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Linear Free Energy Relation of Methanofullerene C_{61}-Substituents with Cyclic Voltammetry: Strong Electron Withdrawal Anomaly

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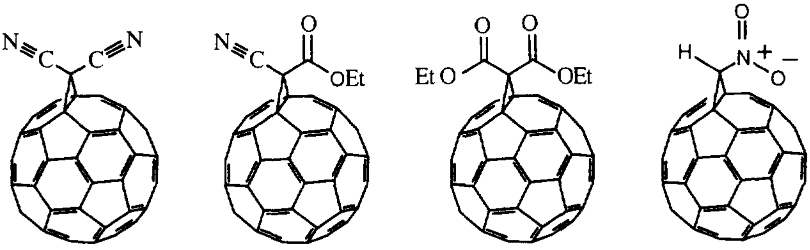
Abstract. Methanofullerenes with cyano, nitro, and carboxyethyl substituents on C_{61} were prepared and characterized. The bis(cyano) methanofullerene shows a first, irreversible, reduction peak at room temperature which is ca 160 mV more positive than the corresponding step in C_{60}. We report for the first time a comparative study of electron-donating and electron-withdrawing substituents on C_{61}, using the Hammett σ_m, which shows that the cyano substituent appears to be more electron-withdrawing than predicted by the Hammett relation. This anomaly could be due to kinetics of a rapid follow-up reaction, periconjugation, or "conjugation" through the cyclopropane Walsh orbitals.

The observation of six reversible reduction waves at very negative potentials in the cyclic voltammogram of fullerene (C_{60}) at low temperature[1,2] is in accord with the theoretically determined three-fold degenerate, low-lying lowest unoccupied molecular orbitals (LUMO) of C_{60}.[3] In principle, chemical modification of fullerenes could alter their electronic properties. Polyfluorofullerenes are reported to be relatively strong oxidizing agents, with the first reduction potential of $C_{60}F_{48}$ being 1380 mV more positive than that of C_{60}.[4] Among the fullerene derivatives, methanofullerenes (C_{61})[5] are of interest in terms of versatility, stability and electronic properties. Recently, we reported[6] the substituent effects and electrochemical evidence for through-space orbital interactions in spiroannulated methanofullerenes.

In this paper we report the synthesis and electrochemical characterization of electron withdrawing-substituted methanofullerenes and discuss the remarkable effect of cyano substitution in the 61 position of methanofullerenes. We show that these compounds follow a linear free energy relation with the Hammet σ_m.

We were surprised to learn that the dicyanomethanofullerene **1** had not been reported until we learned that dicyanodiazomethane failed to react with C_{60} below its decomposition temperature. This is in agreement with the finding that dicyanodiazomethane is inactive as a 1,3 dipole.[7-9] Photolysis or thermolysis (above the decomposition temperature) of dicyanodiazomethane and C_{60} in 1,2-dichlorobenzene (ODCB) yielded, upon chromatographic separation, dicyanomethanofullerene **1** as the single isomer. These results are consistent with the addition of the intermediate electrophilic dicyanocarbene[7-9] exclusively to the [6,6] ring junction of C_{60}.[10,11]

Scheme 1



1 2 3 **4**

The ethyl cyanocarboxymethanofullerene **2** was prepared by a method similar to that reported[12] for the synthesis of bis(carboxyethyl)methanofullerene **3**. Ethyl bromocyanoacetate[13] was allowed to react with C_{60} in the presence of pyridine in ODCB at room temperature. Purification of the product by chromatography, afforded **2**, as a single isomer. A similar procedure using bromonitromethane and triethylamine as base was employed for the preparation of the nitromethanofullerene.

The methanofullerene structures with C_{2v} symmetry for compound **1** and Cs symmetry for compounds **2** and **4** were assigned on the basis of ^{13}C NMR, UV-VIS and IR spectra[14]. The ^{13}C NMR spectrum of **1** exhibited 19 signals (see Experimental Section), sixteen of which were in the sp^2 hybridized fullerene region (139-146 ppm). The sp^3 hybridized bridgehead carbon and methano bridge carbon appeared at 67.9 and 20.3 ppm respectively, while the sp hybridized nitrile appeared at 110 ppm. The sp^2 hybridized fullerene region of **2** and **4** (31 lines expected) shows 20 and 23 signals respectively, some of which are clearly overlapping. The bridgehead and the methano bridge resonances of **2** appeared at 69.7 and 35.3 ppm respectively; while those of **4** had chemical shifts at 70.4 and 70.1 ppm respectively. The nitrile and the carbonyl resonances were observed at 112.7 and 161.0 ppm respectively. A comparison of the methano bridge resonances (ppm) of **1** (20.3), **2** (35.3), **3** (52.3) and **4** (70.1) clearly demonstrate the shielding effect of the cyano group.[15]

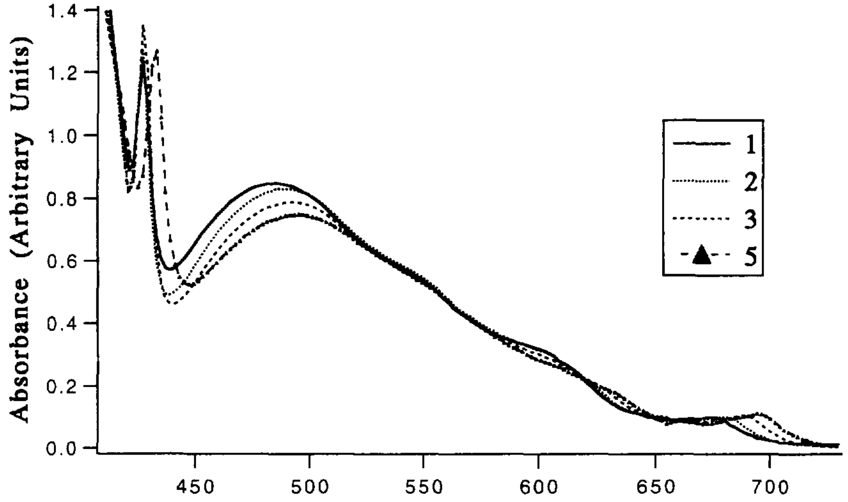


Figure 1. A plot of the visible region of the superimposed UV-Vis spectra of methanofullerenes **1**, **2**, **3**, and **5** in toluene.

The UV-vis absorption spectra of **1**, **2**, **3**, and **4** are similar to the other methanofullerenes. However, a study of the visible region spectra of numerous substituted methanofullerenes showed an hypsochromic shift with the introduction of progressively more electron-withdrawing groups. An overlay of the UV-vis spectra of **1**, **2**, **3**, and a typical methanofullerene **5** is shown in Figure 1.

The cyclic voltammetry (CV) of **1** at room temperature[16] showed at least 9 reduction waves, several of which were irreversible. A study of **1** using OSWV[17] showed one additional reduction wave but several of the waves were still poorly defined. The CV of **1** at low temperature (see Figure 2) consists of 9 reduction steps, of which 6 appear to be electrochemically reversible. The first reduction wave changes from irreversible at room temperature to quasi-reversible at -72 °C, suggesting that a thermally activated process, possibly a cyclopropane ring-opening[6] occurs upon reduction. A -72 °C[18] OSWV study of **1** - **3**, is depicted in Figure 3. The peaks with asterisks and part of the intensity of the first peak[19] are due to C_{60}.[20] It appears as though both **1** and **2** are converted, even at -72 °C, to C_{60}, upon addition of one electron. Compound **3** is more robust, showing complications only after the 4th wave. At room temperature, compound **4** behaves in a manner much like **1** and **2**, showing an initial irreversible reduction peak followed by numerous successive, irreversible reductions.

In general, saturation of a double bond of C_{60} in methanofullerenes (58π electrons) causes a negative shift of about 100-150 mV for the first three reduction waves. The most striking feature of the *room temperature* CV is that the first peak reduction potential of **1** occurs at -967 mV vs. Fc/Fc+, *156 mV more positive* than C_{60}. This value for the first peak reduction of **1** makes this the most electronegative methanofullerene prepared so far. The magnitude of this positive shift becomes even more interesting when we compare the first reduction potential to that of the bis(carboxyethyl)methanofullerene **3** (-1164 mV) and the nitromethanofullerene **4** (-1163 mV), 40 mV *more negative* than C_{60}. Clearly, the presence of the two moderately strong electron-withdrawing ester groups or one single very strong electron-withdrawing nitro group is not sufficient to compensate for the saturation of one C_{60} double bond.

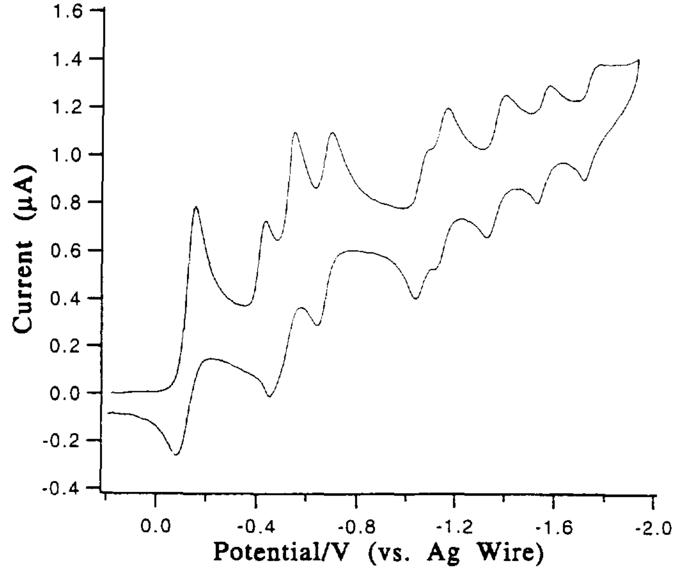


Figure 2. The CV of **1** in 3:2 Toluene/DMF with 0.1 M Bu_4NBF_4 at -72°C; Ag/Ag^+ quasi-reference electrode and Fc/Fc^+ internal reference. Scan rate, 10 mV/s.

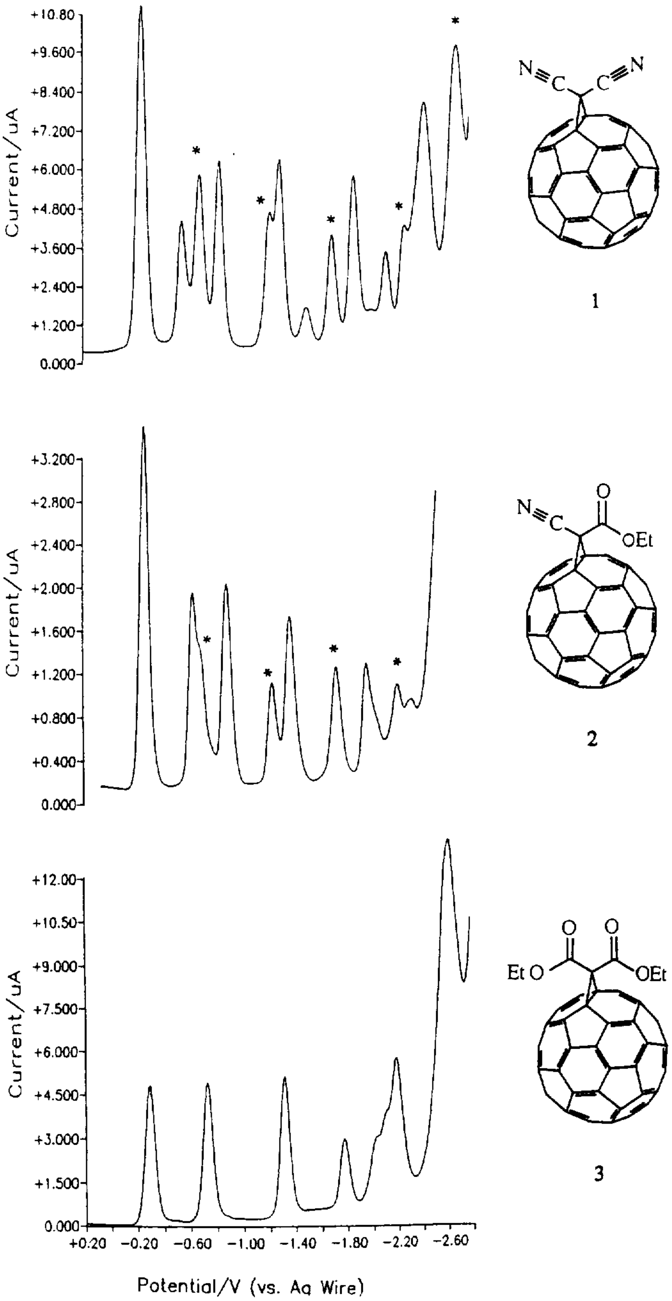


Figure 3. OSWV scans of methanofullerenes **1**, **2**, and **3** in 3:2 Toluene/DMF with 0.1 M Bu_4NBF_4 at -72°C; Ag/Ag^+ quasi-reference electrode and Fc/Fc^+ internal reference; scan rate, 60 mV/s.

On the other hand, the methanofullerene **2**, prepared to study the effect of a single cyano group on the electron-accepting ability of methanofullerenes, showed a first peak reduction potential at -1113 mV, very nearly the same as for C_{60}.

The remarkable "substituent effect" of the electron withdrawing functional groups is exhibited in Figure 4, in the form of a plot of first peak reduction potentials of a number of methanofullerenes[21] vs. the sum of σ_m of the substituents on C_{61}.[22] We used σ_m because the substituents are not conjugated with the fullerene and the effect is expected to be inductive rather than through resonance.[19] Examination of the open circles data in the figure indicates a linear correlation between the first peak reduction potential and σ_m ($r = 0.959$). The fact that compounds 1 and 2 do not fit on the open circle line suggests that the effect caused by the cyano groups in the 61-position of methanofullerenes could be due to orbital interactions between the cyano groups and the buckminsterfullerene skeleton; perhaps of the periconjugation type[6] as shown below:

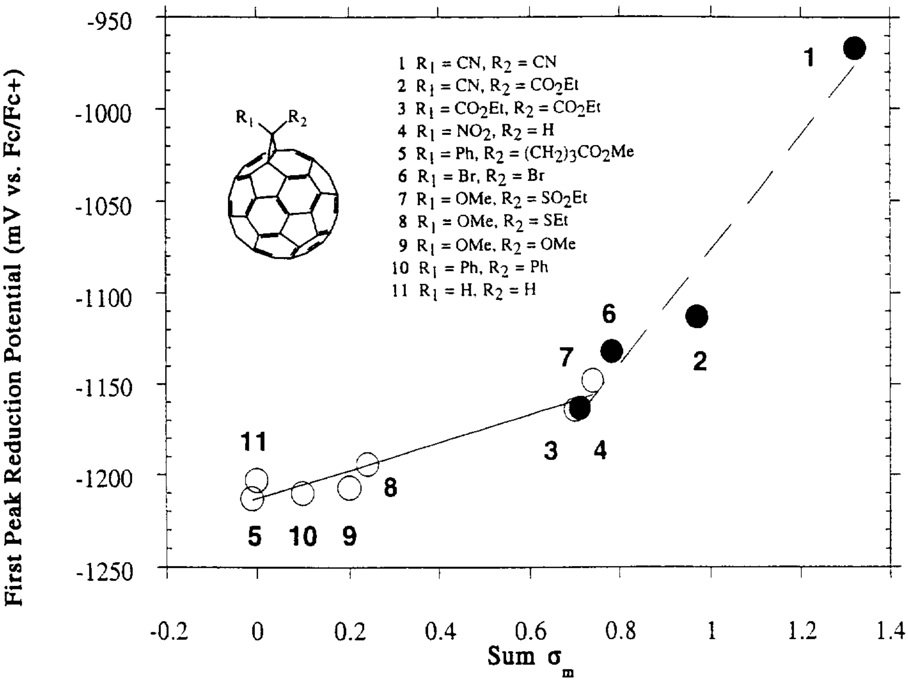
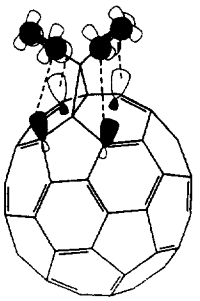
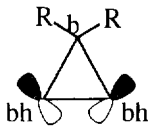


Figure 4. A plot of first peak reduction potential versus the sum of σ_m values for substituents at the 61-position. Open circles, reversible reductions; filled circles, irrversible reductions. Least-squares fits to each data set are solid and dashed lines, respectively.

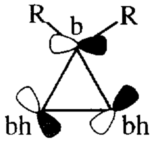


In the diagram above, for clarity, the remaining C_{60} "p-π" orbitals were left out and the in-plane CN p-orbitals are represented phase-less because they are not involved.

Another explanation could involve cyclopropane conjugation[23] as depicted below.



$\psi_{2(s)}$



$\psi_{3(a)}$

	b - bh	bh - bh
R = H	1.521Å	1.620Å
R = CN	1.550Å	1.593Å

Of the HOMO (Walsh) orbitals of a methanofullerene, we need consider only the $\psi_{3(a)}$ because $\psi_{2(s)}$ has a node on the bridge (b) carbon. As the results of calculations show above, substituting a CN for an H, causes weakening of the b - bh bond and strengthening of the bh - bh bond; in full accord with the observed ring-opening upon reduction. Furthermore, this type of conjugative interaction is possible for the CN group but not for the carboxylate because the latter, in its lowest energy conformation, is rotated out of "conjugation" with $\psi_{3(a)}$.

Alternatively, the electrochemical data can be treated separately depending on whether the first reduction step is reversible or irreversible, since the reduction potential of an irreversible process can be affected by the kinetics of a coupled chemical process. When a fast, irreversible chemical reaction follows a reversible, one electron reaction at room temperature, the observed peak potential is shifted from the reversible peak potential[24]

Support for this interpretation is found in Figure 4. The compounds that exhibit reversible first peak reductions (open circles) follow a good linear correlation and the compounds with an irreversible first peak (filled circles), which contain strong electron withdrawing substituents, fall on a steeper-sloped line (r = 0.978), with compound 1 at the very top of the line. It is clear that there is a break, or elbow in the plot and that the steepness of the slope is due to displacement of the onset of the reduction to more positive values by the coupled chemical process of a ring opening reaction.

We are continuing our investigations into both the concept of periconjugation and the effects exhibited by cyano-substituted methanofullerenes and will report on our progress in due time.

Experimental Section

Preparation of Dicyanomethanofullerene

To a solution of C_{60} (1040 mg, 1.44 mmol) in ODCB (80 mL) was added a solution of dicyanodiazomethane (186 mg, 202 mmol) in ODCB (20 mL) under a dry N_2 atmosphere. The mixture was irradiated for 9 h at 25-45 °C and the resulting reddish-brown, homogeneous solution was loaded onto a silica column. The unreacted C_{60} was eluted with cyclohexane/toluene 8:2, and the dicyanomethanofullerene with cyclohexane/toluene 1:1. The solvents were removed under reduced pressure and the residue was washed with cyclohexane, methanol and ether respectively. The product was crystallized from CS_2/cyclohexane as black prisms: 290 mg, 26% (66% based on consumed C_{60}, 405 mg). ^{13}C NMR (ODCB-*d4* /CS_2, one drop, 125 MHz): 145.51, 145.36. 145.30, 144.62, 144.21, 143.74, 143.65, 142.98, 142.85, 142.65, 141.86, 141.74, 141.21, 141.12, 139.36, 109.98, 67.89, 20.31. FTIR (KBr): 2247, 1429, 1185,1183, 743, 716, 559, 562, 523 cm^{-1}. FABMS (NBA): *m/z* 785 (M^+), 720 (C_{60}^+). UV-Vis (CH_2Cl_2) λ_{max} nm (ε) 254 (136480), 324 (40860), 424 (2080), 486 (1650), 686 (220). Anal. Calcd for $C_{63}N_2$. 1/2 cyclohexane: $C_{66}H_6N_2$: C, 95.89; H, 0.73; N, 3.38. Found: C, 95.46: H, 0.30; N, 3.44.

Preparation of Ethyl Cyanocarboxymethanofullerene

To a solution of C_{60} (500 mg, 0.694 mmol) in ODCB (75 mL) was added ethyl bromocyanoacetate (201 mg, 1.04 mmol) and pyridine (2 mL) at room temperature. The mixture was stirred overnight and the resulting reddish-brown solution was treated with 1M solution of H_2SO_4 (3 mL) and diluted with water (100 mL) and chloroform (150 mL). The organic phase was separated and washed with water. When dried over Na_2SO_4, the low boiling solvents were removed under reduced pressure and the remaining ODCB solution was loaded onto a silica column. The unreacted C_{60} was eluted with cyclohexane/toluene 8:2, and the ethyl cyanocarboxymethanofullerene with cyclohexane/toluene 1:1. The solvents were removed under reduced pressure and the residue was washed with cyclohexane, methanol and ether respectively. The product was dried *in vacuo* at 70° C: 180 mg, 31% (47% based on consumed C_{60}, 330 mg). ^1H NMR ($CDCl_3$, 500 MHz): 1.59 (t, J = 7.0 Hz, 3H), 4.63(q, J = 7.0 Hz, 2H). ^{13}C NMR (ODCB-*d4* /CS_2, 1:1, 125 MHz): 161.01, 145.22 (br), 145.10, 145.01, 144.85, 144.59(br), 144.43, 144.27, 144.16, 143.85(br), 143.70(br), 143.07, 142.91(br), 142.70, 142.49, 141.94(br), 141.81, 141.28, 141.07, 140.86, 138.71, 112.69, 69.67, 64.32, 35.25, 14.21. FTIR (KBr): 2971, 2246, 1753, 1458, 1427, 1366, 1254, 1235, 1186, 1016, 739, 714, 556, 526, 524 cm^{-1}. FABMS (NBA): *m/z* 832 (M+1). UV-Vis (CH_2Cl_2) λ_{max} nm (ε) 254 (14500), 326 (45570), 424 (2440), 486 (1730), 678 (200). Anal. Calcd for $C_{65}H_5NO_2$: C, 93.93; H, 0.60; N, 1.68. Found: C, 93.69: H, 0.87; N, 1.66.

Preparation of Nitromethanofullerene

Triethylamine (160 mg, 1.58 mmol) in ODCB (2 mL) was added dropwise to a solution of C_{60} (1.0 g, 0.1.39 mmol) and bromonitromethane (400 mg, 2.86 mmol) in ODCB (80 mL) at room temperature. The mixture was stirred overnight and the resulting reddish-brown solution was quenched with acetic acid (1.0 mL) and loaded onto a silica column. The unreacted C_{60} and the nitromethanofullerene were eluted with cyclohexane/toluene 8:2. The solvents were removed under reduced pressure and the residue was washed with methanol and ether respectively. The product was dried *in vacuo* at 70° C: 210 mg, 19% (32% based on consumed C_{60}, 600 mg). ^1H NMR (ODCB-*d4*, 500 MHz): 6.49 (S). ^{13}C NMR (ODCB-*d4*, 125 MHz): 145.08, 144.91, 144.61, 144.52, 144.47, 144.18, 144.06, 143.91, 143.58, 143.41, 143.09, 142.91, 142.79, 142.70, 142.06, 142.00, 141.91, 141.85, 141.68, 141.09, 140.94, 136.56, 134.82, 70.41, 70.09. FTIR (KBr): 3056 (w), 1553, 1430, 1349, 1186, 1184, 707, 576, 531, 526, 523, 491 cm^{-1}. FABMS (NBA): *m/z* 780 (M+1), 733 (M-NO_2), 720 (C_{60}) UV-Vis (CH_2Cl_2) λ_{max} nm 260, 328, 412 (sh), 424, 492, 602 (sh), 680.

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