Benzoquinone-Linked Fullerenes with a Pyrrolidine Spacer

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The synthesis of 1,4-benzoquinone-linked fullerenes (1 and 2) and an attempted synthesis of 1,2-benzoquinone-linked fullerenes (9 and 10) are described with the interesting redox behavior of these benzoquinone-linked fullerenes.

We have recently reported the [2+3] cycloaddition reactions of C_{60} with α-silylamine derivatives to produce pyrrolidine- and 1-pyrroline-fused fullerenes.[1] Our continuing interests in the interaction between C_{60} and 1,4-benzoquinones[2] prompted us to investigate the benzoquinone-linked fullerenes with a pyrrolidine spacer, i.e., 1 and 2. As shown in Figure 1a, the intramolecular distances between the C_{60}- and quinone-sp^2-carbons are 2.8-3.4 Å. Therefore, a π-π interaction between π-electrons of the C_{60} and quinone moieties in 1 and 2 can be expected.
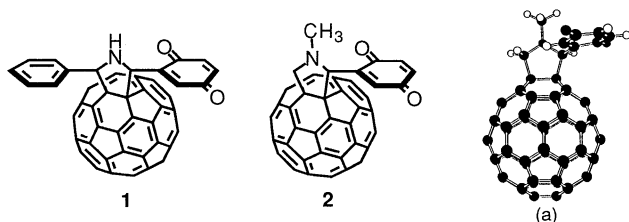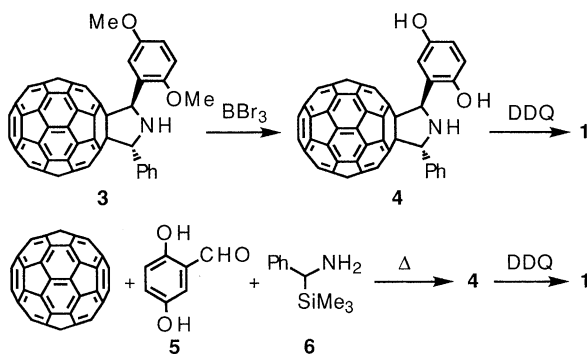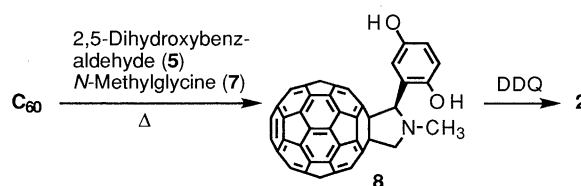

Figure 1. (a) AM1 optimized structure of 2.

For the synthesis of 1, we developed two methods as shown in Scheme 1. The first method starts from 3.[1] The reaction of 3 with excess amounts of BBr₃ in benzene at 5-7 °C for 30 min gave a mixture of the hydroquinone (4) and by-products which were hardly separable. The oxidation of the crude 4 with excess amounts of DDQ in benzene-ethyl acetate produced the desired 1 in 34% yield based on 3.[3] As for the second method, the direct reaction of C_{60} with 2,5-dihydroxy-benzaldehyde (5) and α-trimethylsilylbenzylamine (6)[4] in o-dichlorobenzene at 160-170 °C for 24 h produced the hydroquinone 4 (30%), which was oxidized with DDQ to give 1 in 50% yield.
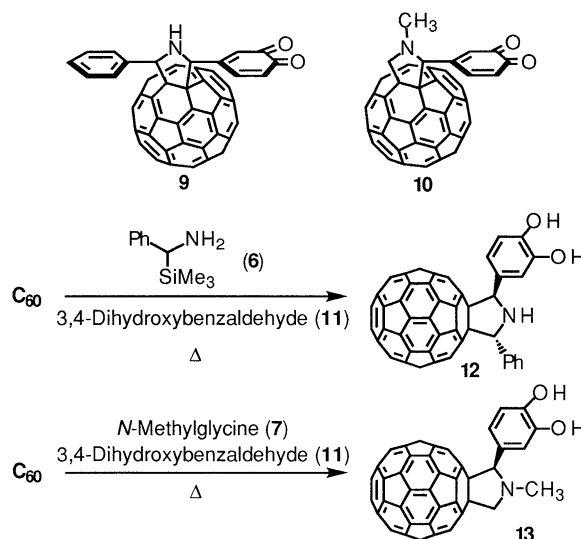

Scheme 1.

Syntheses of many *N*-methyl-fulleropyrrolidine derivatives have been reported by Prato and Maggini.[5] However, no

benzoquinone-linked fulleropyrrolidine has been reported until now. Therefore, we worked on the benzoquinone-linked molecule 2 using Prato-Maggini's method. The reaction of C_{60} with 5 (4 equiv.) and *N*-methylglycine (4 equiv.) in refluxing toluene for 48 h produced the [2+3] cycloadduct 8 in 23% yield with the recovered C_{60} (51%). Although the hydroquinone (8) was hardly soluble in common organic solvents, 8 could be satisfactorily oxidized with DDQ in toluene-ethyl acetate for 3 h at room temperature to lead to the desired 2 in 38% yield.

Scheme 2.

Since 1,2-benzoquinone shows interesting electronic properties, we attempted the synthesis of the 1,2-benzoquinone-linked fulleropyrrolidines (9 and 10). As shown in Scheme 3, the reaction of C_{60} with 3,4-dihydroxybenzaldehyde (11) and 6 in o-dichlorobenzene at 180-190 °C for 24 h produced the 1,2-hydroquinone derivative 12 (60%). A similar reaction of C_{60} with 11 and 7 in refluxing toluene gave the cycloadduct 13 in 76% yield. The oxidation of 12 and 13 with excess amounts of DDQ at room temperature produced the products which might be assigned to the 1,2-quinone derivatives (9 and 10).[6] The isolation and characterization of 9 and 10 are now under investigation.
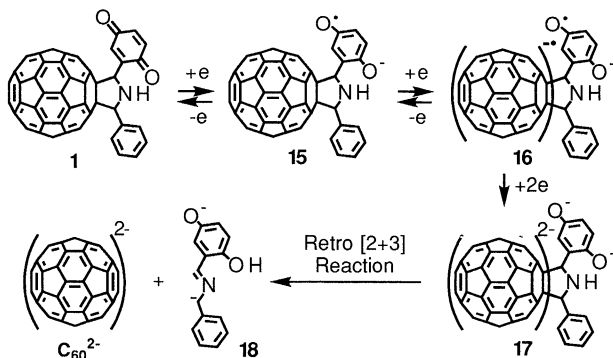

Scheme 3.

In order to examine the redox behavior of the new fullerenes, the reduction potentials of 1,4-benzoquinone (14),

C₆₀, **1**, and **2** were measured by cyclic voltammetry (Table 1). Although the 1,4-benzoquinone-linked fulleropyrrolidine **2** showed five reversible redox waves corresponding to the reduction of the 1,4-benzoquinone and fullerene moieties, **1** was found to be unstable under the redox conditions. Thus, the first and second redox waves of **1** were reversible, but the third, fourth and fifth waves were not clear and were irreversible. Interestingly, the cyclic voltammogram of **1** gradually changed to that of C₆₀ after several scannings swept from 0 to -2.0 V. The decomposition of **1** by the electrochemical reduction can be explained as follows. As shown in Scheme 4, the first step [$E_{red}^1(Q)$] is the reduction of the 1,4-benzoquinone moiety to the corresponding semiquinone radical **15**. The second reduction [$E_{red}^1(C_{60})$] corresponds to the reduction of the fullerene moiety to the fullerene anion radical **16**. The third and fourth reductions seem to form the hydroquinone-fullerene tetraanion **17** which may be destabilized either by the acidic hydrogen (N-H) or by the electronic interaction between the fullerene dianion and the hydroquinone dianion. Thus, the acidic hydrogen bound to nitrogen of the pyrrolidine ring in **17** may be quenched by the hydroquinone dianion, and the retro [2+3] reaction occurs to produce **18** and C_{60}^{2-}.

Table 1. Cyclic voltammetric data of 1,4-benzoquinone (**14**), C₆₀ and fullerenes (**1** and **2**) (V)[a]

Compound	$E_{red}^1(Q)$	$E_{red}^1(C_{60})$	$E_{red}^2(C_{60})$	$E_{red}^2(Q)$	$E_{red}^3(C_{60})$
14	-1.00			-1.85	
C₆₀		-1.12	-1.52		-1.98
1	-1.00	-1.15	_b	_b	_b
2	-0.93	-1.26	-1.61	-1.83	-2.20

[a]Conditions: n-Bu₄NPF₆ (0.05 mol dm⁻³), 1,2-dichlorobenzene, 25 °C, glassy carbon working and Pt counter electrodes, 100 mV s⁻¹. Potentials were measured vs Fc/Fc⁺ using Ag/Ag⁺ reference electrode. [b]Not observed.

Scheme 4.

Since the redox potentials of the benzoquinone-linked fullerene (**2**) show the interaction between the benzoquinone and fullerene moieties, the ab initio calculations on **2** and its mono-anion (**19**) have been carried out.[7] Although the LUMOs of the C₆₀ and benzoquinone moieties in **2** keep their own properties unchanged, some charge transfer can be calculated as shown in Figure 2. Thus, **2** shows a partial charge transfer from the amino group to the C₆₀ core, and the benzoquinone moiety remains unchanged. In the case of the monoanion **19**, a fairly large charge transfer occurs from the amino group (0.200) and the semiquinone moiety (0.103) to the C₆₀ core.
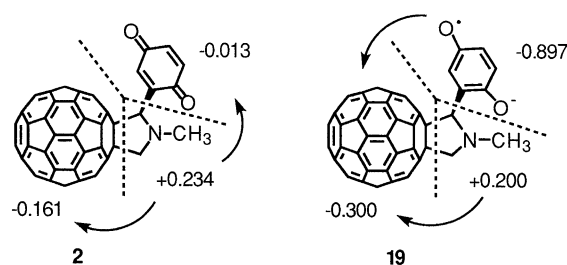

Figure 2. Calculated charge density in **2** and **19**.

The redox behavior of **1** and **2** shown in Table 1 agrees with the MO calculations. The first redox potential of **2** shows a positive shift, reflecting the lowering of the LUMO level which mainly belongs to the benzoquinone moiety. The amino groups in **2** and **19** act as a π-donor to the C₆₀ core, and a similar effect in **1** and **15-17** may increase the acidity of the amino-proton. Consequently, the interaction between the amino-proton and the hydroquinone dianion may result in the retro [2+3] reaction very easily to produce C_{60}^{2-} and **18**.

References and Notes
1 M. Iyoda, F. Sultana, and M. Komatsu, *Chem. Lett.*, **1995**, 1133.
2 M. Iyoda, F. Sultana, S. Sasaki, and M. Yoshida, *J. Chem. Soc., Chem. Commun.*, **1994**, 1929.
3 The structures of all new compounds reported here were fully characterized by the spectroscopic analysis. The selected data are as follows. **1**: black fine cryst., mp 130-140 °C (decomp); FAB-MS (m/z) 946 (M⁺+1); ¹H NMR (acetone-d₆/CS₂) δ 3.76 (s, 1H, NH), 5.95 (s, 1H, CH), 6.14 (s, 1H, CH), 6.76-6.84 (m, 2H, quinone CH), 7.28 (t, J = 7.3 Hz, 1H, p-Ph), 7.36 (t, J = 7.6 Hz, 2H, m-Ph), 7.62 (d, J = 2.4 Hz, 1H, quinone CH), 7.89 (d, J = 8.3 Hz, 2H, o-Ph); UV-vis (C₆H₁₂) λmax (ε) 268 (94800), 311 (43000), 326 (44500), 428 (649), 685 (226), 696 (711). **2**: black fine cryst., mp 200 °C (decomp.); MS (m/z) 885 (M⁺+2); ¹H NMR (CDCl₃/ CS₂) δ 2.81 (s, 3H, CH₃), 4.32 (d, J = 9.5 Hz, 1H, CH₂), 4.93 (d, J = 9.5 Hz, 1H, CH₂), 5.29 (s, 1H, CH), 6.80 (dd, J = 10.1, 2.4 Hz, 1H, quinone CH), 6.83 (d, J = 10.1, 1H, quinone CH), 7.35 (d, J = 2.4 Hz, 1H); UV-vis (CH₂Cl₂) λmax (ε) 310 (35800), 322 (36000), 429 (5120), 686 (486), 698 (530). **4**: black fine cryst., mp 200 °C (decomp.); FAB-MS (m/z) 947 (M⁺); ¹H NMR (acetone-d₆/CS₂) δ 4.50 (br. s, 1H, NH), 5.96 (s, 1H, CH), 5.97 (s, 1H, CH), 6.55-6.58 (m, 2H, hydroquinone CH), 6.91 (br. s, 1H, hydroquinone CH), 7.31 (t, J = 7.5 Hz, 1H, p-Ph), 7.41 (t, J = 7.5 Hz, 2H, m-Ph), 7.85 (d, J = 7.5 Hz, 2H, o-Ph). **8**: black fine cryst., mp 220 (decomp); FAB-MS (m/z) 885 (M⁺); ¹H NMR (CDCl₃/CS₂) δ 2.97 (s, 3H, CH₃), 4.26 (d, J = 10.1, 1H, CH₂), 4.30 (s, 1H, OH), 4.98 (s, 1H, CH), 5.05 (d, J = 9.8, 1H, CH₂), 6.67 (dd, J = 8.6, 2.8 Hz, 1H, hydroquinone CH), 6.73 (d, J = 8.6, 1H, hydroquinone CH), 6.82 (d, J = 2.8, 1H, hydroquinone CH), 10.47 (s, 1H, OH).
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6 The 1,2-quinone derivatives (**9** and **10**) were unstable to atmospheric oxygen, acids, and base.
7 The calculations were carried out at the HF/6-31G level on the AM1 optimized geometries using the GAUSSIAN 94 program. The split valence 6-31G basis set on O was augmented by the diffuse s and p functions (exponent 0.0945).