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Synthesis and Properties of Dialkyl Derivatives of Di[60]fullerenylbutadiyne and Di[60]fullerenylacetylene: the Buckydumbbells

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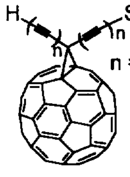
Abstract: The dumbbell-type C_{60} dimers connected by a butadiyne or an acetylene spacer were synthesized and fully characterized. The cyclic voltammetry indicated that the electronic interaction between two C_{60} cores is negligibly small. Copyright © 1996 Elsevier Science Ltd

Combination of fullerene and acetylene units is expected to provide a new kind of carbon allotropes. Thus, an attempt has been made by Diederich, Rubin and co-workers to construct a "charm-bracelet type" carbon network using diethynyl- or dibutadiynylmethanofullerene **1** as a molecular building block.[1] So far the dimeric compound[1b] was obtained from **1**. However, each of the C_{60} core had to be modified with six substituted methano-units for realization of the cyclic trimer and tetramer because of the solubility problem.[1c]

On the other hand, we have prepared ethynyldihydrofullerene **2**,[2] in which only one sp^3 carbon is present between the triple bond and the fullerenyl π-system. Here we report the synthesis and properties of dumbbell-type dimers **3** and **4** , the "buckydumbbells," for which the electronic interaction between the two C_{60} cores is of particular interest.



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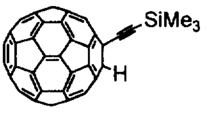

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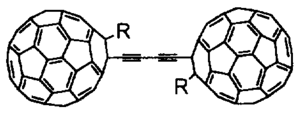
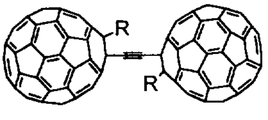


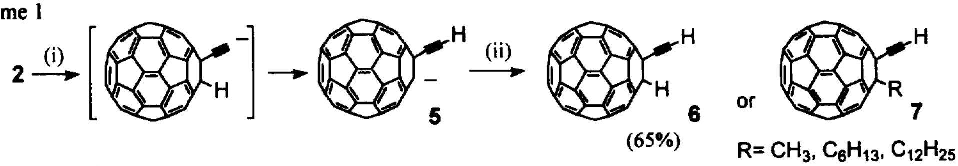
3 R = C_6H_{13}, $C_{12}H_{25}$



4 R = $C_{12}H_{25}$

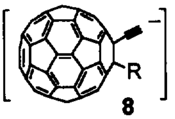
When (trimethylsilyl)ethynyl derivative **2** was desilylated with fluoride ion in THF, the solution immediately turned into dark green[3] indicating the generation of fulleride ion **5** due to the intramolecular transfer of the highly acidic fullerenyl proton[4] to the acetylenic carbon. Quenching of this green solution with trifluoroacetic acid or with alkyl iodide gave ethynylfullerene **6** or **7** (Scheme 1). The simplest acetylene **6** was only sparingly soluble whereas the alkyl derivative **7** was much more soluble in common organic solvents. Then acetylene **7** (R=C_6H_{13}, $C_{12}H_{25}$) was oxidatively coupled by the use of CuCl (80 equiv) and TMEDA (80 equiv) in chlorobenzene under air at room temperature for 6 h. The chromatographic separation of the crude product afforded a dark brown solid, the structure of which was determined as a dumbbell-type dimer **3** (R = C_6H_{13}, 23% yield; R = $C_{12}H_{25}$, 64% yield) based on the spectral data.[5]

Scheme 1



(i) $Bu_4N^+F^-$ (1.2 equiv), THF ; (ii) CF_3CO_2H or R-I (150-350 equiv)

The synthesis of dimer **4** having an acetylene spacer instead of butadiyne met with much greater difficulty. The attempt to add acetylide **8** ($R=C_{12}H_{25}$) to C_{60} was unsuccessful presumably due to the severe steric hindrance caused by the alkyl group, resulting only in the recovery of unchanged starting materials. However, the reaction of dilithioacetylene, generated from trichloroethylene and butyllithium (3 equiv) in THF, with C_{60} in toluene followed by reaction with excess of dodecyl iodide at refluxing temperature for 4 h afforded desired compound **4**,[5] albeit in a low yield (5%)[6] (Scheme 2).



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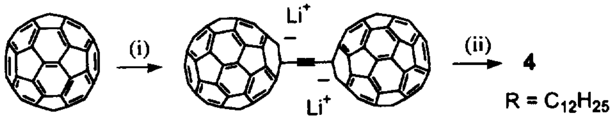
Scheme 2



(i) Li-C≡C-Li (3 equiv) in THF, toluene, rfx, 15 min ; (ii) $C_{12}H_{25}I$ (50 equiv), rfx, 4 h

The FAB or CI MS spectra of all new compounds demonstrated the molecular-ion peaks[5] which were in agreement with theoretical isotopic distributions. In the ^1H NMR spectra, methylene signals at the C-1 to C-3 positions of the dodecyl group in **3** and **4** ($R=C_{12}H_{25}$) are downfield shifted by 0.11 to 0.22 ppm as compared with those for monomer **7** ($R=C_{12}H_{25}$).[5] This can be taken as a piece of evidence that another C_{60} moiety is attached at the other end of the molecule and exerting the deshielding effect.[7] The characteristic features of ^{13}C NMR (partly overlapped 30 signals for sp^2 carbons) and UV-Vis spectra (three strong UV absorptions and a visible absorption at around 430 nm together with the one extending to about 700 nm)[5] indicate that all the new C_{60} derivatives **3**, **4**, and **7** have organic groups attached at the 6,6-juncture bond on the C_{60} surface.

Although the full conjugation between the two C_{60} cores in **3** and **4** is prevented by the presence of quaternary sp^3 carbons present on the C_{60} surface, the acetylenic and fullerenyl π-systems could formally be considered as homoconjugated. However, there is no evidence for such electronic interaction observable upon comparing the electronic spectra of **3**, **4**, and **7**. The electronic interaction between the two C_{60} cores, if present, would only be detected upon electronic perturbation such as reduction/oxidation. In order to examine the possibility of such interaction, cyclic voltammetry was conducted for C_{60}, monomer **7**, and dimers **3** and **4** in *o*-dichlorobenzene. As shown in Figure 1, the reduction potentials of the derivatives **7**, **3**, and **4** are generally 60 to 200 mV more negative than those for C_{60}. However, the most remarkable feature is the gradual increase in peak-to-peak width (ΔE_p) of the individual redox waves in the order, C_{60}, **7**, **3**, and **4**.

If the C_{60} moiety at one end can recognize the electronic perturbation occurring at the other end the individual redox should take place stepwise, whereas the both C_{60} cores would be reduced simultaneously in the absence of such interaction. Even upon careful examination, each redox process in **3** and **4** does not seem to be stepwise. Rather, the observed gradual widening of redox waves, in the order C_{60}, **7**, **3**, and **4**, may better be ascribed to the decrease in rate constant for electron transfer at the electrode, which is directly related to the separation of peak potentials.[8] It would be quite possible that the structural modification with a long and flexible alkyl chain such as a dodecyl group causes the hindrance for the electrode reaction on the C_{60} moiety and this tendency would become more prominent as the two C_{60} cores are placed in closer proximity resulting in gradual widening of the redox waves just as have been observed.

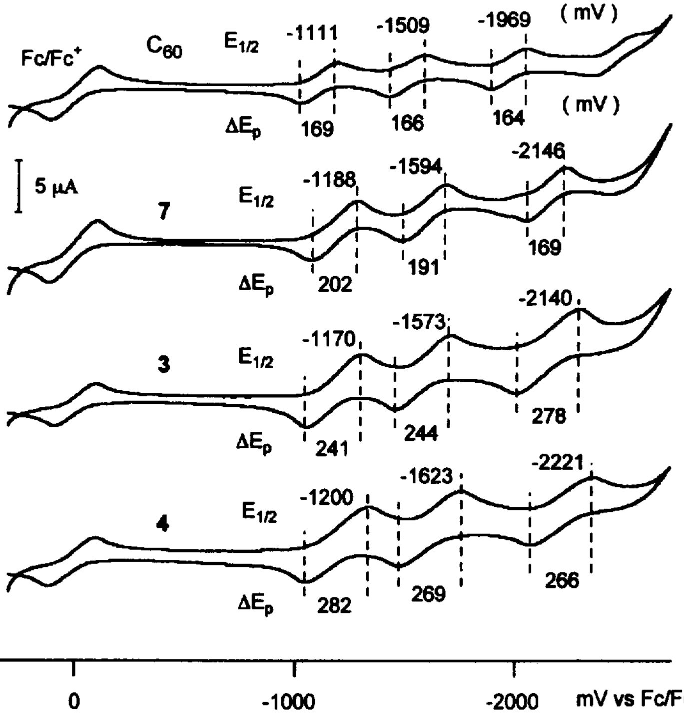


Figure 1. Cyclic voltammograms of C_{60}, monomer 7 ($R=C_{12}H_{25}$), and dimers 3 ($R=C_{12}H_{25}$) and 4 ($R=C_{12}H_{25}$) conducted in *o*-dichlorobenzene with 0.05 M $TBABF_4$; scan rate 20 mV s^{-1}.

Acknowledgments.

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3. a) Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K.; Komatsu, K. *J. Org. Chem.* **1995**, *60*, 1490-1491. b) Murata, Y; Komatsu, K.; Wan, T. S. M. *Tetrahedron*, **1996**, *52*, 5077-5090.
4. The pK_a value in DMSO was determined as 5.7 for *t*-$BuC_{60}H$ (Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697-9699), 4.7 for $HC_{60}H$ (Niyazymbetov, M. E.; Evans, D. H.; Lerke, S. A.; Cahill, P. A.; Henderson, C. C. *J. Phys. Chem.* **1994**, *98*, 13093-13098), and 2.5 for $NCC_{60}H$ (Keshavarz-K, M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371-11372).

5. Most of the C_{60} derivatives were purified only by reprecipitation from CS_2-pentane, and failed to give correct analytical data due to incorporation of the solvent molecule. The example is given for the case of **3** (R = $C_{12}H_{25}$) below.

   6 : MS (negative APCI) *m/z* 746 [M$^-$]; ^{1}H NMR (300 MHz, CS_2-$CDCl_3$ (1:1)) δ 7.05 (s, 1H), 3.11 (s, 1H). (^{13}C NMR data could not be obtained due to the extremely low solubility.)

   7 (R = CH_3) : MS (negative DCI) *m/z* 760 [M$^-$]; ^{1}H NMR (300 MHz, CS_2-$CDCl_3$ (1:1)) δ 3.45 (s, 3H), 3.02 (s, 1H). (^{13}C NMR data could not be obtained due to the extremely low solubility.)

   7 (R = C_6H_{13}) : MS (negative APCI) *m/z* 830 [M$^-$]; ^{1}H NMR (300 MHz, CS_2-$CDCl_3$ (3:1)) δ 3.68 (m, 2H), 2.96 (s, 1H), 2.51 (m, 2H), 1.82 (m, 2H), 1.51 (m, 4H), 1.02 (t, 3H). (^{13}C NMR data could not be obtained due to the extremely low solubility.)

   7 (R = $C_{12}H_{25}$) : MS (negative DCI) *m/z* 914 [M$^-$]; ^{1}H NMR (300 MHz, CS_2-$CDCl_3$ (3:1)) δ 3.66 (m, 2H), 2.94 (s, 1H), 2.49 (m, 2H), 1.79 (m, 2H), 1.57 (m, 2H), 1.28 (m, 14H), 0.89 (m, 3H); ^{13}C NMR (75 MHz, CS_2-$CDCl_3$ (3:1)) δ 155.35, 153.28, 147.60, 147.46, 146.32, 146.23, 146.03, 145.66, 145.45, 145.39, 145.30, 145.18, 145.11, 144.91, 144.51, 144.40, 142.99, 142.41, 141.98, 141.80, 141.69, 141.38, 141.22, 139.97, 139.73, 134.46, 134.28, 82.23, 73.05, 65.25, 58.70, 44.32, 32.13, 30.43-30.05, 29.63, 23.07, 14.39; UV-Vis (C_6H_{12}) λ_{max} 211 nm (log ε 5.16), 257 (5.06), 326 (4.54), 433 (3.55), 700 (2.62).

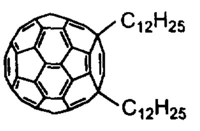
   3 (R = C_6H_{13}) : MS (negative APCI) *m/z* 1658 [M$^-$]; ^{1}H NMR (300 MHz, CS_2-$CDCl_3$ (2.5:1)) δ 3.79 (m, 4H), 2.63 (m, 4H), 1.96 (m, 4H), 1.66 (m, 4H), 1.54 (m, 4H), 1.02 (t, 6H). (^{13}C NMR data could not be obtained due to the extremely low solubility.)

   3 (R = $C_{12}H_{25}$) : MS (negative FAB) *m/z* 1826 [M$^-$]; ^{1}H NMR (300 MHz, CS_2-$CDCl_3$ (3:1)) δ 3.77 (m, 4H), 2.61 (m, 4H), 1.94 (m, 4H), 1.66 (m, 4H), 1.49 (m, 4H), 1.23 (m, 24H), 0.85 (m, 6H); ^{13}C NMR (75 MHz, CS_2-acetone-*d*$_6$ (5:1)) δ 155.17, 152.18, 147.79, 147.62, 146.53, 146.41, 146.25, 146.21, 145.77, 145.64, 145.50, 145.35, 144.95, 144.69, 144.51, 143.17, 142.66, 142.61, 142.15, 141.99, 141.87, 141.60, 141.42, 140.26, 139.99, 134.77, 134.64, 79.46, 69.95, 66.22, 59.71, 44.77, 32.31, several peaks were hidden by the solvent peak between 31 to 29, 23.26, 14.51; UV-Vis (C_6H_{12}) λ_{max} 220 nm (log ε 5.16), 257 (5.12), 313 (4.71), 433 (3.81), 699 (2.71). Anal. Calcd for $C_{148}H_{50}\cdot CS_2$: C, 93.99; H, 2.63%. Found: C, 93.99; H, 2.79%.

   4 (R = $C_{12}H_{25}$) : MS (negative FAB) *m/z* 1802 [M$^-$]; ^{1}H NMR (300 MHz, CS_2-$CDCl_3$ (3:1)) δ 3.88 (m, 4H), 2.62 (m, 4H), 1.67 (m, 4H), 1.24 (m, 32H), 0.87 (m, 6H); ^{13}C NMR (75 MHz, CS_2-$CDCl_3$ (3:1)) δ 155.42, 153.17, 153.12, 147.75, 147.60, 146.49, 146.34, 146.19, 146.16, 145.77, 145.58, 145.54, 145.43, 145.32, 145.28, 145.02, 144.84, 144.68, 144.50, 143.17, 142.59, 142.09, 142.06, 141.95, 141.89, 141.56, 141.34, 140.28, 139.86, 134.64, 84.27, 66.17, 59.62, 45.04, 33.75, 32.10, 31.17-29.57, 28.79, 23.02, 14.33; UV-Vis (C_6H_{12}) λ_{max} 211 nm, 258, 312, 434, 700.

6. To our surprise, the main product was 1,4-didodecyl[60]fullerene (**9**): the mechanism for its formation is not clear yet.

   9 : MS (negative DCI) *m/z* 1058 [M$^-$], 890 [M$^-$-$C_{12}H_{25}$]; ^{1}H NMR (300 MHz, CS_2-$CDCl_3$ (3:1)) δ 3.01 (m, 4H), 2.32 (m, 4H), 1.68 (m, 4H), 1.25 (m, 32H), 0.86 (m, 6H); ^{13}C NMR (75 MHz, CS_2-$CDCl_3$ (3:1)) δ 157.66, 157.33, 151.72, 148.53, 148.39, 147.29, 147.00, 146.72, 146.67, 146.13, 146.08, 145.26, 145.00, 144.93, 144.69, 144.56, 144.22, 144.09, 143.91, 143.72, 143.59, 142.96, 142.77, 142.50, 142.45, 142.28, 141.91, 141.79, 140.56, 138.74, 138.16, 67.58, 43.25, 38.76, 32.12, 30.43-29.61, 27.33, 23.04, 14.35; UV-Vis (C_6H_{12}) λ_{max} 219 nm (log ε 5.18), 256 (5.03), 436 (3.76), 457sh (3.68), 689 (2.54).

   9

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Note added in proof. A similar dumbbell-type dimer **3** (R = $CH_2C_6H_5$) was recently reported by Diederich and coworkers in a completely independant study: Timmerman, P.; Witschel, L. E.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1996**, *79*, 6-20.

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