Redox Properties of 1,2-Dihydro[60]fullerene Derivatives with Electron-Withdrawing Substituents

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The cyclic voltammograms of 1-cyano-2-hydroxy-1,2-dihydrofullerene derivatives indicate a complex redox behavior. The first reduction peak of these new compounds is at less negative values compared to the parent [60]fullerene. This is a consequence of the two electron-withdrawing groups, which are attached directly to the C60 moiety.

Introduction

The high electron affinity of [60]fullerene could be deduced, among others, from its cyclovoltammetric examination, that indicates the reversible acceptance of up to six electrons at low temperature [1]. This unique behavior encouraged the preparative chemists to combine potential electron-donating groups such as ferrocenyl or tetrahydrofurfuryl [2,3] with C60 to obtain fullerene derivatives with novel redox properties. The results however showed, that apart from a negative potential shift relative to C60, which is due to the saturation of one double bond in the fullerene, no significant effects could be found in the cyclovoltammetric behavior of the ground state fullerenes.

The efforts to enhance the electron-accepting ability of organofullerenes by binding electron-withdrawing moieties or atoms covalently to C60 were more successful. Two cyano groups attached to the three-membered ring in the methanofullerene [4] or fixed directly to the fullerene core [5] results in fullerene derivatives which are easier to modify the redox properties and to find intramolecular charge-transfer effects. The spectroscopic data of the new fullerene derivatives 2-5 are mainly identical within the standard deviations of the experiment (±0.01 V) and therefore one can see in Table 1 the data of the compounds 2-5 are mainly identical within the standard deviations of the experiment (±0.01 V) and therefore no significant influence of the spacerlength (0, 1 or 2 methylene groups) between the fullerene skeleton and the potential electron donating group could be observed. As an example, Fig. 1 shows the CV of compound 2, that turned out to be very complex. The electrochemical reversibility of the reduction processes were checked by reversing the scan direction after each peak. The first reduction

Results and Discussion

In this communication we report the redox properties of 1-cyano-2-hydroxy-1,2-dihydrofullerene derivatives 2-5, which could be synthesized by esterification of the corresponding carboxylic acids with the fullerenol 1 [9, 10] in the presence of DCC and 4-(dimethylamino)pyridine (DMAP). The electron-withdrawing cyano and carboxylic groups are directly attached to the fullerene skeleton. This system was combined with potential electron-donating substituents R at the ester group to modify the redox properties and to find intramolecular charge-transfer effects. The spectroscopic data of the new fullerene derivatives 2, 3 and 5 are in agreement with the proposed molecular structures. Furthermore an X-ray crystal structure analysis of compound 4 could be obtained, as we reported recently [11].

The cyclic voltammograms (CVs) were recorded in α-dichlorobenzene at room temperature. As one can see in Table 1 the data of the compounds 2-5 are mainly identical within the standard deviations of the experiment (±0.01 V) and therefore no significant influence of the spacerlength (0, 1 or 2 methylene groups) between the fullerene skeleton and the potential electron donating group could be observed. As an example, Fig. 1 shows the CV of compound 2, that turned out to be very complex. The electrochemical reversibility of the reduction processes were checked by reversing the scan direction after each peak. The first reduction
Table I. Cathodic ($E_{pc}$) and anodic ($E_{pa}$) peak potentials for C$_{60}$ and compounds 2–5 in [V] vs. Fe/Fe*, detected by CV at 25 °C. Scan rate 50 mV/s, o-dichlorobenzene solutions [0.1 mol (nBu)$_4$NPF$_6$].

<table>
<thead>
<tr>
<th>Compound (molarity)</th>
<th>$E_{1, \text{red.}}$</th>
<th>$E_{2, \text{red.}}$</th>
<th>$E_{3, \text{red.}}$</th>
<th>$E_{4, \text{red.}}$</th>
<th>$E_{5, \text{red.}}$</th>
<th>$E_{1, \text{ox.}}$</th>
<th>$E_{2, \text{ox.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$ (0.0023 M)</td>
<td>$E_{pc}$ -1.13</td>
<td>-1.49</td>
<td>-1.93</td>
<td>-2.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_{pa}$ -1.10</td>
<td>-1.46</td>
<td>-1.89</td>
<td>-2.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 (0.0012 M)</td>
<td>$E_{pc}$ -1.07</td>
<td>-1.41</td>
<td>-1.83</td>
<td>-1.91</td>
<td>-2.36</td>
<td>-0.50$^a$</td>
<td>0.25$^a$</td>
</tr>
<tr>
<td>3 (0.002 M)</td>
<td>$E_{pc}$ -1.01</td>
<td>-1.41</td>
<td>-1.79</td>
<td>-1.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (0.0017 M)</td>
<td>$E_{pc}$ -1.05</td>
<td>-1.41</td>
<td>-1.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 (0.0017 M)</td>
<td>$E_{pc}$ -1.01</td>
<td>-1.41</td>
<td>-1.79</td>
<td>-1.90</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In order to obtain these values external standard (Fe/Fe*) was used for this measurement.

step is irreversible at scan rates up to 100 mV/s probably due to an irreversible chemical reaction. As a result the shape and the reversibility of the following peaks depend on the scan rate and the potential window. There is evidence for a second irreversible chemical reaction during the reduction scan and in addition two weak oxidation peaks occur, which are also irreversible. This is in contrast to the CV of the related 1,2-dicyano-1,2-dihydro[60]fullerene [5], which shows four reversible half-wave potentials. Therefore the presence of a cyano group alone is not the reason for the complication in the CVs of our examined compounds. Probably the short nucleophilic intramolecular contact of the carboxyl group to the cyano group, which we observed in the X-ray study of fullerene 4 [11], is responsible for the observed unexpected redox properties.

Due to the irreversible chemical reactions during the scans, in Table I reduction and oxidation peak potentials are given only. The first reduction potential of compounds 2–5 is 100–120 mV less negative compared to that of C$_{60}$. Obviously the two electron-withdrawing groups attached to the fullerene core are responsible for this significant shift.
Experimental

NMR: Bruker AC 300 (300 MHz and 75 MHz, for 1H and 13C, respectively); chemical shifts are given with respect to TMS. Calibration with solvent signal (CDCl3; δH = 7.24, δC = 77.0). – FT-IR: Bruker IFS 66. – FAB MS / FD MS: JOEL JMS-700, positive ion mode (matrix 3-nitrobenzyl alcohol for FAB MS). – MALDI-TOF MS: Bruker Biflex, negative ion mode (matrix 9-nitroantracene). – UV: HP 8452 (diode array). – free radical spin trapping reactions (3.41). – FT IR (KBr): v = 2931 cm⁻¹ (w, CH), 1729 (s, CO), 1335 (s), 996 (s), 527 (m, fullerene). – UV/Vis (CHCl3): λmax (lg ε) = 232 nm (4.93), 256 (5.16), 318 (4.72), 418 sh (3.63), 680 (2.31). – MALDI-TOF MS: m/z (%): 957.2 (11) [M⁺], 746.0 (100) [C60N⁺], 720.0 (4) [C60]. – HR FAB MS: m/z: 957.0637 [C71H11NO3] calcd; 957.0654 found.

2-Cyano-1,2-dihydro[60]fullereny 2-(3,4,5-trimethoxyphenyl)-acetate (3). Yield: 10.9 mg (1.1 x 10⁻² mol, 86%). Rf = 0.53 (silica gel, toluene/acetonitrile 9/1). – 1H NMR (300 MHz, CDCl3): δ = 6.81 (s, 2H, arom.), 4.29 (s, 2H, CH2), 3.87 (s, 3H, CH3). – 13C NMR (75 MHz, CDCl3): d = 167.18 (CO), 153.40 (arom.), 145.49 (2C), 145.45 (2C), 145.62 (2C), 145.47 (2C), 144.70 (2C), 144.64 (2C), 144.45 (2C), 144.24 (2C), 143.73 (arom.), 143.15 (2C), 142.95 (2C), 142.91 (2C), 142.47 (2C), 142.43 (2C), 142.00 (2C), 141.63 (4C), 141.14 (2C), 140.31 (2C), 139.73 (2C), 138.06 (2C), 136.62 (2C), 123.91 (arom.), 116.62 (CN), 108.04 (arom.), 61.06 (CH3), 56.54 (CH3). The sp3-fullerene-carbon-atoms could not be detected due to the long relaxation time. – FT IR (KBr): v = 2931 cm⁻¹ (m, CH), 2323 (w), 2240 (w, CN), 1728 (s, CO), 1335 (s), 996 (s), 527 (s, fullerene). – UV/Vis (CHCl3): λmax (lg ε) = 225 nm (4.93), 256 (5.16), 318 (4.72), 418 sh (3.63), 680 (2.31). – MALDI-TOF MS: m/z (%): 957.2 (11) [M⁺], 746.0 (100) [C60N⁺], 720.0 (4) [C60]. – HR FAB MS: m/z: 957.0637 [C71H11NO3] calcd; 957.0654 found.

General procedure for compounds 2–5: To a solution of 10 mg (1.3 x 10⁻⁵ mol) of the alcohol 1 in 50 ml of toluene/acetonitrile 9/1, were added two equivalents (2.6 x 10⁻⁵ mol) of the acid, 5.4 mg (2.6 x 10⁻⁶ mol) of DCC and 0.3 mg (2.6 x 10⁻⁷ mol) of DMAP under nitrogen. The mixture was stirred at room temperature for 72 h, concentrated in vacuum and filtered through a silica-gel column with benzene/toluene/acetonitrile 1/1. The yields of the black powders varied from 80% to 92%.

2-Cyano-1,2-dihydro[60]fullereny 2-(3,4,5-trimethoxybenzoate) (2). Yield: 10 mg (10⁻⁵ mol, 80%). Rf = 0.46 (silica gel, toluene/acetonitrile 9/1). – 1H NMR (300 MHz, CDCl3/CS2, 1/8): δ = 7.69 (s, 2H, arom.), 4.02 (s, 6H, CH3), 3.93 (s, 3H, CH3). – 13C NMR (75 MHz, CDCl3): δ = 167.18 (CO), 153.40 (arom.), 148.58 (2C), 148.02 (2C), 146.81 (2C), 146.79 (2C), 146.63 (2C), 146.50 (2C), 146.47 (2C), 146.38 (2C), 146.14 (2C), 145.64 (2C), 145.50 (4C), 145.47 (2C), 144.70 (2C), 144.64 (2C), 144.45 (2C), 144.24 (2C), 143.73 (arom.), 143.15 (2C), 142.95 (2C), 142.91 (2C), 142.47 (2C), 142.43 (2C), 142.00 (2C), 141.63 (4C), 141.14 (2C), 140.31 (2C), 139.73 (2C), 138.06 (2C), 136.62 (2C), 123.91 (arom.), 116.62 (CN), 108.04 (arom.), 61.06 (CH3), 56.54 (CH3). The sp³-fullerene-carbon-atoms could not be detected due to the long relaxation time. – FT IR (KBr): v = 2931 cm⁻¹ (m, CH), 2323 (w), 2240 (w, CN), 1728 (s, CO), 1335 (s), 996 (s), 527 (s, fullerene). – UV/Vis (CHCl3): λmax (lg ε) = 232 nm (4.93), 256 (5.16), 318 (4.72), 418 sh (3.63), 680 (2.31). – MALDI-TOF MS: m/z (%): 957.2 (11) [M⁺], 746.0 (100) [C60N⁺], 720.0 (4) [C60]. – HR FAB MS: m/z: 957.0637 [C71H11NO3] calcd; 957.0654 found.
(s, CO), 1511 (s), 1123 (s), 1102 (s), 1082 (s), 527 (s, fullerene). – UV/Vis (CHCl₃): ƛₘₚₓ (log ε) = 232 nm (5.06), 258 (5.24), 318 (4.88), 418 sh (3.80), 684 (2.47). – FD MS: m/z (%) 887.2 (100) [M⁺], 746.2 (7) [C₆₁N⁺⁺], 720.1 (11) [C₆₀⁺⁺]. – HR FAB MS: m/z: 887.0041 [C₆₀H₈N₂O₂S] calcd; 887.0082 found.