J. Org. Chem. **1994,** *59,* 2927–2929 **2927**

Synthesis and Characterization of Diethynylmethanobuckminsterfullerene, a Building Block for Macrocyclic and Polymeric Carbon Allotropes

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Received March 8, 1994[●]

Summary: Diethynylmethanobuckminsterfullerene (**1a** and ^{13}C-labeled **1b**) has been prepared by reaction of the lithium salt of 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-one (*p*-toluenesulfonyl)hydrazone (**5a/b**) with C_{60} followed by desilylation and characterized by NMR, IR, UV–vis, and CI-TQMS spectroscopies.

The functionalization chemistry of buckminsterfullerene (C_{60}) has recently become the focus of ardent research,[1] especially since it was found that the water-soluble derivatives[2–4] show biologically-relevant properties such as HIV-1 protease inhibition[5] and cleavage of DNA by sensitized generation of singlet oxygen.[6,7] The preparation of new materials based on C_{60}-derivatives presents a tremendous potential that should reflect the rich chemistry and physics demonstrated by C_{60} itself, in particular superconductivity,[8] ferromagnetism,[9] and nonlinear optical behavior.[10] Diarylmethanobuckminsterfullerenes have been converted to polyesters and polyurethanes with "pendant chain" structures retaining the redox and electronic properties of the monomeric fullerenes and to fullerene-bound dendrimers.[11,12] We have recently prepared a series of "ball-and-chain" donor–acceptor systems based on C_{60} as models in long-range, photoinduced intramolecular electron-transfer processes.[13] In this paper, we report an approach to new macrocyclic and polymeric carbon allotropes that requires diethynylmethanobuckminsterfullerene (**1a**) as a building block (Scheme 1). The conversion of **1a** to the macrocycles **8a–c** should lead to a new class of molecular carbon allotropes combining both cyclo[*n*]carbon (**8a**, $n = 20$, **8b**, $n = 25$, **8c**, $n = 30$) and fullerene frameworks.[14] Such materials may ultimately be converted to single-sized *giant* fullerenes by coalescence reactions.[15] The oxidative coupling of **1a** to afford oligomeric pendant chains (**9**) offers exciting possibilities in the area of organic conductors where doping could be achieved either by electron addition to the C_{60} framework or by electron hole formation in the homoconjugated poly(diyne) chain. In this regard, homoconjugative effects between the π-systems of C_{60} and the alkynyl substituents or between the diyne units through the cyclopropyl Walsh orbitals are particularly interesting to investigate.[16]

Methanobuckminsterfullerenes and fulleroids have been prepared by [3 + 2] dipolar cycloaddition of diazocompounds to C_{60} followed by thermal or photochemical N_2-elimination from the intermediate pyrazolines.[17] The 3-diazo-1,5-bis(trialkylsilyl)-1,4-pentadiynes **6a**,[18] **6b**, and **6c** required for a similar transformation to the protected methanofullerenes **7a–c** were generated *in situ* by thermolysis of the corresponding lithium salts of (*p*-toluenesulfonyl)hydrazones **5a–c** in the presence of C_{60}.[19] The monoadducts **7a** and **7c** were isolated in 33 and 47% yield, respectively, as dark brown crystals. Originally, we used the new (*i*-Pr)$_3$Si-hydrazone **5c** because it was found to be exceptionally stable[20] and convenient to use. However, when we attempted to remove the (*i*-Pr)$_3$Si protecting group of **7c** ($Bu_4N^+F^-$, aqueous THF) instantaneous polymerization or decomposition took place, presumably through nucleophilic addition of fluoride to the C_{60} framework. This side reaction was avoided when the TMS derivative **7a** was deprotected in the presence of sodium tetraborate in aqueous THF,[21] affording compound **1a** in 68% yield.[19] Carbon-13-labeled methanofullerene **7b** was converted directly from **5b** to deprotected diyne **1b** without isolation in a 22% overall yield.

^{1}H-NMR spectroscopy of **1a** displayed only one singlet at 2.87 ppm for the two ethynyl protons, while ^{13}C-labeled **1b** showed one doublet with $^3J_{C-H} = 4.5$ Hz; the ^{13}C-satellites for this peak gave additional coupling constants

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[●] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

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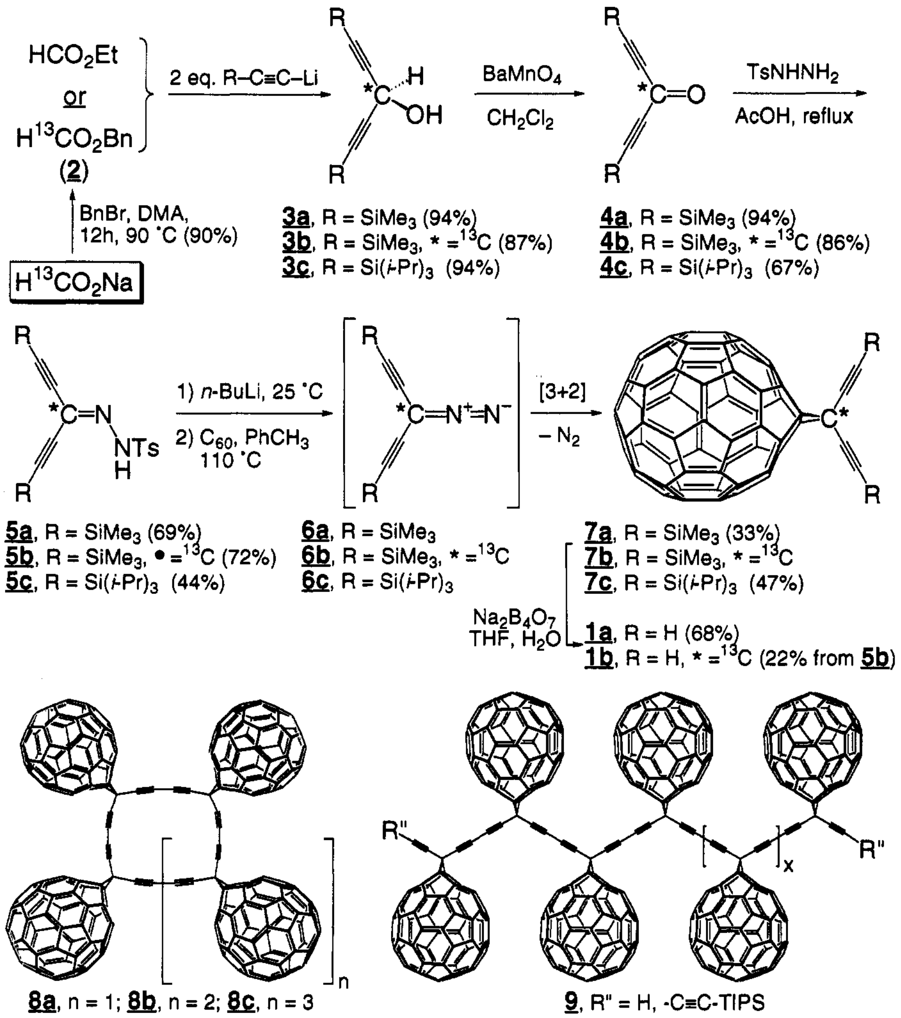
Scheme 1



with ${}^1J_{\mathrm{C\text{-}H}}$ = 256.1 Hz, ${}^2J_{\mathrm{C\text{-}H}}$ = 51.0 Hz. ^{13}C-NMR spectroscopy of the silylated and deprotected compounds **7a**, **7c**, and **1a/b** showed the 17 expected resonances for the fullerene carbons in each compound, indicating that the products are the C_{2v}-symmetric 1,9-methanofullerenes with 6,6-ring junction (Figure 1).[17] The sp^2-hybridized fullerene carbons of **7a**, **7c**, and **1a/b** are observed between 139 and 147 ppm and the sp^3-hybridized carbons at 76.1 ± 0.1 ppm. The methano-bridge carbons for **7a**, **7c**, and **1a/b** appear at 31.2, 29.5, and 26.0 ppm, respectively, while the alkynyl peaks are seen in the expected region (73–100 ppm). In this regard, the methano-carbon of **1a** could not be assigned with certainty due to its very weak absorption and the presence of a difficult to remove alkane impurity in the same region (30.6 ppm, Figure 1A).[22] Thus, the ^{13}C-labeled methanofullerene **1b** was prepared from sodium formate (99 atom % ^{13}C) *via* benzyl formate **2**, alcohol **3b**, and ketone **4b** as shown in Scheme 1. As expected, compound **1b** displays a very large signal for its methano-carbon at 26.0 ppm which is easily seen after just a few accumulations. This should become a clear advantage when **1b** is derivatized further or cyclized to compounds **8a–c**. A gated decoupling experiment confirmed the assignments of the ethynyl and methano-bridge carbons in **1a/b** (Figure 1B). The characteristic ${}^1J_{\mathrm{C\text{-}H}}$ and ${}^2J_{\mathrm{C\text{-}H}}$ doublets for the ethynyl groups in **1a** have coupling constants of 256.3 and 50.8 Hz, respectively, while the methano-bridge carbon in **1b** appears as a triplet with ${}^3J_{\mathrm{C\text{-}H}}$ = 4.6 Hz. In addition, the carbon–carbon coupling constants in **1b** between the ^{13}C-labeled methano-carbon and the alkynyl and C_{60}-sp^3 carbons were obtained: ${}^2J_{\mathrm{C\text{-}C}}$ = 15.1 Hz (${}^{13}CC{\equiv}CH$), ${}^1J_{\mathrm{C\text{-}C}}$ = 18.2 Hz (${}^{13}C$-C_{60} sp^3-C), ${}^1J_{\mathrm{C\text{-}C}}$ = 98.0 Hz (${}^{13}CC{\equiv}CH$) (Figure 1A, inset). These values correlate well with those expected for similar carbon–carbon connections.[23] In the FT-IR spectrum of **1a**, a strong ≡CH stretch is observed at 3295 cm^{-1}, while weak C≡C stretches appear at 2174 and 2124 cm^{-1} (sym and asym). Chemical ionization triple quadrupole mass spectroscopy (CI-TQMS) of **1a** and **1b** gave clear parent ions at m/z = 782 ($C_{65}H_2$) and m/z = 783 ($C_{64}{}^{13}CH_2$), respectively.

The UV–vis absorption spectra of the trialkylsilyl diynes **7a–c** and the diethynyl derivative **1a** (Figure 2) are essentially identical to the parent C_{2v}-methanobuckminsterfullerene ($C_{60}CH_2$).[17c] In particular, the characteristic absorption bands at 256, 330, and 435 nm, as well as the broader absorption centered at 484 nm, are observed. The close similarity of the spectra of the diethynylmethanobuckminsterfullerenes **7a–c** and **1a** with the parent C_{2v}-methanofullerene $C_{60}CH_2$ show that homoconjugative

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[22] Despite our best efforts, we could not obtain a confirming triplet for the methano-carbon of **1a** in several gated decoupling ^{13}C-NMR experiments even in the presence of Cr(acac)$_3$ as a relaxation agent.

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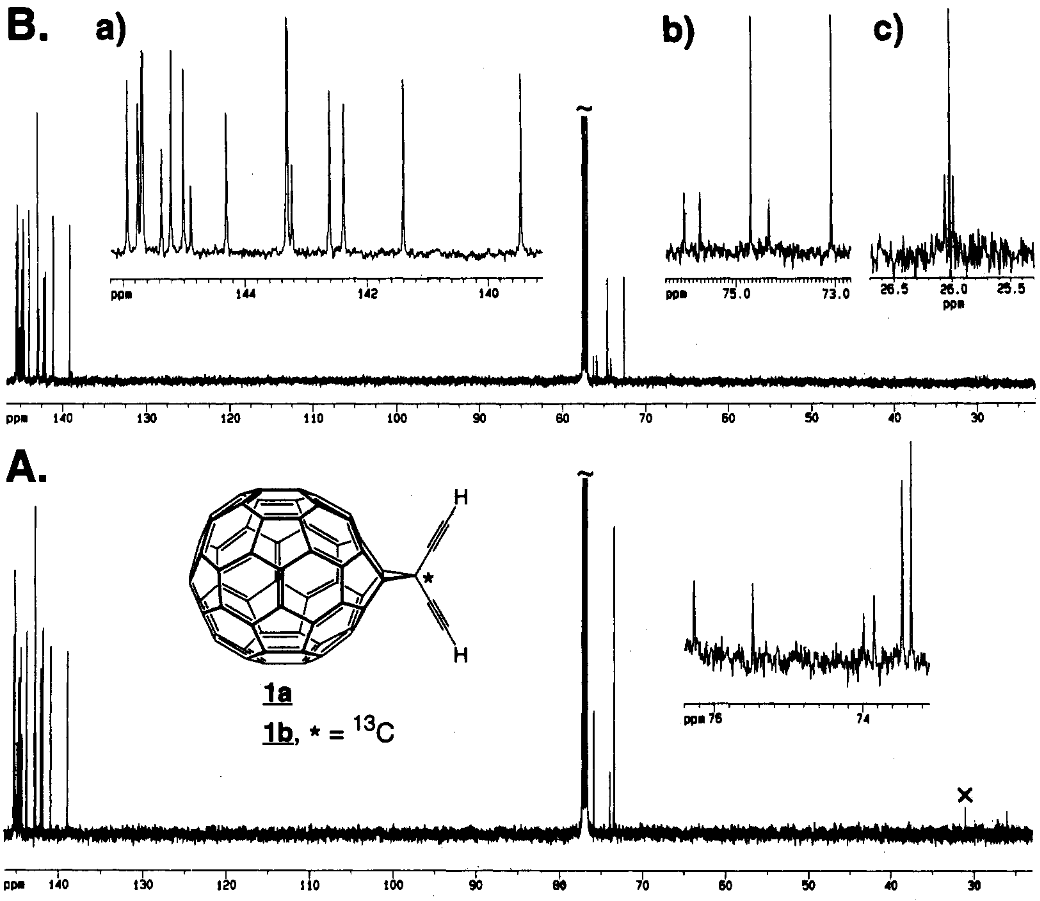

Figure 1. A. Proton-decoupled 125.6-MHz ^{13}C-NMR spectrum of diethynylmethanobuckminsterfullerene (**1a**) in $CS_2/CDCl_3$ (1:1). The peak noted with a × is due to an alkane impurity. The inset shows the expanded spectrum of ^{13}C-labeled compound **1b** between 73.2 and 76.4 ppm; see text for the analysis of coupling constants. B. Gated decoupled ^{13}C-NMR spectrum of **1a**. Inset a shows the expanded spectrum of **1a** in CS_2/C_6D_6 (1:1) where all of the 16 peaks in the fullerene region are well resolved. Inset b shows the expanded spectrum of **1a** between 72.32 and 76.44 ppm and inset c the spectrum of ^{13}C-labeled compound **1b** in the methano carbon region (25.3–26.7 ppm).

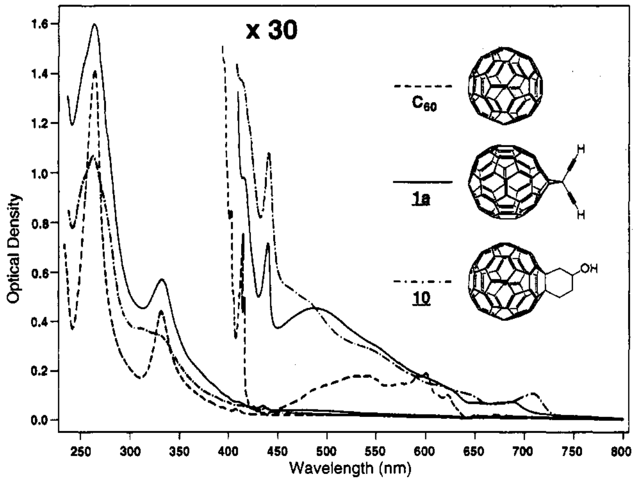

Figure 2. UV–vis absorption spectra of diethynylmethanobuckminsterfullerene (**1a**), buckminsterfullerene (C_{60}), and 1,9-(4-hydroxycyclohexano)buckminsterfullerene (**10**) in CH_2Cl_2: T = 25 °C, d = 1 cm; [C_{60}] = 8.05 × 10^{-6} M (2.82 × 10^{-4} M inset); [**1a**] = 2.21 × 10^{-5} M (6.12 × 10^{-4} M inset); [**10**] = 9.16 × 10^{-6} M (3.61 × 10^{-4} M inset).

effects, if existent, are not observed by this method, as seen previously with other diacetylenic cyclopropanes.[16a] Interestingly, the purple-brown color of **1a**/**b** in solution appears to be intermediate between the deep purple color of C_{60} and the brown color of the unstrained, substituted 1,9-dihydrobuckminsterfullerenes, represented by alcohol **10** (Figure 2). While in the spectrum of **10** there is a steady decrease of absorption from the characteristic peak at 436 nm up to 730 nm, a minimum at 446 nm for **1a**/**b** provides a decrease of absorption in the blue region of the visible spectrum that accounts for its purple hue.

Preliminary oxidative cyclization experiments of dialkyne **1a** to the macrocycles **8a**–**c** using Eglinton–Glaser or Hay coupling conditions gave only intractable material.[24] It is possible that the coupling products are highly insoluble, and a general methodology to render such compounds more handlable by the reversible addition of solubilizing groups to the C_{60}-framework is currently under investigation.

Acknowledgment. We thank the Camille and Henry Dreyfus Foundation and the UCLA College of Letters and Sciences for New Faculty Grants.

Supplementary Material Available: Experimental section, spectroscopic and analytical data for compounds **1a**/**b**, **2**, **3b**/**c**, **4b**/**c**, **5b**/**c**, and **7a**–**c**, and ^{1}H-NMR, ^{13}C-NMR, UV–vis, and mass spectra for representative compounds (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[24] For the oxidative coupling reaction of **1a** with (trimethylsilyl)acetylene under Hay conditions, see: Anderson, H. L.; Faust, R.; Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.*, in press.