Nitration of Fullerene Derivatives under Mild Conditions

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Abstract: A new family of *N*-(2,4-dinitrophenyl)-2-pyrazolino[60]fullerene derivatives has been synthesized by electrophilic nitration using nitronium triflate. As evidenced by CV and OSWV experiments, these species show enhanced electron-accepting properties (up to 90 mV) with respect to C_{60}.

Key words: fullerene, electrochemistry, electrophilic aromatic substitution

Since the first report on the electrochemical properties of C_{60} in 1990,[1] there has been a growing interest in the electron-acceptor character of fullerenes as they can be combined with electron donors for light-induced electron-transfer processes which are of interest for the preparation of photovoltaic devices. C_{60} can accept up to six electrons, and in fact, six reversible reductions have been observed.[2] The electrochemistry of fullerene derivatives is very similar to pristine C_{60} but, usually, with poorer electron-acceptor properties, resulting from both, the saturation of one double bond (raising the energy of the LUMO) and the inductive effect of the addend.[3]

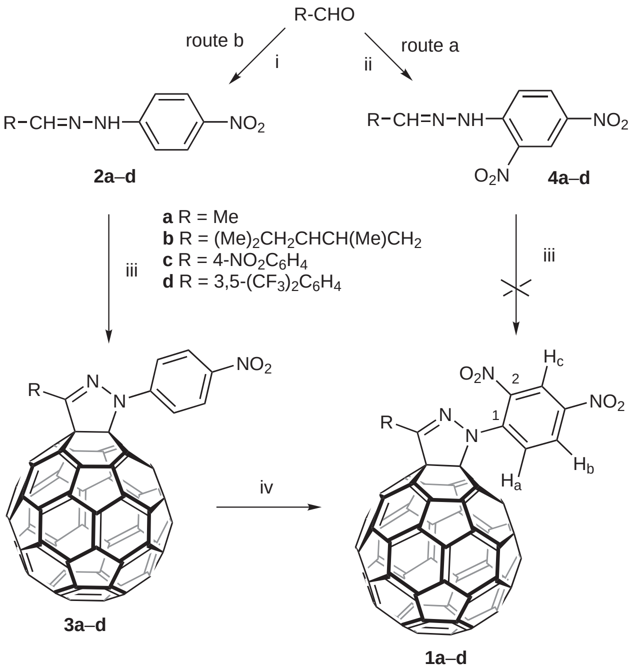
It is clear that the improvement of the electron-accepting properties of C_{60} may lead to more efficient behavior in electron-transfer processes[4] and a better efficiency in photovoltaic devices.[5] Within the past years, several attempts have been carried out directed at the synthesis of stronger acceptors than the parent C_{60};[6] among these attempts are: preparation of pyrrolidinium salts,[7] presence of electronegative groups directly linked to the C_{60} core,[8] incorporation of electron-acceptor substituents[9] and fullerene–metal complexes.[10]

We report here the synthesis and electrochemical properties of *N*-(2,4-dinitrophenyl)-2-pyrazolino-[60]fullerenes **1a**–**d**, which show enhanced electron-accepting ability (up to 90 mV) with respect to C_{60}.

One approach to the preparation of the target compounds **1a**–**d** implies the formation of 2,4-dinitrophenylhydrazones **2a**–**d**, then halogenation followed by the elimination reaction to form the corresponding nitrile imine[11] and ulterior 1,3-dipolar cycloaddition to C_{60} (Scheme 1, route a). Nevertheless, all reaction conditions used by us (NBS or NCS for halogenation, different solvents, classical heating or using microwave irradiation) failed in our hands.[12] The absence of reactivity of these nitrile imines towards C_{60} can be explained by an increased $\text{HOMO}_{\text{dipole}}$–$\text{LUMO}_{\text{alkene}}$ gap, induced by the presence, in the aryl ring, of a new electron-withdrawing group. These results made us turn to the second approach, outlined in Scheme 1 (route b). It is based on the nitration of 4-nitrophenylpyrazolinofullerenes **3a**,[11] **3b**,[13] **3c**,[14] and **3d**.[14] Among the wide variety of nitrating agents available,[15] we chose the nitronium triflate[16] (NO_2OTf) for several reasons: the electrophilic nitration can be carried out under mild conditions (low or room temperature) in organic solvents, the reaction is selective and these conditions are compatible with many pendant electron-donating and electron-withdrawing substituents found in the benzene ring.

The structures of the new cycloadducts **1a**–**d** were confirmed by spectroscopic data (i.e., UV–Vis, FTIR, ^1H NMR, ^{13}C NMR and MALDI–MS spectra).[17]

Whereas nitration of **1a** and **1b** was achieved at low temperature, formation of **1c** and **1d** was performed at room temperature due to the lack of reactivity of the corresponding starting material at lower temperature. In these cases the lower yield is the result of a rapid decomposition of the newly formed nitrated product. Polynitration could



Scheme 1 *Reagents and conditions*: (i) *p*-nitrophenylhydrazine, AcOH, EtOH, reflux; (ii) 2,4-dinitrophenylhydrazine, AcOH, EtOH, reflux; (iii) (a) NBS, $CHCl_3$, r.t.; (b) C_{60}, Et_3N, toluene, reflux or r.t.; (iv) tetramethylammonium nitrate, triflic anhydride, CH_2Cl_2.

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not be achieved, even with a large excess of the nitrating agent. In the case of **1c**, only the N-side aromatic ring, which is the more activated ring, could be nitrated.

The *meta* substitution (with respect to the original NO_2), explained by the presence of a *meta*-directing NO_2 and a *ortho*(*para*)-directing pyrazole moiety, was confirmed by the ^{13}C NMR. When compounds **3** showed four ^{13}C NMR signals corresponding to the nitrophenyl moiety, compounds **1** exhibited six signals. Furthermore, the signal attributed[18] to C2 in **3** (see Scheme 1) was shifted downfield in the case of **1**, due to the introduction of the new nitro moiety.

As a typical example, the expansion of the aromatic region in the ^1H NMR of compound **1b** is shown in Figure 1. The spectrum is well resolved at room temperature, with sharp signals for the protons of the aromatic ring, showing the signals corresponding to the proposed structure: the most deshielded signal appears as a doublet (J_m = 2.5 Hz) and is assigned to H_c (two nitro groups are in *ortho* position). The signal corresponding to H_b appears as doublet of doublets with two coupling constants, J_m = 2.5 Hz and J_o = 9 Hz. Finally, the proton H_a appears as a doublet with J_o = 9 Hz.

Like in other fullerene derivatives,[19] the steric hindrance resulting from the introduction of a nitro moiety at the C2 position seems to be sufficient to increase the rotational energy barrier to the point where free rotation is almost impossible. This fact was supported by the computational studies performed to evaluate the relationship between potential energy and the dihedral angle between the pyrazolinofullerene moiety and the phenyl ring. These studies showed that two conformers can exist with a dihedral angle of 138° and 322°, the energy barrier being higher than 30 kcal/mol, enough to prevent the rotation of the aryl group.[19] In fact, ^1H NMR spectra (recorded in $CDCl_3$ and $C_6D_5CD_3$) at different temperatures revealed no dynamic exchange between the two possible conformers (Figure 1).

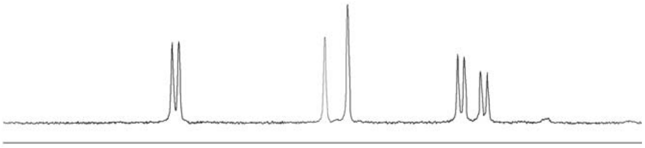

Figure 1 ^1H NMR of aromatic protons of compound **1b** in deuterated toluene

The electrochemical characteristics of the newly synthesized compounds were examined using cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV), in order to evaluate their electron-accepting abilities compared to parent C_{60}.

The redox potentials for **1a**–**d**, parent compounds **3a**–**d** and C_{60} are listed in Table 1. All of the pyrazolino[60]fullerenes (**1a**–**d** and **3a**–**d**) showed four quasireversible reduction waves for the fullerene moiety, similar to that found for the parent C_{60}. In addition, other nonreversible reduction wave(s), corresponding to the reduction of one (**3a**–**d**) or two (**1a**–**d**) nitro moieties, were observed. Interestingly, a remarkable difference was found between the reduction potentials corresponding to the fullerene cage.

Unlike the standard behavior found in most of 1,2-dihydrofullerenes that showed reduction waves shifted to more negative potentials than the parent C_{60},[6,20] compounds **1a**–**d** and **3a**–**d** exhibited reduction potentials which were anodically shifted (30–90 mV) in comparison with the parent C_{60}, similar to other pyrazolino[60]fullerenes.[8] Furthermore, as shown in Table 1,

Table 1 Electrochemical Data for the Redox Processes of Compounds **1a**–**d**, **3a**–**d** and C_{60}-Fullerene[a]

Compound	$E_{red}(1)$[b]	$E_{red}(2)$[c]	$E_{red}(3)$[b]	$E_{red}(4)$[c]	$E_{red}(5)$[b]	$E_{red}(6)$[c]	$E_{red}(7)$[b]
C_{60}	–0.97		–1.38		–1.85		–2.29
1a	–0.92	–1.30	–1.40	–1.62	–1.84	–1.94	–2.30
3a	–0.94		–1.35		–1.77	–1.94	–2.24
1b	–0.91	–1.29	–1.39	–1.63	–1.86	–1.96	–2.28
3b	–0.93		–1.35		–1.77	–1.94	–2.28
1c	–0.89	–1.27	–1.48	–1.63	–1.83	–1.99	–2.30
3c	–0.91		–1.32	–1.51	–1.72	–1.91	–2.30
1d	–0.88	–1.26	–1.55	–1.64	–1.78	–2.08	–2.27
3d	–0.90		–1.32	–1.67	–1.85	–2.24[d]	

[a] V vs. $Ag/AgNO_3$; detected by OSWV in *o*-dichlorobenzene–MeCN (4:1) solution (0.1 M n-Bu_4NClO_4) at r.t. under identical experimental conditions. OSWV data were obtained using a sweep width of 25 mV, a frequency of 15 Hz, a step potential of 4 mV, and a quiet time of 2 s on a Windows-driven Autolab PGSTAT 30 electrochemical analyzer.

[b] C_{60}-based reduction.

[c] *p*-Nitrobenzene-based redox process.

[d] The fourth C_{60}-based reduction wave was overlapped with a *p*-nitrobenzene-based one.

introduction of the second nitro moiety has a striking influence on the redox behavior. In all cases a shift to more positive values by 20 mV with respect to the corresponding mononitro compound was observed, which is a direct consequence of an increase in the electronic effect of the electron-accepting organic addend attached to the pyrazole ring.

These results clearly indicate that these systems are stronger electron acceptors than pristine C_{60}. The remarkable electron-acceptor character of these new molecules is of interest for further applications in the preparation of optoelectronic devices. Work is now in progress for the preparation of blends with conjugated semi-conducting polymers for photovoltaic applications.

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(13) Compound **2b**: A solution of *p*-nitrophenylhydrazine (1.0 g, 6.5 mmol), 3,5,5-trimethylhexanal (0.82 g, 6.5 mmol) and two drops of AcOH in EtOH (50 mL) was heated under reflux for 2 h. The solid was filtered off and recrystallized in EtOH to give **2b** as a red solid (1.47 g, 82%); mp 82.3–82.7 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.13 (d, J = 9.2 Hz, 2 H), 7.90 (s, 1 H), 7.19 (t, 1 H), 6.99 (d, J = 9.2 Hz, 2 H), 2.10–2.40 (m, 2 H), 1.85 (m, 1 H), 1.32 (dd, J_1 = 3.4 Hz, J_2 = 14.0 Hz, 1 H), 1.13 (dd, J_1 = 6.2 Hz, J_2 = 14.0 Hz, 1 H), 1.01 (d, J = 6.6 Hz, 3 H), 0.91 (s, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.3, 145.3, 144.5, 140.4, 139.7, 126.4, 126.3, 112.0, 111.3, 50.8, 50.6, 41.6, 35.7, 31.3, 31.3, 30.1, 28.2, 27.7, 23.0, 22.8. FT-IR (ATR): 3289, 2941, 1617, 1511, 1335, 1266 cm^{-1}. Anal. Calcd for $C_{15}H_{23}N_3O_2$: C, 64.95; H, 8.36; N. 15.15. Found: C, 64.43; H, 8.13; N, 15.21. Compound **3b**: To a solution of hydrazone **2b** (115 mg, 0.41 mmol) in anhyd $CHCl_3$ (10 mL) was added, under an Ar atmosphere, NBS (148 mg, 0.82 mmol). The mixture was kept under agitation during 2 h at r.t. The solvent was removed and an anhyd toluene (250 mL) solution of C_{60} (300 mg) and Et_3N in excess were then added. The reaction was kept under agitation at r.t. for 1.75 h. The toluene was then evaporated under vacuum. The remaining solid was purified by column chromatography (silica gel; toluene–hexane, 2:1) to give **3b** in 41% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.30 (d, J = 9.6 Hz, 2 H), 8.16 (d, J = 9.6 Hz, 2 H), 3.15 (dd, J_1 = 5.9 Hz, J_2 = 16.0 Hz, 1 H), 2.99 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 1 H), 2.53 (m, 1 H), 1.65 (dd, J_1 = 4.2 Hz, J_2 = 14.6 Hz, 1 H), 1.37 (dd, J_1 = 6.6 Hz, J_2 = 14.7 Hz, 1 H), 1.33 (d, J = 6.5 Hz, 3 H), 0.99 (s, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.47, 149.15, 147.94, 147.39, 146.75, 146.67, 146.56, 146.39, 146.34, 146.16, 145.76, 145.61, 145.53, 145.47, 145.34, 144.89, 144.64, 144.35, 143.74, 143.46, 143.20, 143.11, 142.64, 142.60, 142.50, 142.29, 141.82, 141.22, 141.14, 139.52, 139.44, 137.25, 136.24, 136.13, 129.28, 128.47, 125.76, 125.54, 118.58, 88.84, 84.28, 51.56, 39.37, 31.53, 31.21, 30.50, 29.96, 28.64, 23.34. FT-IR (KBr): 2941, 1597, 1535, 1335, 530 cm^{-1}. MALDI–TOF: m/z calcd for $C_{75}H_{21}N_3O_2$: 995.98; found: 995.9.

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(17) **Experimental Procedure**: To an anhyd CH_2Cl_2 solution of the corresponding fullerene derivative **2** (1 equiv) in CH_2Cl_2,

tetramethylammonium nitrate (2 equiv) was added under Ar. The solution was cooled to the desired temperature and triflic anhydride (2 equiv) was added. NO_2OTf was formed in situ and the solution was kept at this temperature until the complete disappearance of the starting material (the reaction progression was followed by TLC). The reaction was then quenched by adding a Na_2CO_3 solution (pH 8). The organic layer was separated, dried and evaporated. The remaining solid was purified by column chromatography affording the desired compounds **1a**–**d**.

Compound **1a**: reaction temperature: –5 °C for 4 h. Column chromatography (silica gel; toluene–hexane, 1:2); yield: 90%. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.80 (d, J = 2.5 Hz, 1 H), 8.45 (dd, J_1 = 2.5 Hz, J_2 = 9.0 Hz, 1 H), 8.40 (sd, J = 9.0 Hz, 1 H), 2.79 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.36, 147.79, 147.21, 146.38, 146.32, 146.08, 145.96, 145.34, 145.49, 145.29, 145.28, 145.24, 144.41, 144.23, 144.09, 143.97, 143.21, 143.07, 143.04, 142.95, 142.93, 142.84, 142.40, 142.24, 142.18, 142.05, 142.02, 141.06, 139.81, 137.31, 136.55, 127.10, 126.28, 122.22, 88.90, 83.39, 15.03. FT–IR (KBr): 2917, 2357, 1601, 1527, 1331, 526 cm^{-1}. UV–Vis: λ (log ε) = 255.0 (6.1), 320.0 (5.6) nm. MALDI–TOF: m/z calcd for $C_{68}H_6N_4O_4$: 942.94; found: 942.0.

Compound **1b**: reaction temperature: –5 °C for 5 h. Column chromatography (silica gel; toluene–hexane, 1:2); yield: 85%. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, J = 2.4 Hz, 1 H), 8.44 (dd, J_1 = 2.5 Hz, J_2 = 9.0 Hz, 1 H), 8.40 (sd, J = 9.0 Hz, 1 H), 3.11 (dd, J_1 = 4.6 Hz, J_2 = 16.5 Hz, 1 H), 2.95 (dd, J_1 = 8.8 Hz, J_2 = 16.5 Hz, 1 H), 2.45 (m, 1 H), 1.54 (dd, J_1 = 4.5 Hz, J_2 = 14.0 Hz, 1 H), 1.33 (dd, J_1 = 6.2 Hz, J_2 = 14.0 Hz, 1 H), 1.27 (d, J = 6.6 Hz, 3 H), 0.99 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.63, 147.77, 147.20, 146.37, 146.36, 146.31, 146.31, 146.07, 146.06, 146.05, 145.96, 145.95, 145.55, 145.53, 145.51, 145.46, 145.43, 145.42, 145.32, 145.29, 145.28, 145.26, 145.25, 144.40, 144.29, 144.24, 144.10, 144.09, 144.06, 143.21, 143.01, 142.97, 142.85, 142.83, 142.75, 142.42, 142.40, 142.26, 142.24, 142.19, 142.16, 142.12, 142.10, 142.01, 142.00, 140.95, 140.90, 139.84, 139.79, 137.31, 136.45, 136.26, 126.99, 126.00, 122.19, 88.84, 83.84, 51.39, 39.25, 31.26, 30.04, 28.07, 22.98. FT–IR (KBr): 2941, 2337, 1597, 1540, 1335, 526 cm^{-1}. UV–Vis: λ (log ε) = 255.0 (6.2), 320.0 (5.7) nm. MALDI–TOF: m/z calcd for $C_{75}H_{20}N_4O_4$: 1040.98; found: 1040.1.

Compound **1c**: reaction temperature: r.t. for 2 h. Column chromatography (silica gel; toluene–hexane, 2:1); yield: 65%. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.87 (d, J = 2.5 Hz, 1 H), 8.52 (dd, J_1 = 2.5 Hz, J_2 = 9.0 Hz, 1 H), 8.49 (sd, J = 9.0 Hz, 1 H), 8.38 (d, J = 9.0 Hz, 2 H), 8.36 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.61, 147.79, 147.32, 147.13, 146.46, 146.42, 146.14, 146.08, 145.60, 145.56, 145.38, 145.33, 145.16, 144.69, 144.33, 144.16, 144.15, 144.08, 143.95, 143.28, 143.07, 142.99, 142.94, 142.49, 142.32, 142.26, 142.08, 141.99, 141.95, 140.64, 140.12, 137.38, 137.21, 136.90, 129.73, 127.32, 127.13, 124.24, 122.20, 91.39, 81.42. FT-IR (KBr): 2357, 1597, 1535, 1335, 526. UV–Vis: λ (log ε) = 245.5 (6.3), 321.5 (5.9) nm. MALDI–TOF: m/z calcd for $C_{73}H_7N_5O_6$: 1049.87; found: 1050.2.

Compound **1d**: reaction temperature: r.t. for 3 h. Column chromatography (silica gel; toluene–hexane, 1:2); yield: 47%. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.88 (d, J = 2.5 Hz, 1 H), 8.67 (br s, 2 H), 8.53 (dd, J_1 = 2.5 Hz, J_2 = 9.0 Hz, 1 H), 8.48 (sd, J = 9.0 Hz, 1 H), 8.00 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.07, 147.58, 146.72, 146.68, 146.40, 146.35, 145.97, 145.79, 145.66, 145.59, 145.12, 144.59, 144.41, 144.16, 144.13, 143.54, 143.33, 143.25, 143.18, 142.73, 142.58, 142.53, 142.31, 142.25, 140.89, 140.40, 137.64, 137.29, 133.46, 132.90, 132.63, 128.93, 127.57, 124.26, 123.99, 122.43, 122.11, 91.81, 81.44. FT-IR (KBr): 2921, 2332, 1597, 1531, 1331, 1274, 1135, 526 cm^{-1}. UV–Vis: λ (log ε) = 254.5 (6.1), 319.0 (5.7) nm. MALDI–TOF: m/z calcd for $C_{75}H_6F_6N_4O_4$: 1140.86; found: 1141.2.

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