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The First Fullerene(C₆₀)-Substituted [2.2](2,7)Fluorenophane

Kwang-Yol Kay^{*}, In Chul Oh

Department of Chemistry, Ajou University, Suwon 442-749, KOREA

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Abstract : The fullerene(C_{60})-substituted [2.2](2,7)fluorenophane 1 was synthesized and spectroscopically characterized. © 1999 Elsevier Science Ltd. All rights reserved.

Our interest in the aesthetically "charming ring" structure of the target compound 1 as well as its possibility of intramolecular charge transfer interactions has prompted us to synthesize the first [2.2]cyclophane that contains a covalently bound fullerene moiety as functional group.



The most straightforward preparation of 1 can be envisaged to proceed through a reaction sequence of the following 11 steps (scheme 1). The first part of the sequence consist of synthesizing the precursor cyclophane 9, which carries solubilizing alkyl-groups in order to obtain a more easily characterizable C_{60} -derivative 1. This was achieved using a typical method of cyclophane synthesis^{1,2} involving cyclization, oxidation and pyrolysis. The second part of the sequence was designed on the basis of the well-documented reactivity of C_{60} towards diazoalkanes already made accessible through a simple and reproducible route.^{3,4} The

cyclopropane bonds (ring closed "methano-fullerene") thus obtained, connecting the C₆₀ and the fluorenophane are expected to exhibit a high π character as already known structures.⁵⁻⁷ This would allow conjugate interaction between the fluorenophane and the fullerene pendant.



SCHEME 1 (R=C₈H₁₇)

a) 1.n-BuLi, $C_8H_{17}Br$ 2. n-BuLi, $C_8H_{17}Br$ b) Br_2 , DMF c) 1.n-BuLi, $(CH_2O)_n$, 2. ether, NaOH, reflux d) PBr_3, THF e) 2,7-bis-(mercaptomethyl)fluorene, K_2CO_3 , EtOH f) mCPBA, CHCl₃ g) pyrolysis at 10⁻³Torr, 750°C, 3 minutes h) Triton B, pyridine i) p-toluenesulfonhydrazide, THF, 20 h reflux j) NaOH, MeOH, CHCl₃, 35 h reflux k) C_{60} , toluene, 30 h, r.t.

Double alkylations of commercially available fluorene (2) gave 3 almost quantitatively. Bromination of 3 proceeded with bromine in DMF at room temperature to afford 4 in 92 % yield. Hydroxymethylation of 4 with n-BuLi and paraformaldehyde provided 5 in 49 % yield and then its hydroxymethyl groups were converted to bromomethyl groups by treatment with PBr₃ in THF, affording 6 in 85 % yield. Subsequently, dropwise addition of a dilute methanolic solution of 6 and 2,7-bis(mercaptomethyl)fluorene⁸ to hot alcoholic K₂CO₃ under dilute conditions gave the dithiaphane 7 in 63 % yield as a major fraction after column chromatography. Oxidation of 7 with mCPBA provided the disulfone 8 in a yield of 92 %, pyrolysis of

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which at 700 $^{\circ}$ and 10⁻³ torr for 3 minutes (so-called "shock pyrolysis")¹ gave the precursor cyclophane 9⁹ as a cold-trap condensate in 25 % yield.

From ¹H- and ¹³C-NMR data of 9, it is evident that compound 9 exists in anti-form, which is also in good agreement with the assignments of analogous anti-[2.2](2,7)fluorenophanes by Haenel;⁸ the chemical shift and splitting patterns of the cyclophane ring protons are diagnostic of this. Compound 9 thus obtained was then oxidized with Triton B in pyridine to give 10⁹ as a yellow crystalline solid in 42 % yield. Conversion of 10 with p-toluenesulfonhydrazide went smoothly to afford pale yellow crystalline tosylhydrazone 11⁹ in a yield of 79 %. Treatment of 11 with NaOH produced the diazo derivative 12, which is unstable under air, and after identification of 12 by IR-band (2054 cm⁻¹, N₂) we allowed 12 to react with 1.4 equivalents of C₆₀ in toluene at room temperature for 24 hours and then refluxed for 24 hours. This led to the thermodynamically favored product 1,⁹ which has the structure of a closed 6,6-bridged methanofullerene : FAB-mass spectrum of 1 showed peaks at m/z = 1327(M⁺) and 720(C₆₀). This provided a direct evidence for the addition of the fluorenophane moiety to the fullerene. ¹H-NMR spectrum of 1 showed the typical resonance signals of the cyclophane moiety. However, the aromatic protons nearest to the C₆₀ spheroid were shifted slightly to the downfield in comparison to 9 and 10.

The ¹³C-NMR signals of aromatic carbons of fluorenophane system were not markedly affected by substitution of C₆₀. However, the signals between $\delta = 140$ and 150 result from the superimposition of fluorenophane ($\delta = 142.95$ in 9) and fullerene carbon atoms. The complex pattern of signals in which two main peaks emerge at 143.1 and 144.6 was assigned to the C₆₀ moiety. This assignment is in good agreement with the previously reported assignments.^{10,11} The resonance peak of the bridgehead carbon in 1 appeared at $\delta = 78.03$ which lies in the usual region (70-90 ppm) of bridgehead carbons for methanofullerenes.^{10,11} These patterns of signals are unambiguously diagnostic for the structure with a 6,6-junction. In addition, the signal for the quaternary spirocarbon in 1 appeared at $\delta = 51.90$ as a distinct peak.

The UV/Vis spectrum of 1 has some significant differences in comparison with 9, but resembled those of other methanofullerene derivatives,^{11,12} showing the characteristic absorption bands for the methanofullerenes at 438, 495 and 695.7 nm, which newly appeared due to the incorporation of C_{60} into 9. Besides these bands, the band at 271.2 nm in 9 is shifted hypsochromicly to 259.4 nm in 1, while the two bands at 306.4 and 316.9 nm in 9 are bathochromically shifted, making a band at 325.8 nm in 1. This shifting phenomenon of the latter bands to the longer wavelength can be attributed to the intramolecular charge transfer interaction between the two moieties However, possibilities of the involvement of complex periconjugation effects,¹²⁻¹⁴ occurred especially when the fluorene rings in the molecule are held perpendicular to the C_{60} spheroid, can not be excluded.

The electrochemistry and the x-ray structural study of the compound 1 are currently under investigation, and we are also working on synthesis of the analogous cyclophanes based on both fullerenes and fluorenes.

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9 : m.p. 132 °C. FT-IR: $\nu = 3025$, 3005, 2952, 2925, 2850, 1603, 1469 cm⁻¹. ¹H-NMR(CDCl₃): $\delta = 7.40-7.20$ (m, 4H), 7.00-6.90(m, 4H), 6.25(d, 4H), 3.40-3.00 (m, 5H), 2.90-2.40 (m, 5H), 1.70 -0.70(m, 34H) ¹³C-NMR(CDCl₃): $\delta = 153.10$, 142.95, 137.57, 137.14, 136.94, 128.89, 127.31, 125.75, 125.56, 125.49, 120.01, 118.23, 52.12, 36.69-14.05 (19 peaks) UV/Vis (cyclohexane) : λ_{max} [nm]=271.2 (log $\varepsilon = 4.68$), 306.4(4.17), 316.9(4.76) at 4.90 × 10⁻⁵M. Satisfactory C,H analysis for C₄₆ H₅₀.

10 : m.p. 80-82 °C. FT-IR: $\nu = 1725$ cm⁻¹. ¹H-NMR(CDCl₃): $\delta = 7.40$ (d, 2H), 7.10-6.90 (m, 6H), 6.40 (s, 2H), 6.30 (s, 2H), 3.40-3.00 (m, 4H), 2.90-2.40 (m, 4H), 1.70-0.70 (m, 34H). UV/Vis(cyclohexane) : $\lambda_{max}[nm]=213$ (log $\varepsilon = 4.71$), 260(4.77), 303(4.04), 313(4.02), 413(2.75) at 5.00 × 10⁻⁵M. Satisfactory C,H analysis for C₄₆ H₅₄O.

11 : m.p. 151-161 °C. FT-IR: $\nu = 3211,1320,1165$ cm⁻¹. ¹H-NMR(CDCl₃): $\delta = 8.10$ (d, 2H), 7.90 (s, 1H), 7.45 (d, 2H), 7.10-6.60 (m, 8H), 6.40 (s, 1H), 6.20 (d, 2H), 3.40-3.00(m, 4H), 3.00- 2.70 (m, 7H), 1.70-0.70 (m, 34H). Satisfactory C,H analysis for C₅₃ H₆₂N₂O₂S.

1 : m.p. >330 °C. FT-IR: $\nu = 3068, 3042, 3012, 2924, 2853$ cm⁻¹. ¹H-NMR(CDCl₃ : CS₂ = 1 : 3): $\delta = 7.60-7.40$ (m, 6H), 7.12 (d, 2H), 6.88 (d, 2H) 6.40 (s, 2H), 3.40-3.15 (m, 4H), 3.00-2.70 (m, 4H), 1.80-0.70 (m, 34H). ¹³C-NMR (CDCl₃ : CS₂ = 1 : 3): $\delta = 152.80, 148.88, 147.80, 145.02-140.67$ (17 peaks), 138.34, 137.87, 137.79, 137.74, 137.48, 136.68, 127.55, 127.18, 126.98, 126.10, 120.18, 119.44, 78.03, 51.90, 39.55-14.15 (18peaks). UV/Vis(cyclohexane) : λ_{max} [nm]=259.4 (log $\varepsilon = 5.14$), 325.8(4.60), 438(3.72)495(3.64), 695.7(3.28) at 9.03 × 10⁻⁶M. FAB-MS : m/z 1227(M⁺) 720(C₆₀). Satisfactory C,H analysis for C₁₀₈H₃₄

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