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The First Fullerene(C_{60})-Substituted [2.2](2,7)Fluorenophane

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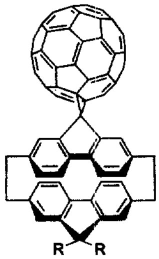
Abstract : The fullerene(C_{60})-substituted [2.2](2,7)fluorenophane **1** was synthesized and spectroscopically characterized.

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.



1 ($R=C_8H_{17}$)

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

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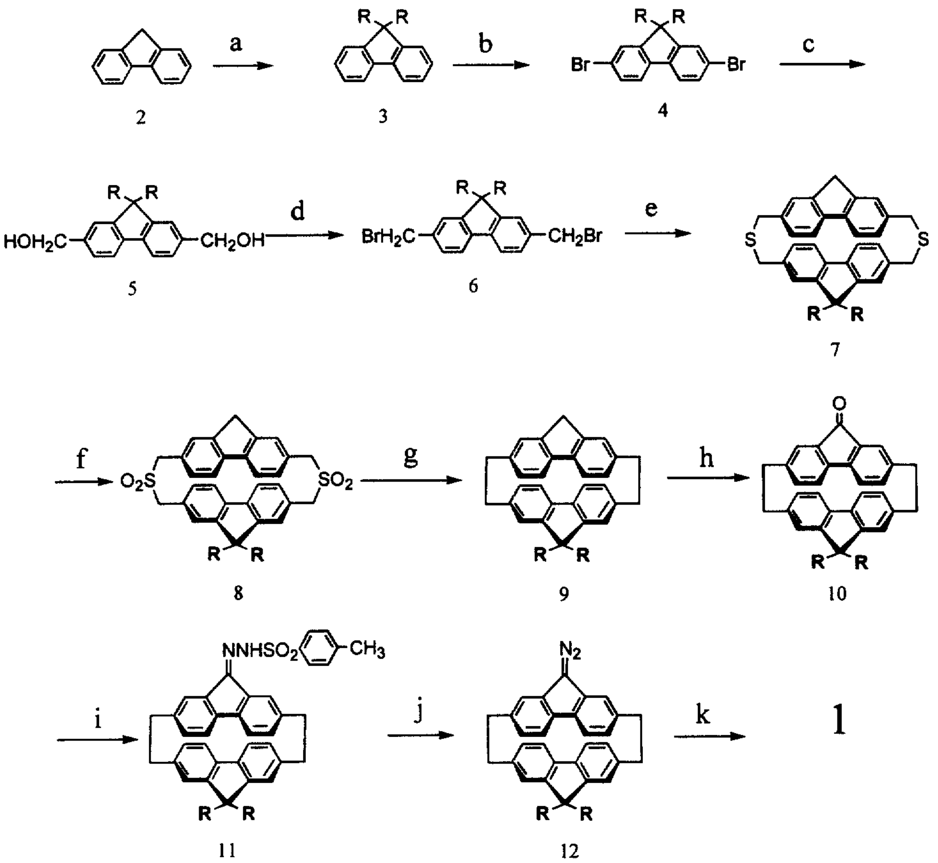
cyclopropane bonds (ring closed "methano-fullerene") thus obtained, connecting the C_{60} and the fluorenophane are expected to exhibit a high π character as already known structures.[5-7] This would allow conjugate interaction between the fluorenophane and the fullerene pendant.



SCHEME 1 ($R=C_8H_{17}$)

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, $CHCl_3$ g) pyrolysis at 10^{-3}Torr, 750°C, 3 minutes h) Triton B, pyridine i) p-toluenesulfonhydrazide, THF, 20 h reflux j) NaOH, MeOH, $CHCl_3$, 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 PBr_3 in THF, affording **6** in 85 % yield. Subsequently, dropwise addition of a dilute methanolic solution of **6** and 2,7-bis(mercaptomethyl)fluorene[8] to hot alcoholic K_2CO_3 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 which at 700 ℃ and 10^{-3} torr for 3 minutes (so-called "shock pyrolysis")[1] gave the precursor cyclophane **9**[9] as a cold-trap condensate in 25 % yield.

From ^{1}H- and ^{13}C-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 **10**[9] as a yellow crystalline solid in 42 % yield. Conversion of **10** with p-toluenesulfonhydrazide went smoothly to afford pale yellow crystalline tosylhydrazone **11**[9] 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}, N_2) we allowed **12** to react with 1.4 equivalents of C_{60} 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(C_{60}). This provided a direct evidence for the addition of the fluorenophane moiety to the fullerene. ^{1}H-NMR spectrum of **1** showed the typical resonance signals of the cyclophane moiety. However, the aromatic protons nearest to the C_{60} spheroid were shifted slightly to the downfield in comparison to **9** and **10**.

The ^{13}C-NMR signals of aromatic carbons of fluorenophane system were not markedly affected by substitution of C_{60}. However, the signals between δ = 140 and 150 result from the superimposition of fluorenophane (δ = 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 C_{60} 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 δ = 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 δ = 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] Selected physical data of **9-11** and **1**

9 : m.p. 132℃. FT-IR: ν =3025, 3005, 2952, 2925, 2850, 1603, 1469 cm^{-1} . ^{1}H-NMR($CDCl_3$): δ = 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) ^{13}C-NMR($CDCl_3$): δ =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 ε = 4.68), 306.4(4.17), 316.9(4.76) at 4.90 × 10^{-5}M. Satisfactory C,H analysis for $C_{46}H_{56}$.

10 : m.p. 80-82℃. FT-IR: ν =1725cm^{-1}. ^{1}H-NMR($CDCl_3$): δ =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) : λ_{max}[nm]=213 (log ε = 4.71), 260(4.77), 303(4.04), 313(4.02), 413(2.75) at 5.00 × 10^{-5}M. Satisfactory C,H analysis for $C_{46}H_{54}O$.

11 : m.p. 151-161 ℃. FT-IR: ν =3211,1320,1165 cm^{-1} . ^{1}H-NMR($CDCl_3$): δ =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 $C_{53}H_{62}N_2O_2S$.

1 : m.p. >330 ℃. FT-IR: ν = 3068, 3042, 3012, 2924, 2853 cm^{-1} . ^{1}H-NMR($CDCl_3$: CS_2 = 1 : 3): δ =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). ^{13}C-NMR ($CDCl_3$: CS_2 = 1 : 3): δ =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 ε = 5.14), 325.8(4.60), 438(3.72)495(3.64), 695.7(3.28) at 9.03 × 10^{-6}M. FAB-MS : m/z 1227(M^+) 720(C_{60}). Satisfactory C,H analysis for $C_{106}H_{54}$

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