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MONO- and DIANION OF BENZOQUINONE-LINKED [60]FULLERENE

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Abstract: Reduction of the benzoquinone-linked [60]fullerene first gives the monoanion containing the semiquinone-radical and C_{60} moieties. The further reduction of the monoanion produces the dianion containing the semiquinone-radical and C_{60}-anion moieties. The EPR spectra of the dianion clearly show the triplet interaction between the semiquinone and C_{60} radical anions.
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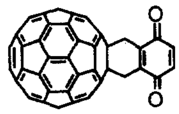
The interaction between C_{60} and alkali metals or π-donors has attracted much attention, because it is known to lead to superconductivity and ferromagnetic behavior.[1] Thus, a variety of fullerene derivatives covalently linked to π-donors,[2] organic radicals,[3] organometallic complexes,[4] and porphyrins[5] has been synthesized in order to examine the intramolecular interactions between the C_{60} core and its substituents. However, the intramolecular interaction between the C_{60} moiety and π-donor groups in these molecules has been observed only in limited cases, although the detectable electron transfer and spin-spin interactions in the donor- or radical-linked fullerenes have been reported under irradiation of UV-vis light.[2e, 3a, 5] Recently, the electrochemical evidence for through-space interactions in spiromethanofullerenes has been reported and the periconjugation has been clarified between the C_{60} core and the electron withdrawing π-systems.[6]

Previously we reported the synthesis and some properties of the C_{60} derivative covalently linked to 1,4-benzoquinone **1**.[7] We intuitively assumed that the first reduction in **1** occurs in the 1,4-benzoquinone part to give **2**, followed by the reduction of the C_{60} moiety to produce **3**. However, there is another possibility for the reduction which leads to the mono- and dianions (**4** and **5**). In order to clarify the LUMO-levels in **1**, the synthesis of **6** was carried out.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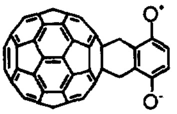
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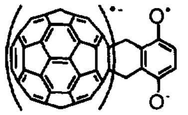
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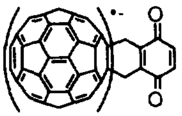
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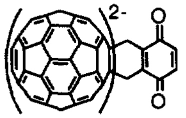
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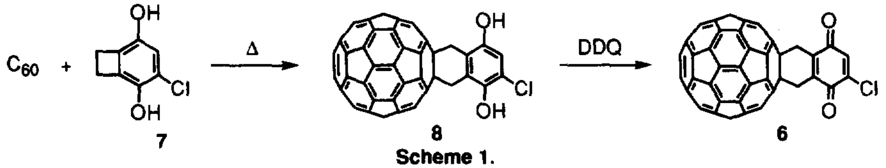
As shown in Scheme 1, the thermal [4+2]cycloaddition of **7** to C_{60} (1 equiv.) in *o*-dichlorobenzene at 240 °C for 24 h produced the 1:1 adduct **8** in 36% yield with a mixture of di- and triadducts, and the 37% yield of C_{60} was recovered unchanged. Oxidation of **8** with DDQ (2 equiv.) in benzene at room temperature for 15 min afforded the desired **6** in a quantitative yield as an air-stable crystalline solid.[8]



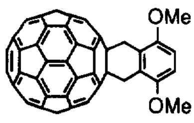
Scheme 1.

The redox potentials of **1**, **6**, **9**, C_{60}, 1,4-benzoquinone (**11**), and **12** measured by cyclic voltammetry are summarized in Table 1. The potentials were measured in *o*-dichlorobenzene as a solvent in order to minimize the solvent effect on the redox potentials. All compounds except for benzoquinones (**11** and **12**) showed three or five reversible electroreductions by cyclic voltammetry. As for 1,2-dihydrofullerenes, a 100 mV negative shift relative to C_{60} was reported for the first and second reduction potentials.[9] Therefore, the potentials (-1.22, -1.22, and -1.24 V for **1**, **6**, and **9**) are assigned for the reduction of the C_{60} moiety to its radical anion such as **10**. The potentials (-1.02 and -0.86 V for **1** and **6**) can be regarded as the reduction of the benzoquinone part to the semiquinone radical, although the reduction potentials of the quinone part in **1** are more positive than those of **12** and rather similar to those of **11**. As expected by a lowering of the LUMO level, the chlorine-substitution in **6** changes two reduction potentials of the quinone part to the more positive ones.

Table 1. Redox potentials (V) of **1**, **6**, **9**, **11**, **12**, and C_{60}.[a]

Compound	E_{red}^1(quinone)	$E_{red}^1(C_{60})$	$E_{red}^2(C_{60})$	E_{red}^2(quinone)	$E_{red}^3(C_{60})$
11	-1.00			-1.85	
12	-1.28			-2.00	
C_{60}		-1.12	-1.52		-1.98
9		-1.24	-1.62		-2.19
1	-1.02	-1.22	-1.63	-1.99	-2.28
6	-0.86	-1.22	-1.62	-1.82	-2.28

[a] Conditions: n-Bu_4NPF_6 (0.05 mol l^{-1}), 1,2-dichlorobenzene, 22 °C, glassy carbon working and Pt counter electrodes. Potentials were measured *vs* Fc/Fc^+ using Ag/Ag^+ reference electrode. [b] Scan rate: 10 mV s^{-1}. [c] Scan rate: 100 mV s^{-1}.



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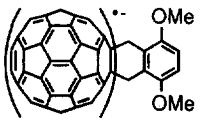

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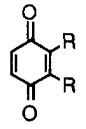

11: R = H
12: R = Me

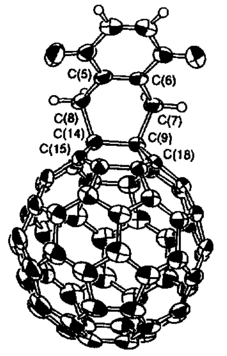

Fig. 1. Molecular structure of **1**; selected bond lengths [Å] and angles [°]: C5-C6 1.328(2), C6-C7 1.495 (2), C7-C9 1.573(2), C9-C14 1.593(2), C9-C18 1.538(2); C5-C6-C7 118.2(2), C6-C7-C9 110.0(2), C7-C9-C14 111.0 (1), C7-C9-C18 109.1(1).

As shown in Fig. 1, the structure of **1** was determined by X-ray analysis.[10] When **1** was crystallized from benzene, black prisms of **1**•benzene (1:1) were obtained. The structure of **1** confirms the expected bridging at the 6-6 ring junction, closely resembling those of *o*-xyleno-bridged fullerenes except for some structural features.[2b] The cyclohexene ring adopts a boat conformation with an angle of 128.19°, and the average intramolecular distance between C(5) and C(15) or C(6) and C(18) is 3.140 and 3.143 Å, respectively. Therefore, a π-π interaction between π-electrons of the C_{60} and quinone moieties in **1** can be expected. There are some close intermolecular contacts between fullerene C-atoms in the crystal, the shortest contact being 3.06 Å.

Although the reduction of C_{60} with alkali metals has been investigated extensively, little has been reported on the alkali-metal reduction of fullerene derivatives covalently linked to organic substituents. The ab initio MO calculations on the fullerene derivative **1** and its anions (**2**, **4** and **5**) show novel electronic properties.[11] The LUMO levels of the C_{60} and benzoquinone moieties in **1** are calculated to be almost the same, and the orbitals of both the C_{60} and benzoquinone moieties keep their own properties unchanged. Consequently, **1** shows only a partial charge-transfer of 0.16 from the quinone part to the C_{60} core. In the case of the monoanions (**2** and **4**), the calculated charge-transfer from the semiquinone part to the C_{60} core in **2** is fairly large (0.34), whereas a small charge-transfer (0.06) in **4** occurs from the quinone part to the C_{60}^- core.

The monoanion **2** is stabilized by 23.6 kcal/mol as compared with **4**. The semiquinone and C_{60} moieties in **2** keep their own properties of MO, and 99.5% of the spin density of the semiquinone part localizes in its own orbital. In the case of the dianion **3**, a similar charge-transfer (0.24) is calculated from the semiquinone to C_{60}^- moieties, leading to the semiquinone and C_{60}^- charges of -0.76 and -1.24, respectively.

On the basis of the ab initio MO calculations, the reduction of **1** and **9** with alkali metals was carried out. The cyclic voltammetric analysis of the fullerene-quinone system **1** shows that **1** easily gives the monoanion **2** and the dianion **3**, whereas a similar reduction of the fullerene-dimethoxybenzene **9** produces the corresponding monoanion **10**.

At first, the reduction of **9** by potassium mirror was monitored by EPR. The spectrum of **10** in THF shows a single signal (g 2.000, ΔH_{PP} = 1.3 G at 292 K; g 2.000, ΔH_{PP} = 5.1 G at 5.7 K), which follows the Curie law in the range 5.9-129 K with g value and ΔH_{PP} constant. Therefore, the monoanion **10** can be regarded as a C_{60} anion radical, although the linewidth narrowing at lower temperature typical of the C_{60} anion radical is not observed.[12]

A similar reduction of **1** with potassium in THF gives the EPR spectra of the dianion **3**•$2K^+$, which consists of a broad signal at the center and a fine structure due to triplet species (g 2.002, D = 45.8 G) at 77 K (Fig. 2a).[13] Both signals obey the Curie law over the range 16-120 K without change in the spectrum, although the $\Delta m_s = 2$ signals were not observed. The THF solution of **3**•$2K^+$ at 293 K shows a spectrum with an unresolved structure (Fig. 2b), which gradually changes to a more simple one composed of a semiquinone radical anion (g 2.005, a_H = 2.1 G (6H)) and a fullerene radical anion (g 2.000, ΔH_{PP} = 1.4 G), presumably due to the disappearance of the dianion, although some monoanionic species (**2** and the degradation products of **2** and **3**) remain in the solution. The sodium reduction of **1** in THF gives almost the same results as potassium (g 2.001, D = 46.0 G at 77K) (Fig. 2c) without any counter cation dependence as known in semiquinone radical anions.[14] The solution of **3**•$2Na^+$ is more stable than that of **3**•$2K^+$ and remains unchanged at 293 K. The distance between two spins estimated from D value by the point dipole approximation (8.5 Å) is comparative to the size of **1** (ca. 8.7 x 14.6 Å). Thus, our results show a marked dipole-dipole interaction between the fullerene core and its substituent at the ground state.

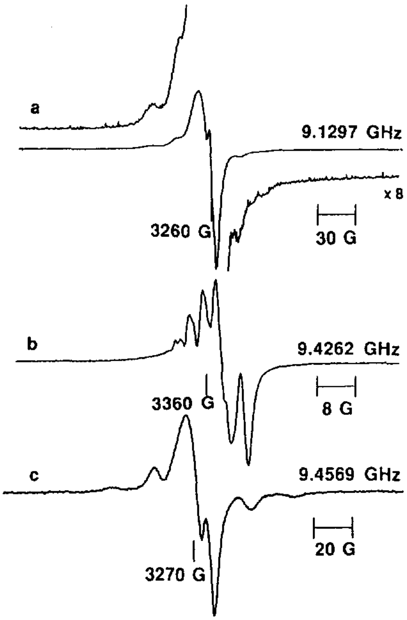

Fig. 2. EPR spectra of **3**•$2K^+$ at 77 K (a), **3**•$2K^+$ at 293 K (b), and **3**•$2Na^+$ at 77 K (c) in THF.

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8 **6**: black cryst., FAB-MS m/z 889 (M^++1); ^1H NMR ($CS_2/CDCl_3$, 1:1) δ 4.51 (s, 2H), 4.56 (s, 2H), 7.29 (s, 1H).

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10 Crystal data for **1**•C_6H_6: $C_{74}H_{12}O_2$, monoclinic, space group: $P2_1/n$, a = 10.541(4) Å, b = 28.543(3) Å, c = 13.519(3) Å, β = 111.55(2)°, V = 3783(1) $Å^3$, Z = 4, D_c = 1.638 g cm^{-3}. The structure was solved by a direct method using MULTAN88. Full matrix least-squares refinement yielded the final R value of 0.039 (R_w = 0.025) for 5628 independent reflections [$2\theta \leq 55.0°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using Mo-Kα radiation (λ = 0.71069 Å) and ω-2θ scan. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre on quoting the full journal citation.

11 The calculations were carried out at the HF/6-31G level[15] on the AM1 optimized geometries using the GAUSSIAN 92/DFT program.[16] The split valence 6-31G basis set on O was augmented by the diffuse s and p functions (exponent 0.0945).

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