Quinone-Type Methanofullerene Acceptors: Precursors for Organic Metals

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Received September 22, 1995[⊗]

We report details on the synthesis and electrochemistry of quinone-type methanofullerene derivatives in which, depending upon the substitution pattern on the cyclohexanedienone moiety, the reduction potential can be tuned, leading to novel fullerene derivatives exhibiting better acceptor properties than C_{60}. We also present the lowest energy conformers of these spiroannulated methanofullerenes. As expected, the anthrone derivative is not coplanar and is not perpendicular to the ball's surface.

The high electron affinity of buckminsterfullerene C_{60} allows the addition of up to six electrons in solution.[1] This led, by reaction with metals and donor species, to the formation of charge transfer salts such as K_3C_{60}[2] and charge transfer complexes of type [TDAE]C_{60} [TDAE: tetrakis(dimethylamino)ethylene],[3] exhibiting superconducting and ferromagnetic properties, respectively.

These findings have encouraged the search of novel fullerene derivatives showing better acceptor abilities. To the best of our knowledge, only one example ($C_{60}F_{48}$)[4] in which the first reduction potential is considerably more positive than in C_{60} is known. Several attempts to prepare chemically modified fullerenes by combining the electrochemical properties of C_{60} with other covalently linked electroactive moieties have been described.[5] However, the lack of conjugation between the two partners, in addition to the loss of conjugation due to saturation of one double bond in C_{60}, was responsible for the observation of adducts which are more electropositive than the parent C_{60}.[6]

In this paper we report more details on the synthesis and electrochemistry of new quinone-type methanofullerene derivatives[7] in which, depending upon the substitution pattern on the cyclohexanedienone moiety, the reduction potential can be tuned, leading to novel fullerene derivatives exhibiting better acceptor properties than C_{60}. This opens up a potential route to fullerene derivatives as precursors for charge-transfer complexes.

The intramolecular electronic interaction (periconjugation)[8] between the p_z-π orbitals of the quinone moiety and the adjacent carbon atoms of C_{60}, separated by a spiro carbon atom, results in more extended conjugated molecules showing good acceptor properties.

The synthesis of the novel methanofullerene derivatives (**3a**−**d**) was carried out according to Scheme 1 by reaction of C_{60} with the corresponding 1,4-diazooxide (**1a**−**d**) by irradiation with a sun lamp (compounds **1a**−**c**) or by heating in 1,2-dichlorobenzene (compound **1d**) under nitrogen atmosphere (Table 1).

The starting diazo compounds **1a**−**d** were prepared by following previously described procedures (**1a**,[9] **1b**,[10] **1c**,[11] **1d**[12]).

It is worth mentioning that, when compounds **1a**−**c** were allowed to react with C_{60} in chlorobenzene or 1,2-dichlorobenzene at 100−115 °C or reflux temperature they afforded the corresponding compounds **3a**−**c** only in trace amounts. However, compound **3d** was obtained by heating at different temperatures (60−70 °C or 100−110 °C) overnight. Compounds **3a**−**d** were purified by flash chromatography (SiO_2, chlorobenzene/hexane or toluene/hexane, 1:1) producing air-stable solids which can be stored at room temperature.

All the methanofullerenes **3a**−**d** were the thermodynamically more stable methanofullerene ("[6,6]") isomer, and the UV spectra showed typical peaks at ca. 440, 500, and 700 nm. The methanofullerene structure was ascertained by the ^{13}C NMR of the bridgehead carbons in the 74−85 ppm region. The FTIR and FABMS are also consistent with the assigned structure, and the ^{1}H NMR spectra show the typical resonance signals of the cyclohexanedienone moiety. However, the aromatic protons nearest to the spheroid in compound **3d** are shifted downfield in comparison to the related anthrone. This effect has also been previously observed in non-quinoid

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

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(8) Wudl, F.; Suzuki, T.; Prato, M. *Synth. Methods* **1993**, *59*, 297. Eiermann, M.; Haddon, R. C.; Knight, B.; Li, Q.; Maggini, M.; Martín, M.; Ohno, T.; Prato, M.; Suzuki, T.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1591. Because the arrangement of "π"-orbitals in C_{60} is orthogonal to those in other spiroannulated molecules, there is no possibility of spiroconjugation in **3a**−**3d**.

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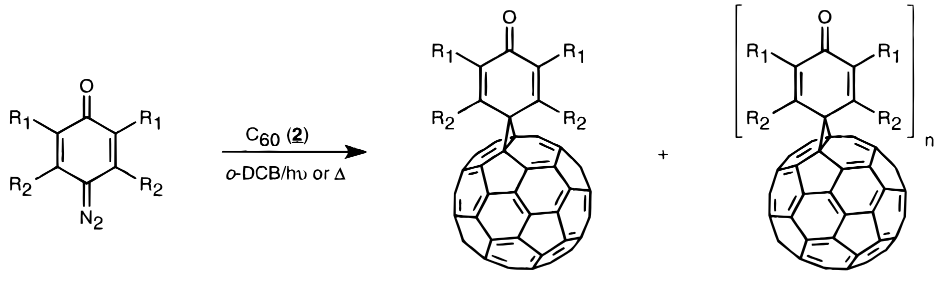
Scheme 1



1

3a-d

4d

Table 1. Novel Methanofullerene Derivatives Prepared

compound	R^1	R^2	solvent	conditions, °C	time (h)	yield (%)
3a	H	H	o-DCB^a	hν 0–10	1	16 (47)^b
3b	Me	H	o-DCB	hν 0–10	1	13 (43)
3c	t-Bu	H	o-DCB	hν 0–10	2	26 (57)
3d	$(-CH{=}CH-)_2$		o-DCB	60–70	24	47 (65)

[a] o-DCB: o-dichlorobenzene. [b] Based on the recovered C_{60}.

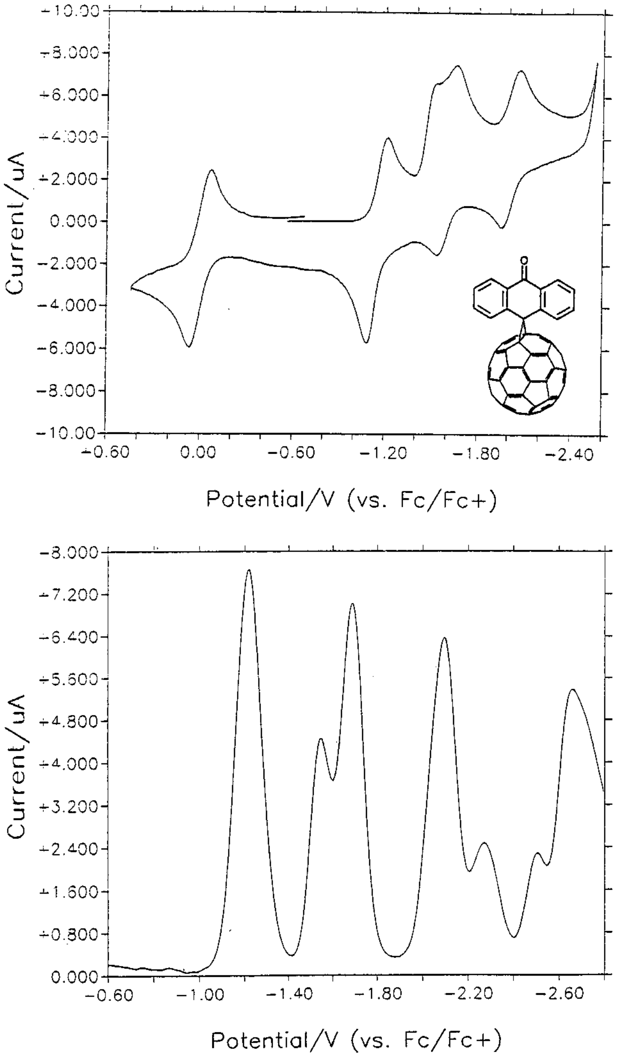


Figure 1. Cyclic voltammogram (CV) and Osteryoung square wave voltammogram (OSWV) of compound **3d** in o-DCB.

related molecules[13] as a consequence of the magnetic deshielding effect of the π-electrons of the buckyball.

No evidence of the fulleroid ("[5,6]") isomer was observed. Attempts to prepare the fulleroid isomer of compound **3d** by carrying out the reaction at lower temperatures (60–70 °C) led solely to the more stable methanofullerene isomer.

Table 2. Peak Reduction Potentials Relative to F_c/F_c+ (mV)

	$E_{1,red}$	$E_{2,red}$	$E_{3,red}$	$E4$,red
3a	−1081^{a,b}	−1559		
3b	−1042^c	1197^c	−1602	−2016
3c	−1097^d	−1620	−2037	
3d	−1215	−1525^c	−1670^c	−2090
C_{60}	−1123	−1455	−1913	−2383
BQ^f	−1166^e	−2026^e		
Me_2BA^g	−1287^e	−2097^c		
$(tBu)_2BQ^h$	−1365^e	−2223^c		
AQ^i	−1587^e	−2172^e		

[a] Peak position depends upon scan rate. [b] Scan rate = 10 mV/s. [c] Electrochemically and chemically irreversible. [d] Two-electron process. [e] Electrochemically irreversible, but chemically reversible. [f] Benzoquinone. [g] 2,5-Dimethylbenzoquinone. [h] 2,5-Di-*tert*-butylbenzoquinone. [i] Anthraquinone.

In addition to the monoadduct **3d**, the bis-adduct **4** (*n* = 2) as well as the tris-adduct **4** (*n* = 3) of the corresponding 1,4-diazoanthrone (**1d**) were also separated by chromatography. However, the mixture of isomers could not be resolved in this way.

The cyclic voltammetry (CV) measurements of the novel acceptors were carried out in 1,2-dichlorobenzene at room temperature with tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The methanofullerene derivatives **3a–c** were found to be better acceptors than the parent C_{60}. In contrast, compound **3d** (Figure 1) showed a more negative first reduction potential (Table 2). All the compounds **3a–d** showed three or four reduction waves and, unlike most organofullerenes reported, these compounds do not behave reversibly in the CV. This finding could suggest the opening of the cyclopropane ring when the molecule accepts an electron.[8] However, attempts to capture the expected phenolate of the radical-anion with strong alkylating reagents were unsuccessful.

Taking into account that compound **3b** presents an irreversible first redox potential, in Table 2 are collected the peak-potentials for the first reduction to the corresponding anion-radical. The OSWV[14] was recorded and also confirms the peaks observed (Figure 1) showing additional waves at more negative values.

The better acceptor ability of compounds **3a–c** could be rationalized by the periconjugation of the p_z-π orbitals of the cyclohexadienone moiety and the orbitals of the

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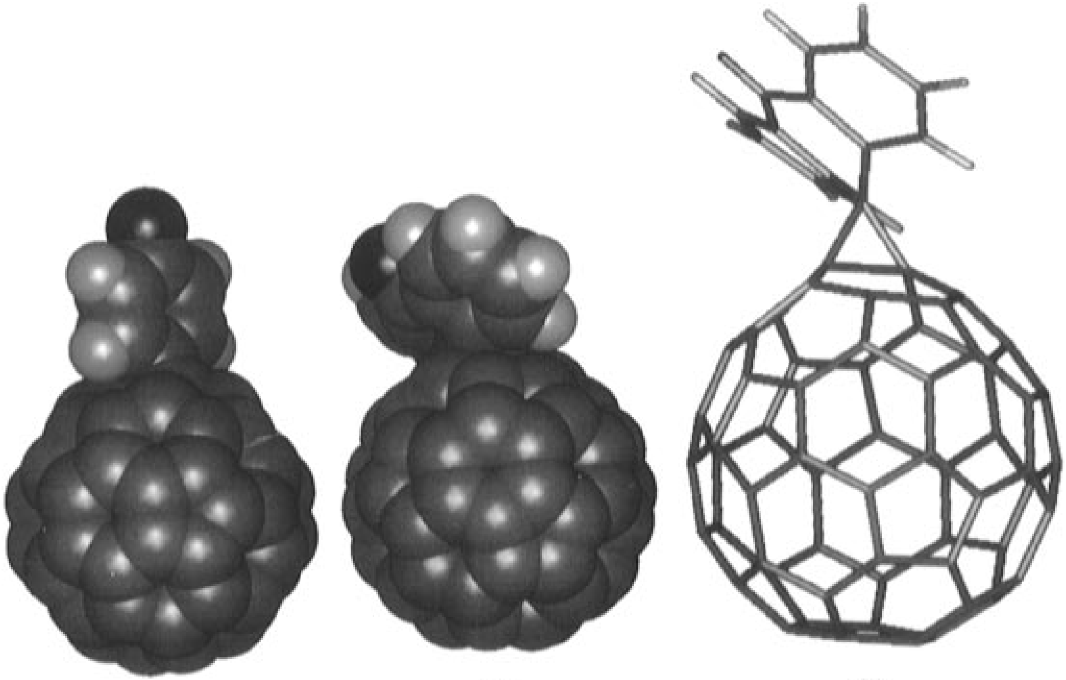
(13) Prato, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 7876.

(14) OSWV acronym for Osteryoung square Wave Voltammetry: Osteryoung, J. G.; O'dea, J. J.; In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1986; Vol. 14.



3a 3d 3d

Figure 2. Molecular geometry of compounds **3a** and **3d** by molecular mechanics calculations. In **3d**, unlike the cyclohexadienone in **3a**, the anthrone moiety is not perpendicular to the ball's surface.

fullerene carbon atoms adjacent to the cyclopropane ring.[8] The more negative reduction potential value found for the anthrone derivative **3d** may be due to the steric interaction of the aromatic peri-hydrogens with the spheroid leading to a significant deviation from the orthogonality and hence to the loss of periconjugation. This result was confirmed by molecular mechanics calculations using a Silicon-Graphics Iris computer (molecular mechanics calculations were performed using the Insight II molecular modeling system, Biosym Technologies Inc., San Diego, CA 92121) which revealed an orthogonal disposition of the quinone moiety for compounds **3a**-**c** and a strong deviation for **3d.** In agreement with these data, the ^{13}C NMR spectra of compound **3b** showed 15 peaks for the fullerene moiety indicating two planes of symmetry, and 23 peaks for **3d** revealing the presence of only one plane of symmetry in this molecule (Figure 2).

In summary, we have carried out the synthesis of novel methanofullerene derivatives bearing a cyclohexanedienone moiety by photolysis of 1,4-diazooxides and C_{60} and also by thermolysis. The good acceptor properties of these molecules, better than C_{60}, could be rationalized in terms of periconjugation. This effect also explains the anomalous behavior of the anthrone derivative **3d.** The ^{13}C NMR and the molecular geometry obtained by molecular mechanics calculations are in good agreement with the CV data. These novel methanofullerene acceptors are precursors for organic metals. Work is in progress in order to form charge-transfer complexes with electron-donor molecules and to prepare the respective TCNQ and DCNQI-type analogs.

Experimental Section

Spiro[10-anthrone-9,61′-methanofullerene]. To a solution of C_{60} (400 mg, 0.55 mmol) in dry *o*-dichlorobenzene (35 mL) was added 10-diazoanthrone (135 mg, 0.61 mmol), and the reaction mixture was stirred at 60−70 °C overnight. The crude reaction mixture was submitted to flash chromatography (SiO_2, 1:1-toluene/hexane) to give 240 mg (47% yield) of pure compound (65% based on consumed C_{60}). Further purification was accomplished by recrystallization in toluene-hexane to yield deep brown crystals. ^{1}H NMR (CS_2/500 MHz): δ 8.40 (dd, $J = 7.5$, 1.5 Hz, 2H), 8.16 (dd, $J = 6.5$, 2.0 Hz, 2H), 7.60−7.54 (m, 4H). ^{13}C NMR (Cl_2CD-$CDCl_2$/CS_2): δ 186.93 (CO), 148.73, 146.31, 145.14, 145.05, 144.84, 144.71, 144.58, 144.52, 144.23, 143.84, 143.49, 143.02, 142.84, 142.76, 141.96, 141.84, 141.31, 140.90, 140.14, 139.26, 138.99, 137.46, 136.26, 130.82, 129.02, 128.58, 127.31, 81.87 (bridgehead C), 74.03 (bridgehead C), 48.08 (bridge). FTIR (KBr): 1670(CO) s, 1595 m, 1465 w, 1450 w, 1430 w, 1300 m, 1260 m, 1185 w, 1160 w, 930 w, 800 w, 770 w, 750 w, 735 w, 715 w, 690 w, 560 w, 527 s cm^{-1}. FABMS (toluene/NBA): *m/z* 913 $(M + H)^+$, 720(C_{60}). Anal. Calcd for $C_{74}H_8O$: C, 97.36; H, 0.88. Found: C, 97.21; H, 0.95. UV-vis (toluene) λ_{max} (nm): 286, 332, 410-(sh), 436, 496, 696.

Preparation of 1,4-Diazooxides. 1-Diazobenzene 4-oxide was prepared by the dehydrochlorination of *p*-diazophenol with freshly prepared silver oxide as described.[9] 3,5-Dimethyl-1-diazobenzene 4-oxide was prepared by reaction of 2,6-dimethyl-1,4-benzoquinone with *p*-tosylhydrazine and subsequent base-catalyzed decomposition.[10] 3,5-di-*tert*-butyl-1-diazobenzene 4-oxide was prepared by the modified method of 3,5 dimethyl-1-diazobenzene 4-oxide and confirmed by comparison of physical data with the literature.[11]

2,6-Di-*tert*-butylbenzoquinone 4-*p*-tosylhydrazone: solid, mp 94−96 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 18H), 2.46 (s, 3H), 7.75 (s, 2H), 7.38 (d, 2H), 7.90 (d, 2H); FTIR (KBR) 3226m, 2957m, 1647m, 1633m, 1625m, 1365m, 1335m, 1319m, 1157s, 902m, 890s, 884m, 682m cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_3N_2S$: C, 64.92; H, 7.26; N, 7.21; S, 8.26. Found: C, 64.63; H, 7.18, N, 7.39; S, 8.50.

3,5-Di-*tert*-butyl-1-diazobenzene 4-oxide: ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 18H), 7.19 (s, 2H); FTIR (KBR) 3007w 2955m, 2076s, 1593s, 1565s, 1353m, 1183s, 882m cm^{-1}; UV-vis (cyclohexane) λ_{max} 210, 262, 350, 500.

General Procedure for Photolysis of 1,4-Diazooxides in *o*-Dichlorobenzene Solution of C_{60}. To a solution Of C_{60} (100 mg, 0.14 mmol) in *o*-dichlorobenzene (7 mL), 1,4-diazooxide (0.19 mmol) was added, and the reaction mixture was irradiated with a sun lamp at 0−10 °C under N_2 for 1 h. Flash chromatography of the reaction mixture gave pure adducts.

Spiro[2,5-cyclohexadienone-4,61′-methanofullerene]: very insoluble solid, 16% yield (47% based on consumed C_{60}); FTIR (KBr) 1657 (C=O)s, 1499m, 1174m, 856m, 527s cm^{-1}; FABMS *m/z* 814 (M + H)$^+$. Anal. Calcd for $C_{66}H_4O$: C, 97.54; H, 0.50. Found: C, 95.21; H, 0.78. UV-vis (cyclohexane) λ_{max} 225, 262, 327, 440.

Spiro[2,6-dimethyl-2,5-cyclohexadienone-4,61′-methanofullerene]: solid, TLC R_f 0.4, chlorobenzene; isolated in 26% yield (57% based on consumed C_{60}) by flash chromatography with chlorobenzene; ^{1}H NMR (CS_2) δ 2.20 (s, 6H), 7.77 (s, 2H); FTIR (KBR) 2920w, 1658m, 1636 (C=O)s, 1427m, 1033m, 738m, 714m, 555m, 527s cm^{-1}. FABMS *m/z* 842 (M + H)$^+$. Anal. Calcd for $C_{68}H_8O$: C, 97.14; H, 0.96. Found: C, 95.83; H, 1.06. UV-vis (cyclohexane) λ_{max}: 222, 260, 330, 440, 500.

Spiro[2,6-di-*tert*-butyl-2,5-cyclohexadienone-4,61′-methanofullerene]: flash chromatographed with a 1/1 solution of chlorobenzene and hexane; TLC R_f 0.6, 1/1 hexane/chlorobenzene; 19% yield (43% based on consumed C_{60}); ^{1}H NMR (CS_2) δ 1.42 (s, 18H), 7.72 (s, 2H). ^{13}C NMR (CS_2) δ 29.56, 40.20, 77.21, 85.81, 131.74, 138.03, 141.38, 141.42, 142.27, 143.13, 143.35, 144.08, 144.74, 144.90, 145.13, 145.30, 145.57, 147.87, 151.45, 183.70. FTIR (KBr) 2952w, 1653 (C=O)s, 1635m, 1463m, 1456m, 1454m, 1427m, 1356m, 1188m, 897m, 757m, 738m, 713m, 587m, 554m, 526s cm^{-1}; FABMS *m/z* 926 (M + H)$^+$, 721 (C_{60} + H). Anal. Calcd for $C_{74}H_{20}O$: C, 96.09; H, 2.18. Found: C, 94.68; H, 1.99. UV-vis (cyclohexane); λ_{max}: 220, 260, 315, 440, 520.

Thermolysis of 3,5-Dimethyl-1-diazobenzene 4-Oxide in Chlorobenzene Solution of C_{60}. To a solution of C_{60} (100 mg, 0.14 mmol) in chlorobenzene (7 mL) was added 3,5-dimethyl 1,4-diazooxide (0.19 mmol), and the reaction mixture was refluxed under N_2 for 24 h. Though comparison of TLC (eluent, chlorobenzene) with an authentic sample indicated generation of the adduct, it could not be isolated.

Acknowledgment. We are grateful to the National Science Foundation for support through Grant DMR 95-00888. N.M. is indebted to Universidad Complutense for a research fellowship (Beca del Amo).

JO951738F