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1,3,5 / 2,4,6-Differentiated Hexaalkynylbenzenes: Absorption and Fluorescence Properties of a D_{3h}-Symmetric Donor-Substituted System

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Abstract: The synthesis of 1,3,5 / 2,4,6 differentially functionalized hexaethynylbenzene derivatives is described. Interesting solvatochromic behavior was observed for **9b** in the absorption and emission spectra. A twisted intramolecular charge transfer (TICT) state in polar solvents appears to be involved.
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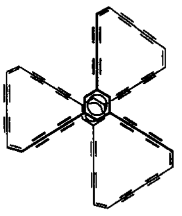
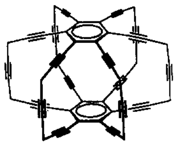
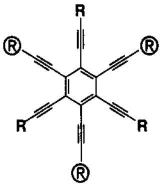
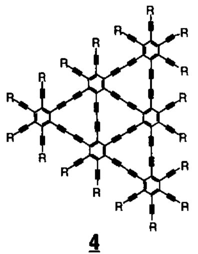
Highly unsaturated sixty-carbon macrocycles such as **1** and **2** can be regarded as potential precursors of buckminsterfullerene (C_{60}) and its endohedral metal complexes.[1] While our preparation of **1** has recently been reported,[1a] the approach to cyclophanes of type **2**, based on the hexaethynylbenzene (HEB) core, has necessitated the development of a method for the preparation of selectively functionalized HEB derivatives such as **3**.


1 ($C_{60}H_{18}$)


2 ($C_{60}H_{24}$)



3 (D_{3h})



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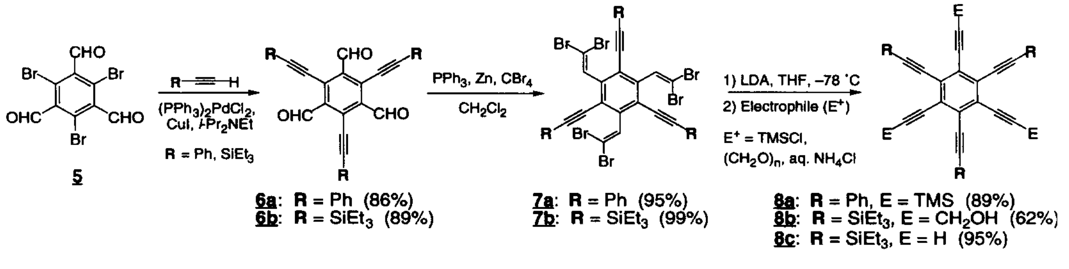
In this paper, we report a versatile method for the preparation of 1,3,5 / 2,4,6 differentially functionalized hexaethynylbenzenes **3** and the interesting absorption and fluorescence properties of the electron rich system **9b**. Beyond the scope of fullerene total synthesis, hexaalkynylbenzenes can be used in the stepwise construction of molecular pieces (e.g. **4**) of hypothetical 2-dimensional carbon allotropes such as graphyne or the corresponding diynyl system.[2] Furthermore, D_{3h}-symmetric hexaalkynylbenzene derivatives (**3**) could lead to new discotic

Scheme 1.



liquid crystals,[3] while those substituted at the 1,3,5 and 2,4,6-positions, respectively, with electron-donating and electron-withdrawing substituents may exhibit strong second-order nonlinear optical properties of multipolar origin.[4]

The synthesis of hexaalkynylbenzenes currently available involves a six-fold palladium-catalyzed ethynylation of hexabromobenzene, leading to a D_{6h} derivative **3** (**R** = ®).[5] We attempted to use the selective alkynylation of 1,3,5-tribromo-2,4,6-triiodobenzene in a similar fashion to prepare the desired D_{3h} derivatives **3**.[6] Unfortunately, the conditions required to dissolve even small amounts of this poorly soluble compound (Et_3N, $(PPh_3)_2PdCl_2$, CuI, refluxing toluene) precluded any type of selective alkynylation. However, we found the synthetic methodology shown in Scheme 1 to be a remarkably efficient route to the desired compounds, considering that 3-fold conversions are carried throughout this sequence. Starting from mesitylene, the versatile trialdehyde **5** was prepared in five steps in 36% overall yield.[7] Facile Pd-catalyzed coupling of aldehyde **5** with a silyl or aryl alkyne provided the triethynyl trialdehydes **6a** and **6b**, which were readily converted into the respective hexaethynyl compounds by application of the Corey-Fuchs dibromo-olefination followed by treatment with LDA.[8]

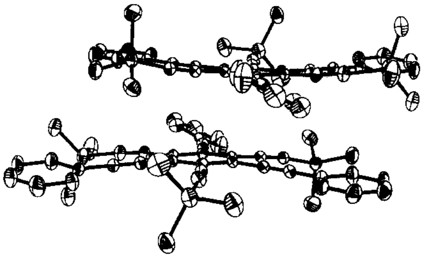
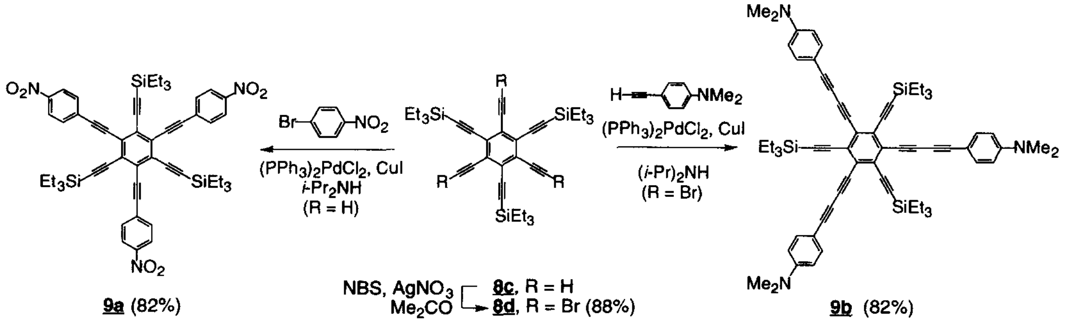


Figure 1. Pair of compound **8a** in the X-ray crystal structure.

The lithiated triphenyl HEB prepared by treatment of **7a** with LDA was quenched with Me_3SiCl to yield the stable silylated derivative **8a** (Scheme 1). The X-ray structural analysis of this compound is presented in Figure 1.[9] Interestingly, the hexaethynylbenzene core of this derivative is bent out of planarity (within 0.19 Å) by crystal packing forces. The molecule crystallizes as pairs of associated molecules; the central benzene ring of each member of the pair is in close contact with the other (3.532 Å closest C-C distance), forcing the peripheral alkynes to "bow" outward, forming a cup-shaped system. Note that the peripheral phenyl rings rotate out of plane in a complementary fashion to accommodate two of the TMS-methyl groups of the partner molecule. Contrary to **8a**, hexakis[(trimethylsilyl)ethynyl]benzene,[5a] which is also distorted from planarity but with alternating up-down alkynyl units, does not pack in pairs in the crystal.

From the lithiated triethylsilyl derivative prepared from **7b**, we could easily prepare the tris(propargyl alcohol) **8b** and the surprisingly stable terminal alkyne **8c** (Scheme 1). The remarkable chemical stability of **8c** allowed further derivatization to the stable, *electron-poor*, tris(nitrophenyl) derivative **9a** in good yield by using standard Sonogashira coupling of the terminal acetylene moieties with 1-bromo-4-nitrobenzene (Scheme 2).

Scheme 2.



The terminal acetylene moieties in **8c** were brominated with NBS to afford the tris(bromoalkyne) **8d**.[10] X-ray analysis of **8d** reveals that this compound is planar (Figure 2).[11] The exceptionally large steric hindrance around the bromoalkyne units, provided by the TES groups on the adjacent alkyne moieties, allowed us to perform an ***unusually selective*** palladium-catalyzed alkyne cross-coupling reaction between **8d** and 4-dimethylaminophenylacetylene to form the tris(dimethylamino) compound **9b** in high yield (Scheme 2). The cross-coupling reaction at two sp-carbon centers under Sonogashira or Stille conditions is notoriously unselective, usually affording a statistical mixture of products.[12] The reason for the high selectivity observed with **8d** lies in the fact that the axial sites of the square-planar palladium(II) intermediate (**10**) are completely shielded from the competing approach of another acetylide unit (e.g. R-C≡C-Cu) to form a Pd(IV) complex,[13] which would reductively eliminate to a symmetrical alkyne (R-C≡C-C≡C-R). We are currently investigating this principle in the design of new palladium ligands to achieve the selective Pd-catalyzed cross-coupling of alkynes.

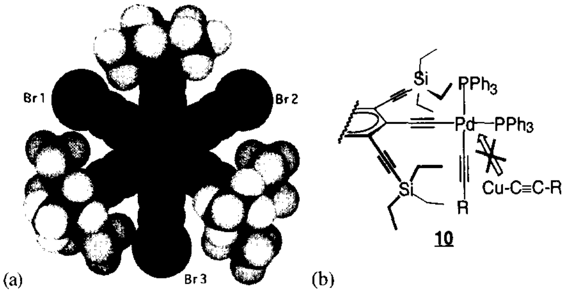


Figure 2. (a) Space-filling model of the X-ray structure of **8d**. (b) structure of Pd(II) intermediate **10** in the reaction of **8d** to **9b**.

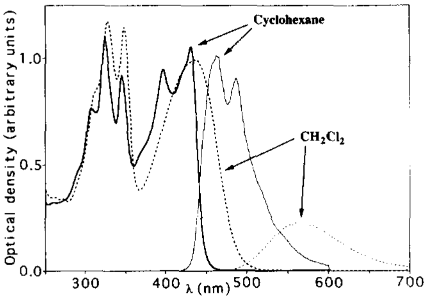


Figure 3. UV-vis absorption (solid lines) and fluorescence spectra (dashed lines) of **9b** in cyclohexane and CH_2Cl_2.

All of the hexaethynylbenzene derivatives reported here, except for **8d** and **9a**, are highly fluorescent. However, the optical properties of the dimethylamino derivative **9b** are particularly intriguing. The UV-vis absorption spectrum of **9b** shows strong solvatochromic behavior – the spectrum in cyclohexane is markedly different from spectra taken in more polar solvents such as CH_2Cl_2 (Figure 3), and the maximum absorption proceeds to longer wavelengths as solvent polarity is increased up to 2-methyltetrahydrofuran (MTHF) and acetonitrile (not shown).

This solvatochromism is carried over into the fluorescence spectra – the emission band is much more resolved and comes at a lower wavelength in nonpolar solvents. This suggests that an intramolecular charge-transfer interaction occurs between the electron-rich dimethylaminophenyl moieties situated on the perimeter of the molecule and the electron-accepting hexaethynylbenzene core of **9b**.[14] Furthermore, the fluorescence occurs at higher energy in a MTHF glass at 77 K than in the solution state at ambient temperature. This is a strong indication that a twisted intramolecular charge transfer (TICT) state is involved in more polar solvents.[15]

Acknowledgment. This work was supported by the Office of Naval Research, and by Beckman and NSF Young Investigator Awards to Y.R.

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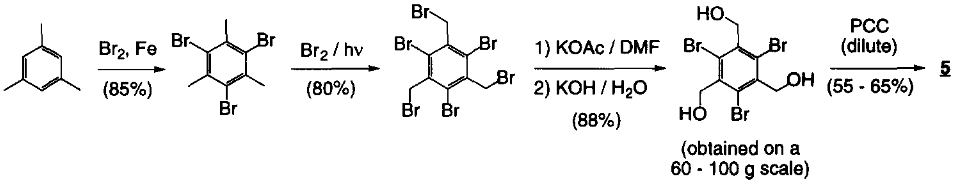
(7) Tribromotrialdehyde **5** was prepared in the following way:



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(9) Compound **8a** ($C_{45}H_{42}Si_3$; M_r = 667.08) crystallized in the monoclinic space group $P2_1/a$ with cell dimensions of a = 14.909(9) Å, b = 18.88(1) Å, and c = 16.00(1) Å; β = 110.55(1)°, V = 4219(5) Å^3, and an occupation of Z = 4 in the unit cell. Data were collected at 20 °C on a Syntex (Crystal Logic) diffractometer using graphite-monochromated Cu K_α radiation, to a maximum 2θ = 115°, giving 6253 total reflections; the structure was solved by direct methods (SHELX86) and refined with full matrix least squares, yielding R = 0.049, R_w = 0.059 for 3309 independent reflections with $I > 3\sigma(I)$.

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(11) Compound **8d** ($C_{36}H_{45}Br_3Si_3$; M_r = 801.72) crystallized in the monoclinic space group C2/c with cell dimensions of a = 33.10(2) Å, b = 17.39(1) Å, and c = 14.848(9) Å; β = 112.66(2)°, V = 7888(9) Å^3, and an occupation of Z = 8 in the unit cell. Data were collected at 156 K on a Picker (Crystal Logic) diffractometer using graphite-monochromated Mo K_α radiation, to a maximum 2θ = 50°, giving 7326 total reflections; the structure was solved by direct methods (SHELX86) and refined with full matrix least squares, yielding R = 0.075, R_w = 0.092 for 2908 independent reflections with $F > 6\sigma(F)$. Some of the disordered ethyl carbons were refined at two alternate positions with geometrical constraints.

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(14) A low first reduction wave at −1.6 V (*vs* Ag/AgCl, CH_2Cl_2, 0.1 M TBAP) is observed for **8a**, indicating mild electron accepting character of the HEB system.

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