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Synthesis, Properties, and Reactions of a Stable Carbanion Derived from Alkynyldihydrofullerene: 1-Octynyl-C_{60} Carbanion

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Abstract: Stable 1-octynyl-C_{60} carbanion (2^-) was generated by the reaction of 1-octynyl-C_{60}-H with *t*-BuOK in THF, and its structure was confirmed by ^1H and ^{13}C NMR spectra. The redox properties were studied by cyclic voltammetry, and were shown to involve a one electron oxidation process affording a dimer of the corresponding radical, in addition to stepwise reduction processes. In accord with the results of semiempirical MO calculations (AM1), the reaction of anion 2^- with various carbon electrophiles afforded the 1,2- or 1,4-disubstituted dihydrofullerenes. The reaction site was apparently controlled by electron density of anion 2^- and the steric effects.

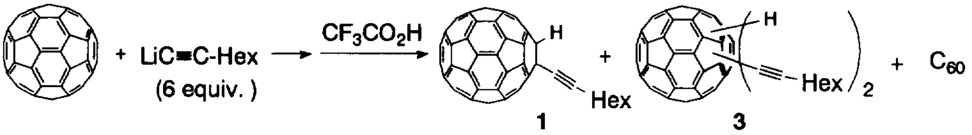
INTRODUCTION

Owing to the recent extensive studies, it is well recognized that buckminsterfullerene C_{60} is a highly electronegative molecule,[1] which readily undergoes nucleophilic reactions. After the pioneering work by Wudl et al.,[2] Hirsch and co-workers[3] studied the reaction with various organolithium and Grignard reagents, which gave monoalkyldihydrofullerenes with well-defined structures after protonation. On the other hand, Fagan et al.[4] reported synthesis and properties of *t*-butyl-C_{60} anion by means of nucleophilic addition of *t*-butyllithium to C_{60}. The fullerenyl proton in the *t*-butyl derivative was shown to be highly acidic with the pK_a value of 5.7.[4] Since an ethynyl group has electron-withdrawing inductive effects[5] as compared with alkyl groups, it was expected that C_{60} bearing an ethynyl group, R-C≡C-C_{60}-H, would give even more stable carbanion than *t*-Bu-C_{60}^-. Recently we reported synthesis and properties of the first acetylene derivatives of C_{60} having a trimethylsilylethynyl group or a phenylethynyl group.[6] However, these derivatives were not quite suitable for the study of their anions, since the phenylethynyl derivative was only sparingly soluble in common organic solvents and the trimethylsilylethynyl derivative was rather unstable under basic conditions. In the present work, we newly prepared an 1-octynyl derivative, Hex-C≡C-C_{60}-H (**1**), which was expected to be more soluble and chemically stable. In this paper we wish to report the synthesis, properties, and reactions of 1-octynyl-C_{60} anion (2^-) bearing 60 π-electrons on the C_{60} core, which was readily generated from **1**.

RESULTS AND DISCUSSION

Synthesis of 1-octynyldihydrofullerene, Hex-C$\equiv$C-C_{60}-H

At the outset of this study, it was anticipated that the nucleophilicity of lithium acetylides would be too low, and thus we carried out the reaction of C_{60} with acetylides in refluxing toluene in our previous study.[6] Later it turned out that a reaction of C_{60} with 1-octynyllithium proceeds smoothly at room temperature in THF giving a dark green solution of the anion $\mathbf{2}^-$. After the reaction of 10 min and quenching with trifluoroacetic acid, the monoethynylated derivative **1** was isolated in 75% yield with unchanged C_{60} recovered in 21%. No bisethynylated compound was detected. In comparison, the reaction in refluxing toluene, which gives black suspension of the lithium salt of the anion $\mathbf{2}^-$, afforded, after quenching and separation, the monoadduct **1** and bisadduct **3** in 52% and 5% yields, respectively, while unchanged C_{60} was recovered in 16% (Scheme 1).



	1	3	C_{60}
THF / r.t.	75 %	——	21 %
toluene / 111 °C	52 %	5 %	16 %

Scheme 1. Synthesis of 1-octynyldihydrofullerene, Hex-C$\equiv$C-C_{60}-H (**1**).

As will be discussed later and also as reported by Hirsch,[3a] theoretical calculations indicate that the negative charge in organofulleride ion is rather localized on carbons which are close to the carbon bearing the organic group. A degree of such negative-charge localization should be greatly influenced by a degree of ion-pairing, which also depends upon solvent polarity. It is quite possible that the 1-octynyl-$C_{60}^-Li^+$ ion pair is less tight in THF with higher solvating power, causing more charge delocalization than in toluene. Such charge delocalization would prevent the attack of the second necleophile and lead to the selective formation of the monoadduct **1**.

Owing to the presence of a long and flexible *n*-hexyl group, the monoadduct **1** has an advantage of considerably high solubility in common organic solvents such as hexane, toluene, $CHCl_3$, THF, and CS_2 as compared with that of original C_{60} or phenylethynyl-C_{60}-H.

The structure of the monoadduct **1** was fully characterized by standard spectroscopic methods. The APCI (atmospheric pressure chemical ionization) mass spectrum displayed the molecular ion peak at *m/z* 829 (M-H). The ^1H NMR showed a singlet signal at δ 6.96 corresponding to the proton directly attached to the C_{60} nucleus together with signals of the *n*-hexyl group. Considerable down-field shift of the fullerenyl proton reflects the presence of a triple bond in close proximity. The ^{13}C NMR spectrum exhibited signals for acetylenic carbons (δ 84.68 and 83.62) and sp^3 carbons in the C_{60} core (δ 62.07 and 54.62), together with 28 signals for the sp^2 carbons of the C_{60} core in the region between δ 151.99 and 134.75, as shown in Figure 1. Assuming that two more signals are hidden by incidental overlapping, it is possible that this adduct has C_s symmetry similar to the structure of trimethylsilylethynyl and phenylethynyl derivatives reported previously.[6] Also the UV-vis spectrum showed a strong resemblance to the spectra of the C60 derivatives in which one of the 6,6-junction bonds was saturated by addition reactions,[3b, 7] thus supporting the structure **1**.

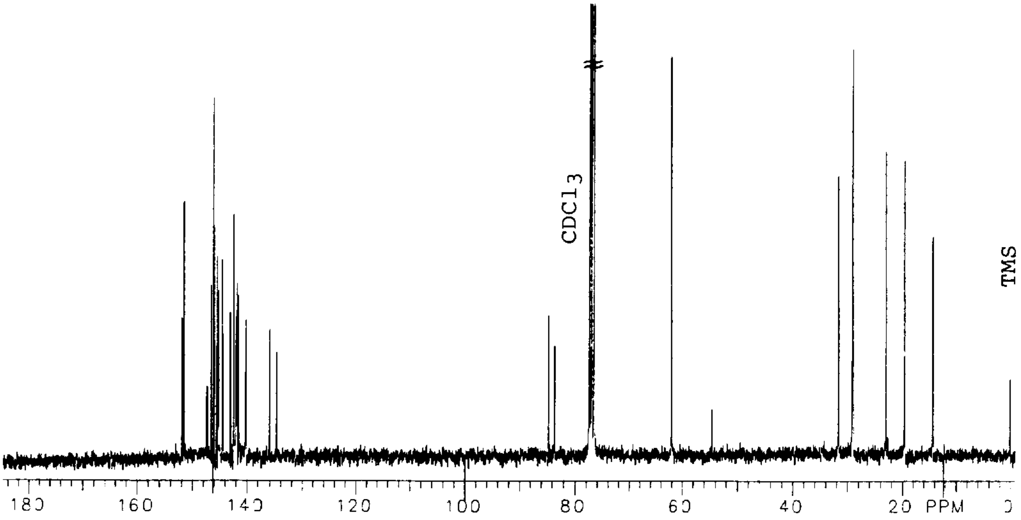
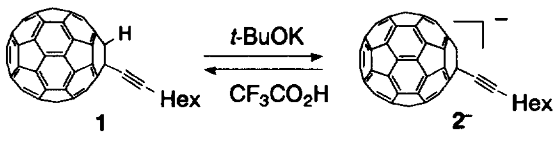


Figure 1. ^{13}C NMR spectrum of 1-octynyl-C60-H (**1**) in CS_2-$CDCl_3$ (1:1).

The redox properties of the monoadduct **1** was studied by the use of cyclic voltammetry in benzonitrile. The voltammogram exhibited one irreversible oxidation peak at +1.41 V vs ferrocene/ferrocenium and four reversible reduction waves at -1.01, -1.42, -1.82, and -2.30 V. These reduction potentials are about 0.1 V less negative than the values for most of the reported C60 derivatives,[7c, 8] and are rather close to those of C60 itself (+1.41, -0.93, -1.36, -1.85, -2.30 V) probably owing to the inductive electron-withdrawing effect of the triple bond.[5]

Generation of 1-octynyl-C60 anion

When the THF solution of the alkynylfullerene **1** was treated with 1 equiv of *t*-BuOK, the initially brown solution immediately turned into a dark green solution (Scheme 2). This solution was protonated again with trifluoroacetic acid to give an original monoadduct **1**, and is considered to contain the 1-octynyl-C60 anion (**2**$^-$) based on the ^1H and ^{13}C NMR data described below. The solution of **2**$^-$ is sensitive to air, but it can be kept without decomposition if stored under argon or nitrogen, for more than half a year.



Scheme 2. Generation of 1-octhnyl-C60 anion (**2**$^-$).

In the ^{1}H NMR spectrum of the solution no signal corresponding to the proton attached to the C60 core was observed any more, while all signals of the *n*-hexyl group in octynyl group are observed nearly identical to those of **1**. In the ^{13}C NMR spectrum shown in Figure 2, there appeared signals for acetylenic carbons (δ 86.47 and 83.40) and an sp^3 carbons in the C60 core (δ 54.61), together with 30 signals for the sp^2 carbons of the C60 core in the region between δ 175.24 and 120.99, which indicates *Cs* symmetry of this species. It is to be noted that the 30 signals of the C60 core of the anion **2**$^-$ appear in a wider range as compared with the spectrum of the precursor **1** with the signals between δ 151.99 and 134.75. This spectrum of **2**$^-$ compares well with that of *t*-Bu-C60 anion, whose sp^2-carbon signals cover the range between δ 179.40 and 126.50 as reported by Fagan et al.[4] This spreading of signals appears to reflect the more extended distribution of negative charge on the C60 core. The signal at δ 120.99 is most probably assigned to the carbon next to the one connected to the 1-octynyl group, which bears the highest negative charge according to semiempirical MO calculations (AM1).

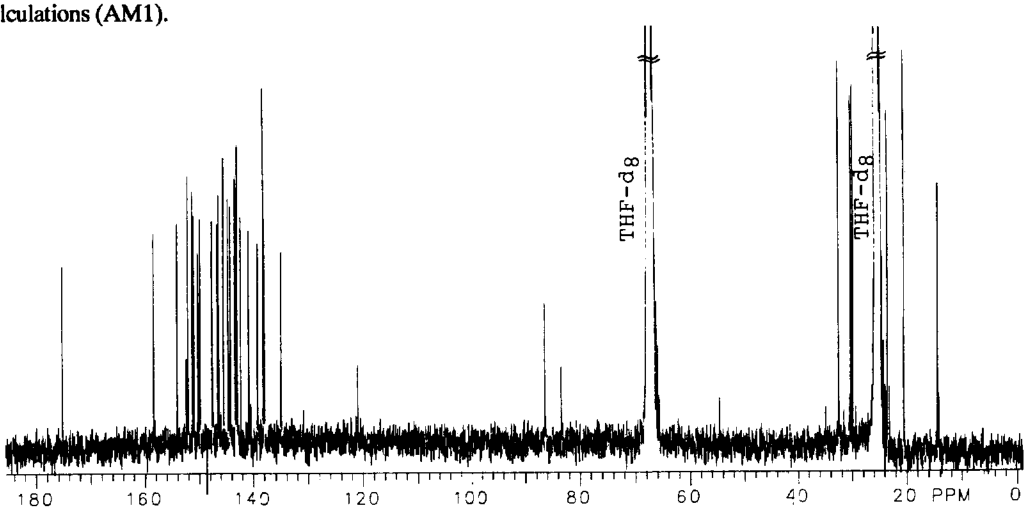


Figure 2. ^{13}C NMR spectrum of 1-octynyl-C60 anion (**2**$^-$) in THF-*d8*.

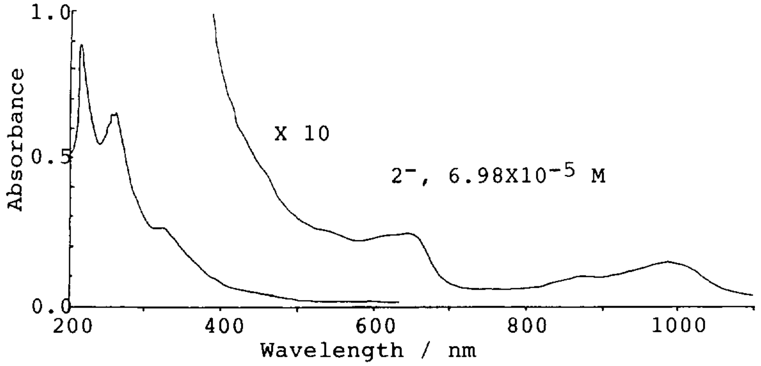


Figure 3. UV-vis-near IR spectrum of 1-octynyl-C60 anion (**2**$^-$) in THF.

It has been reported that C_{60}^- in benzonitrile has an absorption in the near IR region,[9] and that *t*-Bu-C_{60} anion in DMSO or DMSO-CS_2 also has absorption bands at 656 and 995 nm in the visible/near IR region spectra.[10] Similarly, the UV-vis-near IR spectrum of the green THF solution of **2**$^-$ exhibits absorption bands at 643 and 990 nm, together with 214, 257, 262, and 324 nm as shown in Figure 3.

Redox properties of the 1-octynyl-C60 anion

The redox behavior of 1-octynyl-C_{60} anion (**2**$^-$) was examined by the use of cyclic voltammetry in THF and DMSO. A characteristic voltammogram was observed as shown in Figure 4, and the data are presented in Table 1 together with those reported for *t*-Bu-C_{60} anion.[4] Apparently the most unusual feature is associated with the redox cycle at the lowest potential. For example, anion **2**$^-$ in THF is oxidized to its radical at -0.39 V vs ferrocene/ferrocenium, but the corresponding reduction is shifted to -1.20 V, the difference of peak potentials being 0.81 V. This large negative shift of the cathodic peak is ascribed to some chemical process associated with the electron transfer, which is most probably a very rapid dimerization of the 1-octynyl-C_{60} radical (Scheme 3). The reduction of this dimer to the original monomeric anion **2**$^-$ requires extra energy for dissociation and also for subtle structural change in C_{60} framework, which could have caused the cathodic shift as has been observed. The second and third reductions were nearly reversible as observed in individual redox waves (see Figure 4).

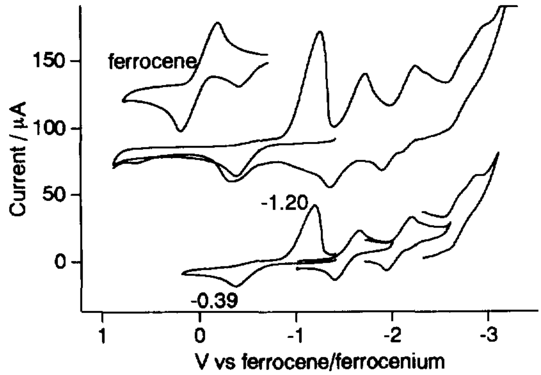
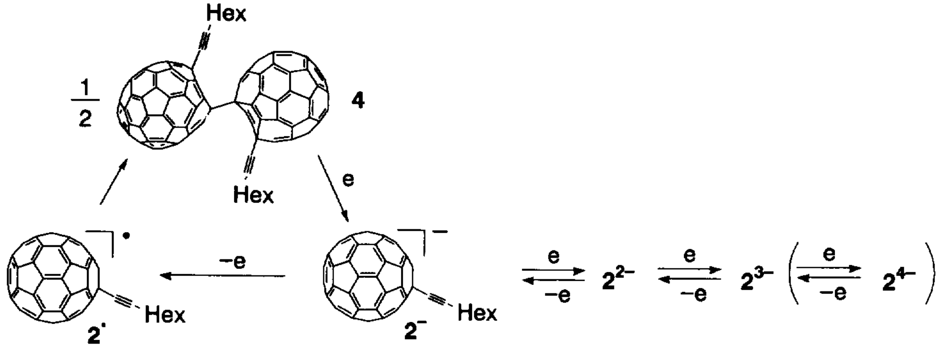


Figure 4. Cyclic voltammogram of 1-octynyl-C_{60} anion (**2**$^-$) in THF.

Table 1. Comparison of CV data (V vs Fc/Fc$^+$)

Compd	solv.	E_{ox}		E_{red}^1	E_{red}^2	E_{red}^3
		E_{pa}	E_{pc}			
t-Bu-C_{60}^- Li^+ [a]	THF			-1.53	-2.04	-2.61
t-Bu-C_{60}^- Li^+ [a]	DMSO	" -0.33 "		-1.27	-1.77	
Hex-C$\equiv$C-C_{60}^- K^+ [b]	THF	-0.39	-1.20	-1.55	-2.08	-2.75
Hex-C$\equiv$C-C_{60}^- Li^+ [b]	DMSO	-0.32	-0.94	-1.21	-1.72	-2.33

[a] Ref. 4. [b] scan rate, 0.1 V/s; supporting electrolyte, Bu_4NBF_4 (0.1 M).



Scheme 3. Redox system of 1-octynyl-C_{60} anion (2^{-}).

In fact, when the anion was chemically oxidized with iodine in THF, an immediate color-change from dark green to brown was observed, and a dimeric compound **4** was obtained.[11] In contrast to a dimer of C_{60} derivative having a bulkier *t*-butyl group, no homolytic dissociation seems to be occurring as judged from the ^{1}H NMR spectrum, which did not exhibit any line broadening due to paramagnetic species. Particularly noteworthy is the down-field shift of the 3-methylene signal ($-C{\equiv}C-CH_2-$, δ 3.56) as compared with the original monomer **1** (δ 2.62), reflecting the deshielding effect of another C_{60} core enforced to be located near the octynyl group.

Semiempirical MO calculations (AM1) of anion 2^{-}

In order to examine the structure and properties of anion 2^{-}, semiempirical MO calculations (AM1) were conducted as has been done by Hirsch and co-workers for *t*-Bu-C_{60} anion.[3a] As shown by the optimized structure shown in Figure 5 (a), anion 2^{-} becomes more spherical upon change of the hybridization of C-2 from sp^3 to sp^2. The negative charge (Figure 5 (b)) is distributed mostly on C-2 and C-4 similarly to those of *t*-Bu-C_{60}^{-}. In accord with the highest negative charge at C-2, protonation occurred selectively at this carbon. The coefficients of the HOMO (Figure 5 (c)) are also localized at C-2 (0.54) and C-4 (0.38), and these carbons are expected to selectively react with electrophilic reagents.

Reaction with electrophiles

In order to seek the possibility to synthesize disubstituted dihydrofullerenes in isomerically pure form, anion 2^{-} was treated with carbon nucleophiles such as methyl iodide, ethyl iodide, tropylium ion, and benzoyl chloride. When these electrophiles were added to anion 2^{-} in THF, a brown suspension resulted, from which were isolated disubstituted dihydrofullerenes **5** to **9** in 72~98% yield as shown in Scheme 4. Their structures were determined based on MS, ^{1}H and ^{13}C NMR, IR, and UV-vis spectra.

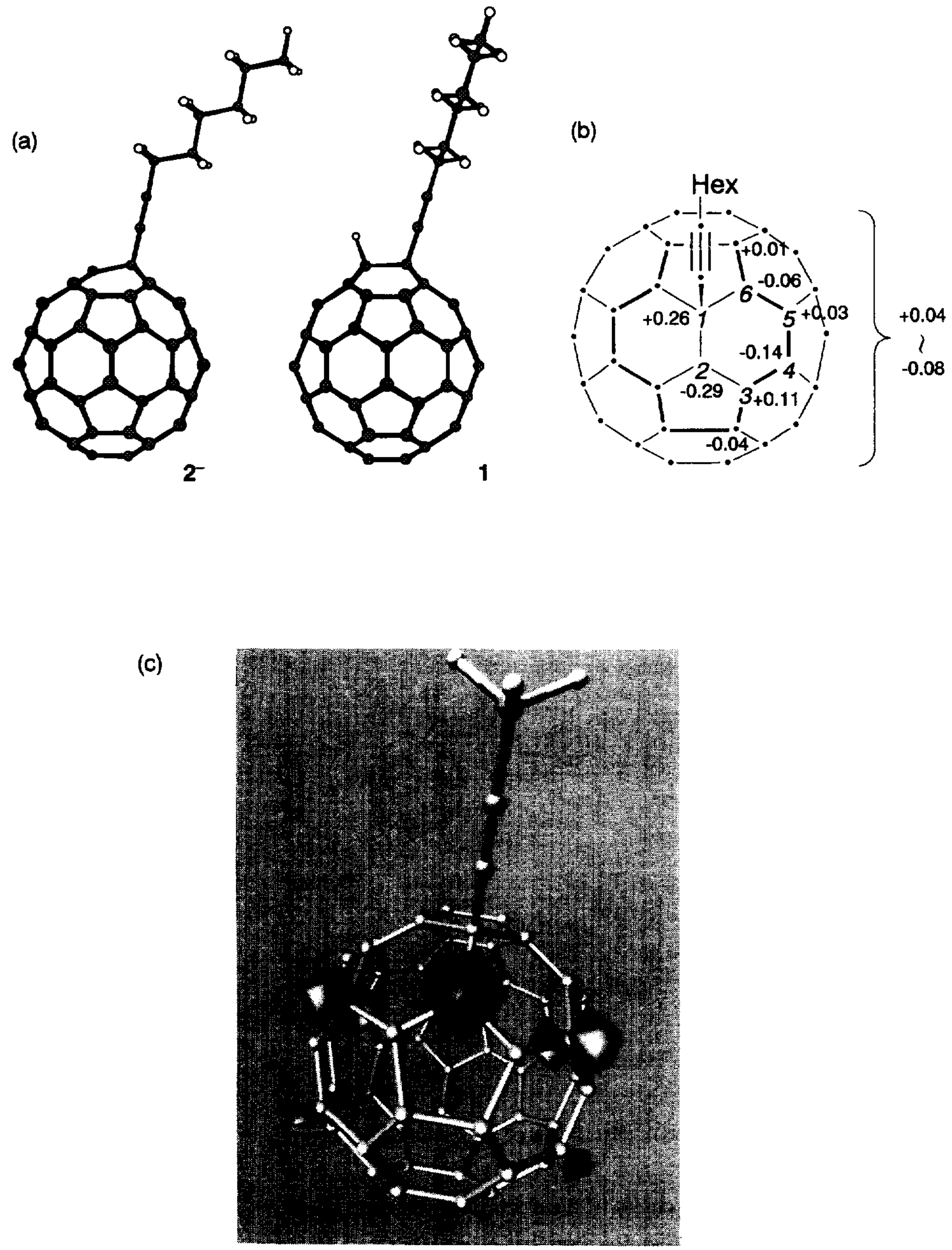
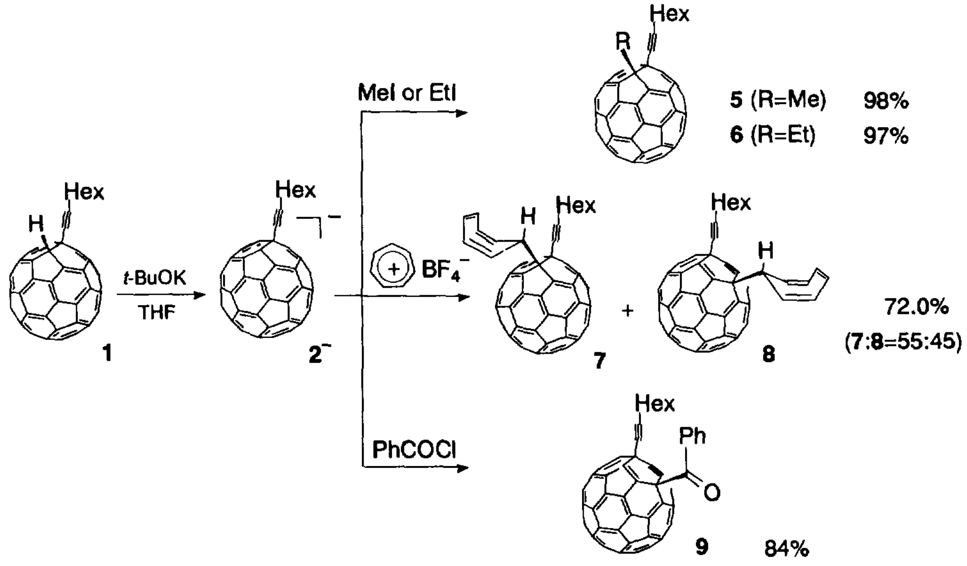


Figure 5. Results of AM1 calculations: (a) optimized structures of **2**$^-$ and **1**; (b) calculated charge densities of **2**$^-$; (c) calculated HOMO of **2**$^-$, produced by the UniChem, Cray Research, Inc. Its *n*-hexyl group is replaced by a methyl group for clarity.

They revealed that the methyl and ethyl adducts were isomerically pure and had C_s symmetry, that is, both methyl and ethyl iodides added selectively at the C-2 position of anion $\mathbf{2}^-$. In contrast to the reaction with the anion having a bulkier *t*-butyl group, which gave rise to only 1,4-adduct,[10] the reaction of tropylium ion with anion $\mathbf{2}^-$ afforded a mixture of both 1,2- and 1,4-adducts **7** and **8** in a 55:45 ratio. On the other hand, the reaction of $\mathbf{2}^-$ with benzoyl chloride selectively gave only the 1,4-adduct **9** as evidenced from the following NMR data. Thus, the ^{1}H NMR spectrum exhibited the presence of only one isomer, and the ^{13}C NMR spectrum showed signals for acetylenic carbons (δ 85.29 and 77.07) and sp^3 carbons in the C_{60} core (δ 71.28 and 62.37), together with 54 signals for the sp^2 carbons of the C_{60} core and *ipso*-carbon in the range between δ 152.82 and 138.17 in addition to signals for CH in a phenyl group (δ 133.21, 129.26, and 128.64) and a carbonyl carbon (δ 194.16). Assuming that five signals are incidentally overlapped, this spectrum is considered to have the structure **9**.



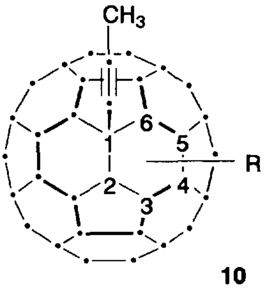
Scheme 4. Syntheses of disubstituted dihtdrofullerenes.

The observed positional selectivity of the electrophilic addition might have resulted from steric effects in addition to the negative-charge distribution described above. The heat of formation was calculated by AM1 for the products of electrophilic addition at C-2 and C-4 of 1-propynyl-C_{60} anion as a model compound. The calculated energies obtained for the optimized structures of each product are shown in Table 2. Apparently, as the size of the electrophile increases in the order, hydrogen, methyl, cycloheptatrienyl, and benzoyl, the relative stability of the 1,4-adduct with reference to the 1,2-adduct increases. In the case of the benzoyl adduct, no energy minimized structure of the 1,2-adduct was obtained. These results are qualitatively in accord with the experimental results, which demonstrated the predominant formation of thermodynamically more stable products except for the addition of tropylium ion.[12]

Table 2. Heat of formation for CH_3-C≡C-C_{60}-R (**10**) calculated by AM1

R	ΔH_f	
	1,2-adduct	1,4-adduct
H	983.22	987.17
CH_3	984.19	984.75
C_7H_7	1043.55	1040.34
PhCO	——[a]	996.86

[a] No energy minimum was obtained for this structure.



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SUMMARY

A previously reported technique of nucleophilic addition of the acetylide to fullerene C_{60} was modified and applied for the synthesis of 1-octynyldihydrofullerene (**1**) in good yield. Deprotonation of **1** with *t*-BuOK quantitatively yielded the corresponding carbanion **2**$^-$ with its negative charge localized at the C-2 and C-4 positions. Various carbon electrophiles react at these carbons to give the corresponding disubstituted dihydrofullerenes with the site of addition controlled by the size of the electrophiles. Redox properties of anion **2**$^-$ were also studied and revealed that the fullerenyl radical generated upon oxidation of the anion dimerizes immediately after its formation.

EXPERIMENTAL

General remarks and materials.

Elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto. NMR spectra were taken at 300 MHz for ^1H and 75 MHz for ^{13}C on Varian XL-300 spectrometer. UV-vis-near IR spectrum was recorded on a Hitachi U-3400 spectrometer. UV-vis and IR spectra were taken on Shimadzu UV-2100PC and FTIR-8000 spectrometers respectively. MS spectra were measured with Finnigan TSQ7000 spectrometer. Cyclic voltammetry was conducted on a BAS electro-analyzer CV-50W using a three-electrode cell with a glassy carbon working electrode, a platinum counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The potential was corrected against ferrocene used as an internal standard added immediately after each measurement. The AM1 calculations were conducted using standard methods as implemented in the MOPAC 6.0 semiempirical molecular orbital package on a CRAY Y-MP2E/264 machine. TLC analyses were conducted with hexane over silica gel 60 F-254 (E. Merck). Medium-pressure liquid chromatography (MPLC) was carried out using silica gel 60 (E. Merck, particle size 0.040-0.063 mm, 230-400 mesh ASTM) as a stationary phase.

C_{60} was separated from a commercial mixture of C_{60} and C_{70} (92:8 by weight, MER) by the use of a Norit carbon–silica gel column eluted with toluene.[13] THF was freshly distilled from sodium benzophenone ketyl before use. Toluene and benzonitrile were distilled from Na and P_2O_5, respectively. A solution of *n*-butyllithium in hexane was titrated using a solution of *N*-pivaloyl-*o*-toluidine in THF.[14] Reactions were conducted under argon atmosphere in pre-dried glasswares.

1-(1-Octynyl)-1,9-dihydrofullerene-60 (1)[15]*; preparation in toluene.*

A solution of 1-octynyllithium was prepared by adding 0.83 mL of 1.68 N *n*-BuLi in hexane to a stirred solution of 1-octyne (158 mg, 1.43 mmol) in 1.9 mL of THF at 0 °C and stirring the mixture at 0 °C for 0.5 h. To a vigorously stirred solution of C_{60} (85.2 mg, 0.118 mmol) in refluxing toluene (40 mL), was added the solution of 1-octynyllithium dropwise by the use of a syringe. After a total of 1.5 mL (0.70 mmol) of the solution was added over 1 min, a black suspension resulted. The mixture was treated with CF_3CO_2H (0.2 mL, 2.6 mmol) to give a dark brown suspension, which was then evaporated under vacuum. The residual solid was extracted with CS_2 and the extracted mixture separated by MPLC on silica gel eluted with hexane. From the first fraction was obtained unchanged C_{60} (13.7 mg, 16.1%); TLC R_f 0.56. From the second fraction was isolated **1** (51.1 mg, 52.1%) as a brown powder: mp > 300 °C; TLC R_f 0.44; ^1H NMR ($CDCl_3$-CS_2 (1:1)) δ 6.96 (s, 1H, $C_{60}H$), 2.62 (t, 2H, CH_2), 1.84 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 1.44 (m, 4H, CH_2CH_2), 0.97 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$-CS_2 (1:1)) δ 151.99, 151.61, 147.47, 147.20, 146.58, 146.25, 146.17, 146.08, 145.69, 145.51, 145.46, 145.35, 145.27, 145.21, 144.56, 144.43, 143.08, 142.91, 142.45, 142.00, 141.91, 141.88, 141.55, 141.47, 140.23, 140.17, 136.03, 134.75 (28 signals, sp^2-carbons in the C_{60} core), 84.68 ($C\equiv C$), 83.62 ($C\equiv C$), 62.07 (CH in the C_{60} core), 54.62 (quaternary sp^3-C in the C_{60} core), 31.67, 29.09, 28.95, 22.98, 19.58, 14.37 (six signals, *n*-hexyl); UV-vis (cyclohexane) λ_{max} (log ε) 213 nm (5.13), 256 (5.08), 326 (4.58), 432 (3.61), 637 (2.65), 690 (2.55), 702 (2.68); negative APCI MS *m/z* 829 (M-H^+). Anal. Calcd for $C_{68}H_{14}$: C, 98.30; H, 1.70. Found: C, 98.05; H, 1.76. The third fraction (eluted with 5% benzene in hexane) afforded a mixture of positional isomers of bisadduct **3** (5.6 mg, 5.4%) as a dark brown powder: TLC R_f 0.26; ^1H NMR ($CDCl_3$-CS_2 (1:1)) δ 6.53 (s), 6.16 (s), 5.83 (s), 5.68 (s), 2.6 - 2.1 (br m); positive APCI MS *m/z* 940 (M^+), 830 ((M^+–$HC\equiv C$-Hex).

1-(1-Octynyl)-1,9-dihydrofullerene-60 (1); preparation in THF.

In the same way as described above, 1.50 mL (0.42 mmol) of a 0.28 M THF solution of 1-octynyllithium was added dropwise to a vigorously stirred suspension of C_{60} (50.3 mg, 0.0698 mmol) in THF (50 mL) at room temperature over 1 min. After 10 min, the resulting dark green solution was treated with excess CF_3CO_2H, worked up in the same way as above, and chromatographed to give unchanged C_{60} (10.3 mg, 20.5%) and monoadduct **1** (43.4 mg, 74.8%).

(1-Octynyl)fulleride ion (2^-).

As a typical procedure, monoadduct **1** (6.34 mg, 0.00763 mmol) was weighed into a glass tube (outer diameter, 8 mm) having an NMR tube and another branched glass-tube as side-arms. In the side-arm was placed 0.23 mL of a 0.0361 M THF solution of *t*-BuOK (0.0083 mmol) by the use of a long-needle syringe under argon. The whole system was connected to a vacuum line, and the solvent was evaporated. For the purpose of NMR measurement, 0.8 mL of pre-dried THF-d_8 (over Na) was transfered onto *t*-BuOK, the whole system was sealed under vacuum, and the solution of *t*-BuOK was mixed well with **1** to give a dark green solution. The solution was poured into the NMR tube, which was sealed off and subjected to NMR measurement. The similar procedure was applied for UV-vis-NIR measurement: UV-vis-near IR (THF) λ_{max} (log ε) 214 nm (5.11), 257 (4.97), 262 (4.97), 324 (4.58), 643 (3.54), 870 (3.18), 990 (3.35), Cyclic voltammetry was conducted under argon atmosphere.

1-(1-Octynyl)-9-methyl-1,9-dihydrofullerene-60 (5).

To a stirred solution of 1-octynyldihydrofullerene **1** (9.43 mg, 0.0113 mmol) in THF (20 mL) was added 0.29 mL of a 0.0393 M solution of *t*-BuOK (0.0114 mmol) in THF under argon to give a dark green solution. After being stirred for 3 min, 0.07 mL (0.16 g, 1.13 mmol) of methyl iodide was added and the reaction mixture was stirred at room temperature for 22 h. The solution turned to a dark brown suspension. After removal of THF and excess methyl iodide under vacuum, the residue was purified by dissolving in CS_2 and passing through a short silica gel column to give 9.4 mg (98%) of **5** as a dark brown solid: mp > 300 °C; ^1H NMR (CS_2-acetone-d_6 (4:1)) δ 3.41 (s, 3H, C_{60}-CH_3), 2.61 (t, 2H, CH_2), 1.83 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 1.43 (m, 4H, CH_2CH_2), 0.96 (t, 3H, CH_3); ^{13}C NMR (CS_2-acetone-d_6 (4:1)) δ 157.12, 154.10, 147.73, 147.59, 146.34, 146.29, 146.10, 145.81, 145.32, 145.23, 145.08, 145.01, 144.62, 144.58, 143.06, 142.95, 142.46, 142.03, 141.98, 141.49, 141.36, 140.11, 140.00, 139.61, 134.31, 133.99 (26 signals, sp^2-carbons in the C_{60} core), 86.55 (C≡C), 78.84 (C≡C), 61.13, 59.18 (two signals, quaternary sp^3-C in the C_{60} core), 32.87 (C_{60}-CH_3), 31.77, 28.93, 28.80, 23.09, 19.71, 14.43 (six signals, *n*-hexyl); UV-vis (cyclohexane) λ_{max} (log ε) 211 nm (4.98), 257 (4.88), 327 (4.44), 433 (3.73), 667 (2.80), 689 (2.85), 701 (2.90); positive APCI MS *m/z* 844 (M^+), 829 ($M^+$$-$$CH_3$), 720 ($C_{60}$). Anal. Calcd for $C_{69}H_{16}$: C, 98.09; H, 1.91. Found: C, 97.53; H, 1.89.

1-(1-Octynyl)-9-ethyl-1,9-dihydrofullerene-60 (6).

Similarly, a dark green solution of 2^- in THF was prepared from 1-octynyldihydrofullerene **1** (4.80 mg, 0.00577 mmol) and 0.060 mL of a 0.0958 M solution of *t*-BuOK (0.0057 mmol) in THF under argon. To this solution was added 0.050 mL (98 mg, 0.62 mmol) of ethyl iodide and the reaction mixture stirred for 40 h to give a dark brown suspension. The mixture was separated in the same way as above to yield 4.8 mg (97%) of **6** as a dark brown solid: mp > 300 °C; ^1H NMR (CS_2–$CDCl_3$ (1:1)) δ 3.74 (q, 3H, CH_3 in the ethyl group)) 2.58 (t, 2H, CH_2) 2.00 (t, 2H, CH_2 in the ethyl group) 1.81 (m, 2H, CH_2) 1.63 (m, 2H, CH_2) 1.42 (m, 4H, CH_2CH_2) 0.96 (t, 3H, CH_3); ^{13}C NMR (CS_2–$CDCl_3$ (1:1)) δ 155.42, 154.38, 153.05, 150.35, 147.59, 147.48, 146.22, 146.03, 145.98, 145.80, 145.67, 145.22, 145.12, 144.48, 144.39, 144.16, 142.95, 142.84, 142.38, 141.96, 141.86, 141.78, 141.36, 141.16, 140.35, 139.97, 139.55, 134.82, 133.84 (29 signals, sp^2-carbons in the C_{60} core) 85.77 (C≡C), 79.29 (C≡C) 65.77, 59.48 (two signals, quaternary sp^3-C in the C60 core) 37.46 (CH_2 in the ethyl group), 31.65, 29.92, 28.93, 23.05, 19.70, 14.76 (six signals, *n*-hexyl), 14.38

(CH_3 in the ethyl group); UV-vis (cyclohexane) λ_{max} (log ε) 212 nm (5.05), 257 (4.98), 328 (4.47), 433 (3.37), 636 (2.47), 668 (2.15), 690 (2.31), 702 (2.40); positive APCI MS *m/z* 859 ($M+H^+$), 858(M^+), 829 ($M^+-C_2H_5$), 720 (C_{60}). Anal. Calcd for $C_{70}H_{18}$: C, 97.89; H, 2.11. Found: C, 97.06; H, 2.08.

1-(1-Octynyl)-9-cycloheptatrienyl-1,9-dihydrofullerene-60 (7) and 1-(1-octynyl)-7-cycloheptatrienyl-1,7-dihydrofullerene-60[16] *(8).*

Similarly, a dark green solution of 2^- in THF was prepared from 1-octynyldihydrofullerene **1** (21.2 mg, 0.0255 mmol) and 0.26 mL of a 0.105 M solution of *t*-BuOK (0.0273 mmol) in THF under argon. To this solution was added 5.5 mg (0.031 mmol) of tropylium tetrafluoroborate and the reaction mixture stirred for 1 h to give a dark brown suspension. The mixture was separated in the same way as above and chromatographed to yield 16.9 mg (72%) of the mixture of **7** and **8** (ratio, 55:45) as a dark brown solid. Even by repeated MPLC or HPLC using Buckeyprep column (Nakalai), separation of **7** and **8** could not be attained: **7** and **8** ; mp > 300 °C; ^1H NMR (CS_2-CDCl_3 (1:1)) δ 6.9 (m), 6.7-6.4 (m), 3.83 (t), 2.53 (t), 2.39 (t), 1.8-1.2 (m), 0.9 (m); UV-vis (cyclohexane) λ_{max} (log ε) 207 nm (5.01), 256 (4.87), 315 (4.46), 433 (3.60), 688 (2.80), 700 (2.82); negative DCI MS *m/z* 920 (M^-), 830 ($M^--C_7H_6$), 720 (C_{60}). Anal. Calcd for $C_{75}H_{20}$: C, 97.81; H, 2.19. Found: C, 96.09; H, 2.06.

1-(1-Octynyl)-7-benzoyl-1,7-dihydrofullerene-60 (9).

Similarly, a dark green solution of 2^- in THF was prepared from 1-octynyldihydrofullerene **1** (20.0 mg, 0.0241 mmol) and 0.28 mL of a 0.0958 M solution of *t*-BuOK (0.027 mmol) in THF under argon. To this solution was added 0.40 mL (0.48 g, 3.4 mmol) of benzoyl chloride at 0 °C and the reaction mixture stirred at 0 °C for 1.5 h to give a dark brown suspension. Removal of the THF and excess benzoyl chloride under vacuum left a dark brown residue. The residue was dissolved in CS_2 and quickly passed through a short SiO_2 column for the purpose of purification. Evaporation of CS_2 gave 20.5 mg of a mixture containing **9** (84% yield as estimated by ^1H NMR) and **1** (7.3% yield as estimated by ^1H NMR), as a dark brown solid. Complete separation was unsuccessful owing to ready transformation of **9** to **1** during chromatography over either silica gel or deactivated alumina: mp > 300 °C; ^1H NMR (CS_2-CDCl_3 (1:1)) δ 8.55 (d, 2H, *o*-Ph), 7.60 (m, 3H, *m,p*-Ph), 2.43 (t, 2H, CH_2), 1.68 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.36 (m, 4H, CH_2), 0.92 (t, 3H, CH_3); ^{13}C NMR (C_6D_6) δ 194.16 (C=O), 152.82, 152.08, 151.97, 149.28, 149.11, 148.97, 148.77, 148.25, 147.87, 147.77, 147.56, 147.48, 147.33, 147.18, 146.84, 146.70, 146.52, 146.15, 145.87, 145.74, 145.65, 145.54, 145.02, 144.97, 144.74, 144.69, 144.66, 144.59, 144.46, 144.33, 144.10, 143.99, 143.79, 143.62, 143.57, 143.54, 143.46, 143.27, 143.09, 142.89, 142.80, 142.62, 143.58, 142.55, 142.46, 142.39, 142.30, 141.92, 141.77, 140.77, 139.22, 139.20, 139.12, 138.17 (54 signals, sp^2-carbons in the C_{60} core and *ipso* carbon), 133.21, 129.26, 128.64, (three signals, CH in phenyl group), 85.29 ($C\equiv C$), 77.07 ($C\equiv C$), 71.28, 62.37 (two signals, sp^3-C, in the C_{60} core), 31.71, 28.98, 28.89, 22.92, 19.46, 14.31 (six signals, *n*-hexyl); UV-vis (cyclohexane) λ_{max} (log ε) 212 nm (5.14), 257 (5.05), 325 (4.57), 434 (3.86), 680 (2.59); positive APCI MS *m/z* 934 (M^+), 830 ($M-COPh+H^+$), 720(C_{60}). Anal. Calcd for a mixture of **9** and **1** (molar ratio 92:8): C, 96.56; H, 1.91; O, 1.87. Found: C, 89.25; H, 1.78; O, 1.52.

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