

Preparation and Characterization of a Macro-cyclic Fullero-pyrrolidine

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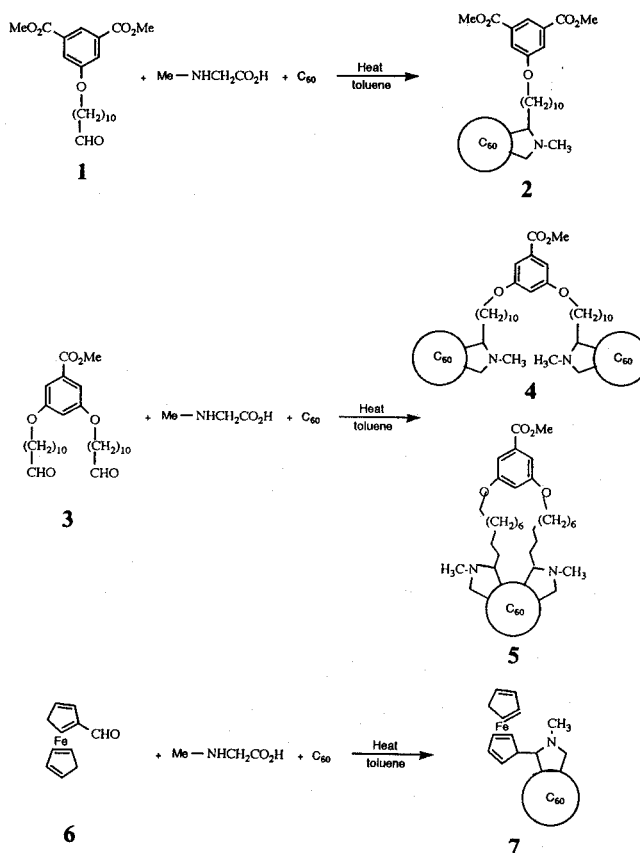
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After the discovery of fullerenes,¹ physical and chemical properties of fullerenes and their derivatives have been investigated by many research groups.² A lot of organic reactions with fullerenes have been performed to derivatize fullerenes and the resulting products show unique physical and chemical properties.³ Diels-Alder adducts,⁴ methano-bridged fullerenes from carbene addition reactions⁵ and five membered ring adducts synthesized by [3+2] cycloadditions of trimethylenemethanes,⁶ are examples of well characterized fullerene derivatives. Furthermore, a wide range of potential applications of fullerenes and their derivatives in material science have been unveiled.⁷ For instance, application to superconductor, optical devices, ferromagnetic materials, batteries, catalysts, sensors, and membrane are under investigation.

We have studied the photophysical and electrochemical properties⁸ of fullerenes. Especially electron transfer reactions with electropositive metals or some strong organic donor molecules are of great interest due to unique photophysical⁹ or electrochemical^{10,11} properties of fullerenes and their derivatives. The electrophilicity of fullerenes is recognized by electrochemical reductions. In the course of looking for the intramolecular electron transfer system of fullerenes connecting metal complexes by covalent bonds, we need to attach a long-alkyl chain to fullerenes. In this paper, we report some preliminary results on the preparation of novel macrocyclic fullero-pyrrolidine derivatives and their physical and electrochemical properties. A novel macrocyclic fullero-pyrrolidine **5** has been prepared (see Scheme). 1,3-Dipolar cycloaddition of azomethine ylide, in situ generated from sarcosine and aldehyde in refluxing toluene, to C₆₀ yields fullero-pyrrolidines.¹² The aldehydes used in this work are synthesized from corresponding alcohols, which are obtained by alkylation of phenols, for example, dimethyl 5-hydroxyisophthalate for **1** and methyl 1,3-dihydroxybenzoate for **3**, respectively. When C₆₀ is treated with the aldehyde **1** and sarcosine in refluxing toluene, the fullero-pyrrolidine **2** is obtained.¹² The crude product has been characterized by Matrix Assisted Laser Desorption Ionization-Mass Spectrometry (MALDI-MS) showing bis-, tris-, and tetra-adducts as well as mono-adduct.¹³ HPLC analysis of crude product shows 2 peaks. The mono-adduct is found in the second peak at retention time of 6.9



Scheme

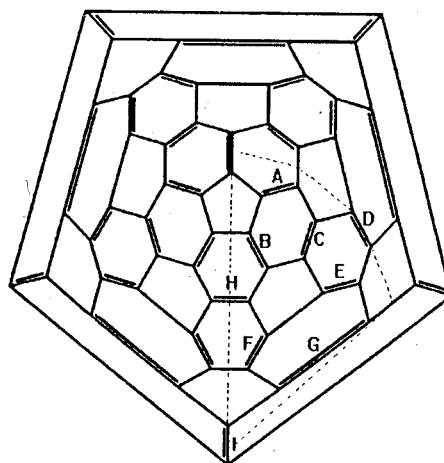


Figure 1. Nine possible binding positions(double bonds) of compound **5** regarding an arbitrary binding position that is marked as a bold line at the center of this diagram. Each conformer may represent three isomers considering relative position of alkyl chains in five-membered rings. The region enclosed by dotted lines connotes a quarter of C₆₀ necessary in considering relative binding positions along with symmetry.

min, while the first one with a shoulder at the retention time of 6.3 min contains multi-adducts.

In order to bind two C₆₀ molecules to a donor ligand, bisaldehyde **3** is employed expecting the one-to-two product **4**.¹² Rather MALDI-MS of the product purified by column chro-

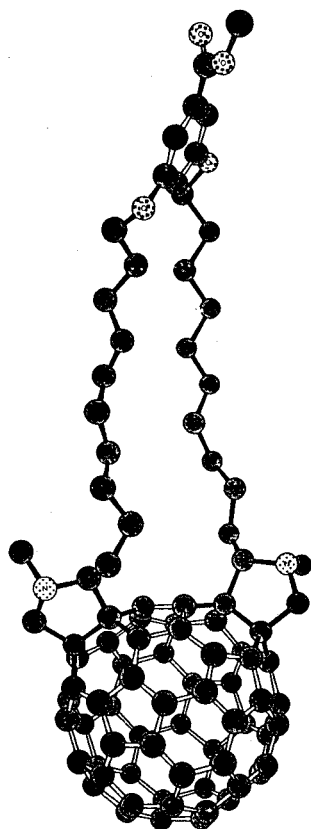


Figure 2. Semiempirical minimum energy structure calculated for **5** using Chem3D Plus showing the approximate dimension of the molecule.

matography shows one-to-one mono-adduct such as compound **5** and bis-adduct as well.¹³ The peak of $m/e=1282$ is considered as a molecular ion peak of **5**. Theoretically this one-to-one adduct has more than 27 isomers as shown in Figure 1 because each conformer may represent three regioisomers when counting relative position of alkyl chains in two five-membered rings into consideration (see Figure 2). Actually HPLC separation showed three peaks of monoadduct at retention times of 1.60, 1.89, and 2.53 min and each fraction showing identical mass spectrum seemed to show an isomer of a macrocyclic fulleropyrrolidine **5**. These isomers might be stable ones. In an effort to search for stable isomer, a computer simulation study is in progress using CERIU² (Molecular Simulations Inc.). Conformer E has the lowest ground state conformational energy while conformer I has the highest value even. Detailed results will be published elsewhere.¹⁴ Though it is not possible to assign the exact structures for three portions of HPLC separation, they are a mixture of various isomers of **5**. The known ferrocene fulleropyrrolidine **7** was prepared for spectroscopic and electrochemical comparison.¹¹

Compounds **2** and **5** were further characterized using spectroscopic means such as UV-Vis,¹⁵ NMR,¹⁶ and FT-IR¹⁵ and the results matched well. Electrochemical behaviors of **2**, **5**, and **7** in solution have been studied by Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV). All the experiments are performed in 1:3 CH₃CN/toluene solution, containing (n-Bu)₄NPF₆ (0.1 M) as a supporting electrolyte,

Table 1. Cathodic potential values (V vs Ag/AgCl) of DPV (scan rate: 20 mV/s) in 1:3 CH₃CN/toluene (0.1 M (n-Bu)₄NPF₆) at ambient condition under argon atmosphere

	Fc ⁺ /Fc	C ₆₀ /C ₆₀ ⁻	C ₆₀ ⁻ /C ₆₀ ²⁻	C ₆₀ ²⁻ /C ₆₀ ³⁻	C ₆₀ ³⁻ /C ₆₀ ⁴⁻
C ₆₀		-0.42	-0.85	-1.35	-1.79
2		-0.58	-1.01	-1.56	-2.00
5		-0.75	-1.19	-1.87	-2.34
7	0.58	-0.60	-1.02	-1.57	-1.99

with glassy carbon as the working electrode, a Pt counter electrode and a Ag/AgCl reference electrode under Ar at ambient condition. Reduction potential data between 1.0 and -2.6 V are shown in Table 1. Four peaks at -0.42, -0.85, -0.35 and -1.79 V are observed in C₆₀.¹⁰ Compound **7** shows four step reduction for C₆₀ moiety and one for ferrocene.^{10b} Four reduction peaks for **2** and **5** have been observed in the potential range investigated, respectively. It is known that loss of conjugation in C₆₀ moiety due to the saturation of double bonds causes negative shifts of reduction peaks.^{10b} As expected, reduction potentials for **2**, **5** and **7** are shifted to negative values compared to those of C₆₀. It is interesting to examine reduction potentials of three compounds closely. It is well understood that reduction potentials for **2** and **7** are very similar because both compounds have lost one double bond due to cycloaddition reactions. However, **5** has lost two double bonds comparing C₆₀ and thus the shift ($\Delta E_c = -35$ –55 mV) in cathodic potential is almost twice with respect to **2** or **7**. CV seemed likely to show that **5** exhibits irreversible redox peaks. Currently, reactivity of reduced species is under investigation. In addition, application to LB film with these materials is being carried out.

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References

1. Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
2. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *254*, 1186.
3. Hirsch, A., *The Chemistry of the Fullerenes*, Georg Thieme Verlag Stuttgart, New York, 1994.
4. Tsuda, M.; Ishida, T.; Nogami, T.; Kuronr, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296.
5. Vasella, A.; Uhlmann P.; Waldruff, C. A. A.; Diederich, F.; Thilgen C. *Angew. Chem. Int. Ed. Engl.* **1992**, *104*, 1383.
6. Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594.
7. Kroto, H. W.; Fisher, J. E.; Cox, D. E. *The Fullerenes*, 1st ed., Pergamon Press, Oxford 1993.
8. Seo, K.; Shin, M.; Jeon, I. C., submitted to *Bull. Kor. Chem. Soc.*

9. (a) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 3575. (b) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* **1992**, *114*, 5454. (c) Krusic, P. J.; Roe, C. D.; Johnston, E.; Morton, J. R.; Preston, K. F. *J. Phys. Chem.* **1993**, *97*, 1736.
10. (a) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. (b) Maggini, M.; Karlsson, A.; Scorrano, G.; Sandona, G.; Fania, G.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1994**, 589.
11. Maggini, M.; Scorrano, G. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
12. Preparation of compound **2**: To a solution of 29 mg (0.041 mmol) of C_{60} in 30 mL of toluene of 7 mg (0.082 mmol) of sarcosine and 31 mg (0.082 mmol) of **1** were added. After the resulting mixture was stirred at room temperature for 20 min under nitrogen, the mixture was heated to reflux under nitrogen for 43 hr. The solvent was removed in vacuo. The crude solid product was purified by flash chromatography on silica gel using a mixture n-hexane and toluene as eluent. The yield of **2** was 55% (based on the consumed C_{60}). Preparation of compounds **5** and **7**: The compounds were prepared by procedure as compound **2** (yield 77%). Physical Measurements UV-visible spectra were recorded in n-hexane at room temperature on a BECKMAN DU7500 Spectrophotometer. 1H NMR and ^{13}C NMR spectra of **2** and **5** were obtained in $CDCl_3$ and of **7** were obtained in $CDCl_3/CS_2=1:2$ (v/v) on an FT-NMR 400 MHz JEOL Spectrometer. MALDI-MS spectra were recorded on a Shimadzu Compact MALDI II Spectrometer. IR spectra were recorded on a Nicolet 5DXB FT-IR Spectrometer. CV and DPV were obtained in 1:3 acetonitrile-toluene (0.1 M (n-Bu) $_4$ NPF $_6$) at room temperature on a BAS 100B/W potentiostat. HPLC conditions; RP-18 Column, acetonitrile-toluene (6:4 v/v) (compound **2**); SIL-5B Column, methanol-dichloromethane (1:9 v/v) (compound **5**); SIL-5B Column, methanol-dichloromethane (1:9 v/v) (compound **7**).¹³ MALDI-MS for crude samples: 408 (M^+-720) (base peak), 1128 (M^+), 1536 (bisadduct), 1940 (trisadduct), and 2344 (tetraadduct) (compound **2**); 562 (M^+-720) and 1282 (M^+) (base peak) (compound **5**); 720 (C_{60}^+), 961 (M^+), 1097 (bisadduct-FeCp) (base peak), and 1205 (bisadduct) (compound **7**). Purified samples by HPLC show molecular ion peaks as base peaks.
13. Issacs, L.; Haldimann, R. F.; Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2339.
14. Hwang, S.; Lee, J. M.; Jeon, I. C. to be published.
15. UV-visible spectra(n-hexane) of **2** and **5** show the pyrrolidine derivative retains the main electronic features of C_{60} , except for a new band at 307 nm. FT-IR (dispersed on KBr plate), 1728 (C=O), 1243 (C-O), 1349 (C-N), 2931, 2853, 1595, 1433, 1180, 1117, 1053, 758, 716, 667, 561 and 519 cm^{-1} . (compound **2**).
16. 1H NMR (400 MHz) of **2**: δ 8.25 (ring CH), δ 4.03 (OCH $_2$), δ 4.0 (ring CH $_2$), δ 3.93 (CO $_2$ Me), δ 2.98 (N-CH $_3$), δ 1.76 (CH $_2$ -pyrrolidine, broad), δ 1.25 ((CH $_2$) $_8$, multiplet). ^{13}C NMR of **2**: δ 159.1, δ 122.7, δ 119.8, δ 131.6 (ring C), δ 166.2 (-CO $_2$ -), δ 52.3 (-Methyl), δ 68.5 (ring CH $_2$), δ 70.3 (ring CH), δ 40.0 (-NCH $_3$), the signals of C_{60} are scattered between 142.1 ppm and 146.5 ppm. 1H NMR

and ^{13}C NMR of **5**: similar signal pattern was appeared. Regarding **7**, results matched the previously published data well.

NMR Study on Dynamics of Double Helical d(GCGCGCGC) $_2$ and Its Complex with Berenil

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Since Pohl and Jovin reported that poly(dG-dC)·poly(dG-dC) showed quite a different CD spectrum from that of a regular B-DNA structure at high NaCl concentration,^{1,2} lots of studies have been carried out in order to investigate the effects of the base sequences and the buffer conditions on the transition between B- and Z-DNA.³⁻⁸ The GpC or CpG rich region appears frequently in the genomic DNA and the structural flexibility of this region is regarded to play an important role in gene expression.^{9,10}

In this study, we have prepared a self-complementary, synthetic oligonucleotide d(GCGCGCGC) containing the GpC sequences associated with the B-Z transition and have studied the dynamics of the d(GCGCGCGC) $_2$ double helix and its

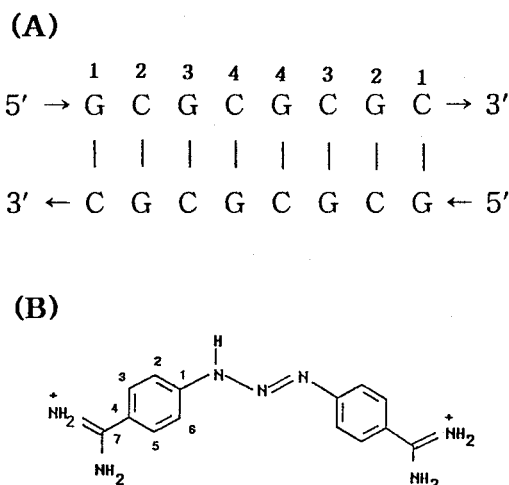


Figure 1. structure of the duplex d(GCGCGCGC) $_2$ (A) and berenil(B).

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