion angle 13.4°) of TCHS hexacene (**3c**) in comparison to all other derivatives (<5°), which likely arises to alleviate strain in crystal packing due to the bulky cyclohexyl substituents.

Our study of the decomposition pathways of hexacenes began during the recrystallization of TIBS hexacene **3a** under ambient laboratory lighting, where a small amount of yellow crystals formed along with the green hexacene. Single-crystal X-ray diffraction analysis of this byproduct showed that this compound was a symmetrical dimer formed between the reactive C7 and C14 carbons of two hexacene molecules (**4**, Figure 2). Unlike the two dimer products proposed for TIPS pentacene decomposition,[15] only the centrosymmetric dimer product was observed, as the planosymmetric product is significantly more sterically hindered.

When pure crystals of TIBS hexacene were kept in air in the dark, they slowly (~1 month) turned from crystalline

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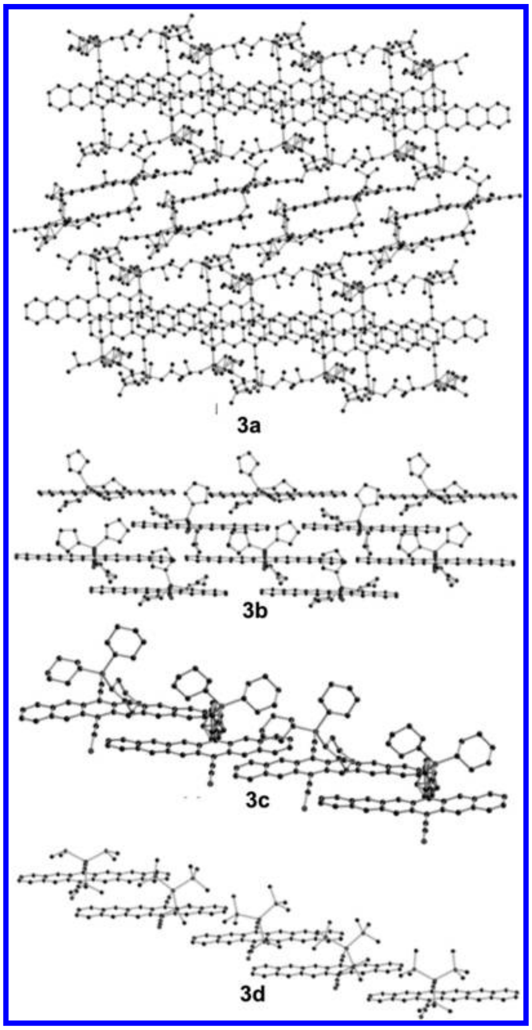

Figure 1. Crystal packing arrangement of hexacenes **3a**−**d** (front-most trialkylsilyl groups removed for clarity).

green needles into a reddish brown powder. Purification of this powder by silica gel chromatogrphiy to remove unreacted hexacene followed by recrystallization and single crystal X-ray diffraction analysis showed that this material was another dimerization product formed between the C7 and C14 carbons of one hexacene molecule with the C8 and C13 carbons of another to give a dimer with tetracene and anthracene chromophores (**5**, Figure 2). The change in the regiochemistry of dimerization arises simply from the orientation of the chromophores in the solid state.

Another byproduct observed during the synthesis of hexacene **3a** was initially isolated as a deep green material that turned yellow-orange during chromatographic purification on silica gel. X-ray crystallographic analysis of this purified material showed that initial decomposition arose from a Diels−Alder reaction of the hexacene core with the alkyne substituent of another molecule, to yield the initially observed green species, followed by endoperoxide formation during chromatography (**6**, Figure 2), which bleached the remaining hexacene chromophore. Thus, the only photo-oxidation product observed in this series of hexacenes arose from reaction on a chromophore where one of the alkyne substituents had been compromized. Noteworthy for these dimeric products are their mass spectra: *all* of these well-characterized decomposition products showed only signals for pristine monomer **3a** when subjected to laser-desorption ionization mass spectrometry (LDI-MS, see Figure S6 in Supporting Information). This result suggests that LDI-MS may not be a viable method to determine structure or purity of the larger acenes.

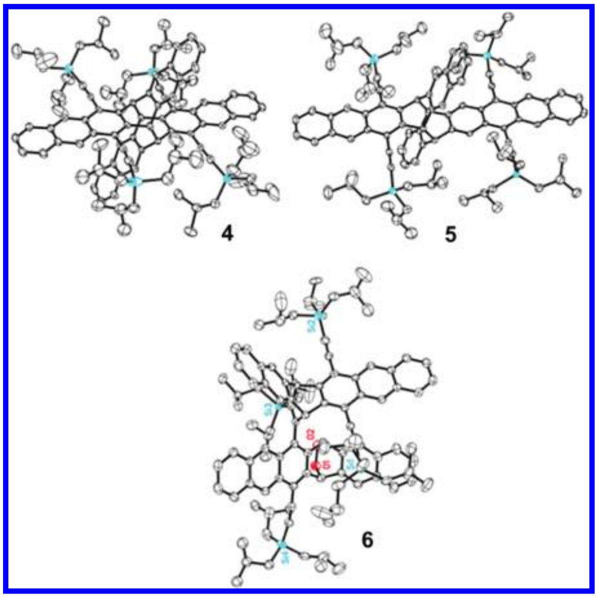

Figure 2. Thermal ellipsoid plots of symmetrical dimer (**4**), offset dimer (**5**), and alkyne dimer−endoperoxide (**6**).

Differential pulse voltammetry was performed on all of the hexacene derivatives to determine the oxidation and reduction potentials of these molecules (ferrocene used as internal standard, Table 1). TTMSS hexacene (**3d**) has the lowest oxidation potential compared to the other derivatives due to the electropositive tris(trimethylsilyl)silylethynyl group. The lower energy gap is also evident from a ∼13 nm red shift in toluene compared to other derivatives.

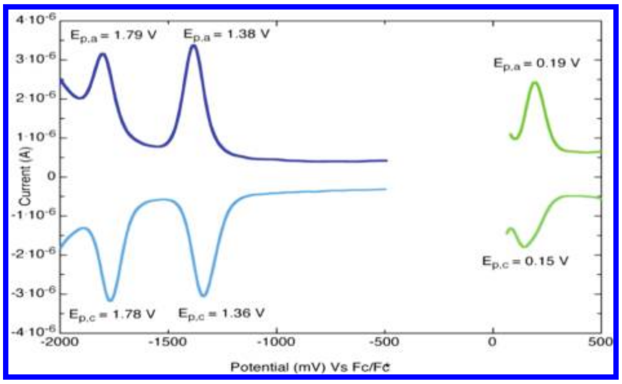

Figure 3. Differential pulse voltammetry of TCPS hexacene.

Table 1. Electrochemical Data and Solution Half-Life of **3a−d**

acene	E_{ox} (mV)	E_{red} (mV)	HOMO (eV)	LUMO (eV)	$t_{1/2}$ (min)
TIPS pentacene					296
3a	181	−1376	−4.98	−3.42	93
3b	172	−1370	−4.97	−3.43	38
3c	198	−1370	−5.00	−3.43	45
3d	123	−1421	−4.92	−3.38	19

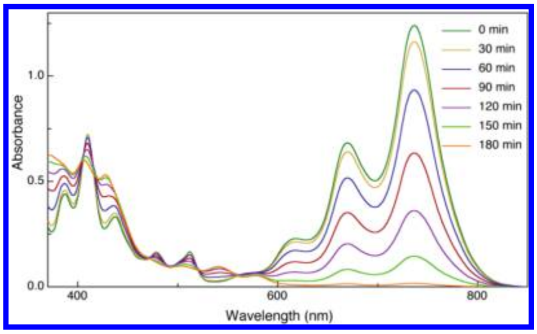

Figure 4. UV−vis spectra of **3a** recorded at regular interval during exposure to light.

To study their relative stabilities in solution, all of these hexacene derivatives were subjected to UV−vis stability studies (Table 1) and compared with TIPS pentacene. Disappearance of the long-wavelength hexacene absorptions is coupled with the appearance of a strong absorption at 430 nm, characteristic of an anthracene chromophore, and weak absorbances at ∼550 nm, characteristic of tetracene (Figure 4). Comparison of the decomposition UV−vis spectrum with absorption spectra of **4** and **5** (Figure S4 in Supporting Information) suggests that these are indeed the major decomposition products in solutions illuminated in air. Similar decomposition products were observed for hexacene derivatives **3b−d** (Figures S1−S3 in Supporting Information). It is noteworthy that TTMSS hexacene **3d**, which was expected to have higher stability due to the effectiveness of the bulky substituents in preventing dimerization, had a half-life of only 19 min in solution (Figure S3 in Supporting Information). This lower stability may be due to the photolysis of the silane into hexamethyldisilane and a radical byproduct,[16] which effectively reduces the size of the silyl group and hence its efficacy in stabilizing the hexacene.

A ^{1}H NMR stability study was also performed on TIBS hexacene **3a** in deuterated benzene at a concentration of 1 wt % (Figure S5 in Supporting Information). The ^{1}H NMR spectra of both N_2- and O_2-purged solutions before and after exposure to bright light again showed that dimerization, rather than oxidation, was the dominant degradation pathway in these silylethyne-functionalized hexacenes. These results suggest that, unlike most other acene derivatives, the electronic properties of silylethyne-substituted acenes need not be tuned to prevent oxidation. Instead, identifying approaches to prevent dimerization may be the best route to stabilize these materials.

In conclusion, we have presented a series of soluble hexacene derivatives using our peri-functionalization approach to study the modes of decomposition of these materials. In contrast to other reports, photooxidation was not found to be a significant decomposition pathway[17] and was only observed in materials where one of the alkyne substituents had been compromised. Instead, dimerization was the most common decomposition pathway. We have developed materials with reasonable solution and solid-state lifetimes, and with suitable precautions to minimize exposure to light, studies of the thin film properties of these materials are currently underway.

Acknowledgment. The authors thank the National Science Foundation (CHE 0749473) for support of this project.

Supporting Information Available: Experimental details and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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