N-Arylation of Pyrrolidino[3′,4′:1,2][60]fullerene: Synthesis under Solvent-Free Conditions and Electrochemistry of New C_{60}–Acceptor Dyads

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Several pyrrolidinofullerenes were *N*-arylated by phase-transfer catalysis in the absence of solvent. The electrochemical behaviour of the novel C_{60}–acceptor dyads was studied by cyclic voltammetry which showed that the nitro groups on the *N*-phenyl ring have a strong influence on the reduction potential values. Theoretical calculations at the semiempirical PM3 level fully support the experimental redox potential values.

Introduction

The design and synthesis of organofullerenes with better reduction potentials than C_{60} is currently under intensive research by several groups[1], because C_{60}−acceptor compounds may find application in photovoltaic cells.[2] To improve the electron affinity of the C_{60} sphere, several types of derivatives with electron-withdrawing substituents (EWG) such as cyano groups,[3] fluorine atoms,[4] TCNQ and DCNQI derivatives,[5] or ammonium salts, were prepared.[6] An enhanced effect of the EWG group has been attributed to a through-space orbital interaction phenomenon called "*peri* conjugation"[7] or to inductive effects.[6]

In recent years, the 1,3-dipolar cycloaddition of azomethine ylides to C_{60}[8] has been used extensively to prepare fullerene derivatives,[9] and among the different methods available to generate the reactive intermediates, the most successful approach has been the decarboxylation of immonium salts derived from condensation of α-amino acids with aldehydes. To functionalise the nitrogen atom in pyrrolidinofullerenes, either an *N*-substituted amino acid may be used or the parent pyrrolidinofullerenes may be modified at the N−H functionality. It was reported that reaction with an acylating agent affords the corresponding amide.[10] An important feature is that the fullerene cage influences the acid−base properties of the pyrrolidine nitrogen atom: It was shown that pyrrolidinofullerenes are almost six orders of magnitude less basic than their non-C_{60}-linked analogues.[9] Moreover, the methylation of the pyrrolidine nitrogen atom by excess methyl iodide is much slower for pyrrolidinofullerenes, confirming the diminished availability of the nitrogen lone pair.

Phase-transfer catalysis (PTC) in the absence of solvent is especially useful for reactions that are particularly difficult, or require harsh conditions.[11] We recently described the facile synthesis of a series of *N*-alkylpyrrolidino[60]fullerenes by PTC in the absence of solvent under microwave irradiation.[12] Despite the low reactivity of the nitrogen atom of the pyrrolidinofullerenes, this procedure allowed its *N*-alkylation.

Now we report the arylation of the readily available pyrrolidinofullerenes under very easy experimental conditions, thus improving the arsenal of available reactions for the functionalisation of [60]fullerene. The new compounds were electrochemically characterised by cyclic voltammetry measurements, and semiempirical PM3[13] calculations were performed to determine the geometry and the HOMO−LUMO levels of these molecules.

Results and Discussion

PTC in the absence of solvent is a useful technique for anionic activation and has been applied to several types of nucleophilic substitution reactions.[14] However, there has been only a few reported examples in which solvent-free PTC has been applied to nucleophilic aromatic substitution reactions (S_NAr).[15] In this paper, we report the solvent-free phase-transfer catalysed S_NAr reactions of a series of pyrrolidinofullerenes, where the latter are the nucleophiles and 1-chloro-2,4-dinitrobenzene is the substrate, to prepare new C_{60}−acceptor dyads, which incorporate a 2,4-dinitrophenyl moiety as acceptor.

Reactions were carried out according to Scheme 1: 1-Chloro-2,4-dinitrobenzene was treated with 2-arylpyrrolidino[60]fullerenes **1a−c**,[16] with TBAB as PTC agent and potassium carbonate as base, at 150 °C for 8−12 h (see Experimental Section). Our group[17] and other authors[18] have shown that if PTC in the absence of solvent is combined with microwave irradiation, yields are improved, and reactions that usually require harsh conditions which result in partial decomposition of reagents and products, may be carried out with better results. In this context we described

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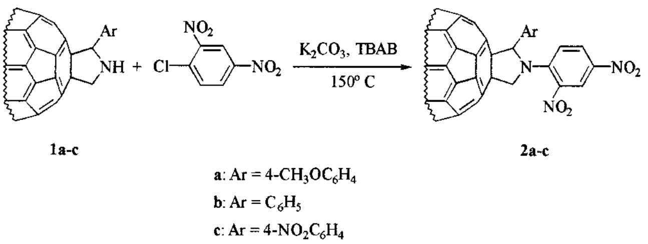
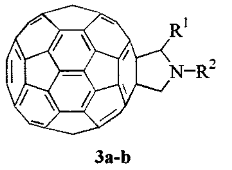
the first application of this technique to fullerene chemistry.[12] However, we could not apply the microwave technique to the new reactions described in this paper: After a few seconds of irradiation an electrical arc occurred in the microwave cavity and no starting material could be recovered. Attempts with other concentrated solutions of different compounds also resulted in sparking.[19]



Scheme 1. Synthetic approach for compounds **2a−c**

The structure of the novel pyrrolidinofullerenes **2a−c** was confirmed by their analytical and spectroscopic data. The UV/Vis spectra show a typical absorption band at around 430 nm. The ^{1}H-NMR spectra contain signals for the pyrrolidine protons at δ = 4.8−5.6 (doublets, $J \approx$ 10 Hz) and 6.2−6.4 (CH), in agreement with other related derivatives; the resonances for the 2,4-dinitrophenyl moiety occur at δ = 8.3−8.9. The FAB and electrospray mass spectra contain MH^+ peaks of **2a−c** at *m/z* 1036, 1006 and 1051, respectively.

Cyclic voltammetry (CV) was employed to study the electrochemical behaviour of species **2a−c** in solution. We also studied the electrochemical behaviour of **1b−c** and **3a,b**[20] (Figure 1) for comparison, to determine the influence of the 2,4-dinitrophenyl moiety on the redox properties of compounds **2a−c**. The results are reported in Table 1 along with the data for C_{60} as reference.



3a-b

Compound	R¹	R²
3a	C_6H_5	$4\text{-}NO_2\text{-}C_6H_4\text{-}CH_2$
3b	$CH(CH_3)_2$	H

Figure 1. Model compounds for electrochemical study

Compounds **2a−c** and the reference compounds show quasi-reversible electrochemical behaviour with five one-electron waves corresponding to the first four reductions of the [60]fullerene cage and the organic addend. The reduction potential values of **1b−c** and **3a,b** shifted to more negative values than those of the parent C_{60}, as expected for most 1,2-dihydrofullerenes,[9] and rationalised on the basis of the saturation of a double bond in the C_{60} core.[1] In contrast, the cyclic voltammograms of the newly synthesised compounds **2a−c** are characterised by small reduction potential shifts towards more positive values than those of reference compounds **1b−c** and **3a,b**, and very close to the values of the parent, C_{60}. This finding can be attributed to the inductive effect of the 2,4-dinitrophenyl group. Moreover, compound **2c**, with a second EWG (*p*-nitrophenyl group) on the pyrrolidine ring, has a slightly more positive (10 mV) first reduction potential than C_{60},

Table 1. Redox properties of C_{60}, **1b-c**, **3a,b** and novel compounds **2a-c**[a]

Compound	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}
C_{60}	−0.60	−1.00	−1.52	−2.04
1b	−0.72	−1.13	−1.70	−2.18
1c	−0.66	−1.10 (br.)	−1.60	−2.14
2a	−0.62	−1.06 (−1.48)	−1.67	−2.15
2b	−0.64	−1.06 (−1.41)	−1.64	−2.25
2c	−0.59	−1.00 (−1.46)	−1.45	−2.25
3a	−0.65	−1.05 (−1.23)	−1.64	−2.19
3b	−0.67	−1.06	−1.63	−2.10

[a] All potentials in V vs. SCE; $Bu_4N^+ClO_4^-$ (0.1 M). Solvent: toluene/acetonitrile (4:1). Sweep rate 0.2 V s^{-1}.

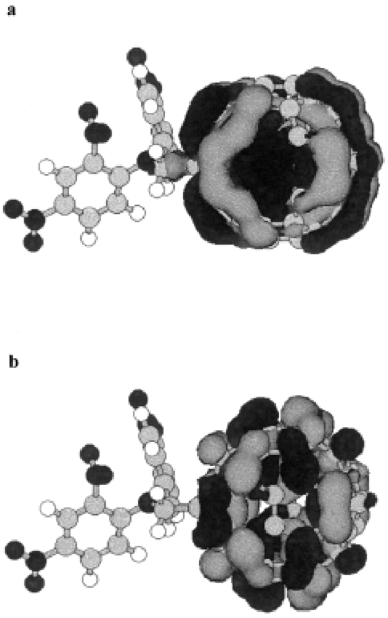


Figure 2. PM3-calculated frontier orbitals of **2c**: (a) HOMO; (b) LUMO

Table 2. Calculated HOMO and LUMO energies (PM3) in eV.

Compound	HOMO	LUMO
1b	−9.128	−2.786
1c	−9.307	−2.946
2a	−9.338	−2.975
2b	−9.339	−2.973
2c	−9.506	−3.121
3a	−9.309	−2.949
3b	−9.133	−2.793

thus confirming that the effect results from the *N*-aryl group.

The optimised geometries of compounds **1b−c**, **2a−c** and **3a,b** were obtained by semiempirical calculations (PM3) and their orbital energies are listed in Table 2. Figure 2 displays the most stable conformation of adduct **2c** and the HOMO and LUMO which are both localised on the C_{60} cage. As shown in Table 2, all compounds except those without nitro groups have a lower LUMO energy level than C_{60} has, with the lowest value belonging to **2c**, as found by CV too. According to Suzuki,[21] the first reduction potentials of compounds **1b−c**, **2a−c** and **3a,b** correlate well (r = 0.87) with the LUMO energy levels calculated by the PM3 method; this shows that the calculated LUMO levels can be used to estimate the reduction potentials of organofullerenes.

Conclusions

The synthesis of new C_{60}−acceptor dyads incorporating a 2,4-dinitrophenyl group[22] was accomplished, with moderate yields, by facile nucleophilic aromatic substitution reactions by PTC in the absence of solvent. The new *N*-arylpyrrolidinofullerenes have interesting reduction potentials compared to those of other pyrrolidinofullerenes; **2c** was shown to be a slightly better acceptor than C_{60}. The electrochemical properties were rationalised with the aid of semiempirical PM3 calculations: The first reduction potential correlated well with the LUMO level.

Experimental Section

General: ^{1}H NMR: Varian Mercury 200 or Varian Unity 300 instruments. − MS-FAB: VE-Autospec EBE spectrometer, with *m*-nitrobenzyl alcohol as matrix. − Electrospray MS: Micromass Lt. Platform II single quadrupole spectrometer. − FT IR: Nicolet Magna IR spectrometer 550. − UV: UV Beckman DU-70 spectrophotometer. −TLC: Merck, silica gel F_{254}. − Products were isolated by gravitational column chromatography (SDS, silica gel particle size 70−230 mesh). − Electrospray MS data were recorded with a Micromass Ltd. Platform II single quadrupole mass spectrometer. For continuous infusion experiments, a syringe pump (Harvard Apparatus. Inc.) and a glass syringe were used to deliver sample solutions to the ESI interface. These solutions were pumped at a rate of 15−30 μL/min through a short length of 0.1 μm i.d. Samples were prepared immediately before injection, 0.1 mg of sample was dissolved in 1 mL of $CHCl_3$, 100 μL of this solution was added to 100 μL of the reacting solution (100 mL $CHCl_3$, 3 mg DDQ, 0.2 mL TFA) and 100 μL of CH_3OH was also added to improve the spray. The samples were sonicated for 30 s before injection. ES MS parameters: Capillary voltage: 3.5 kV. Sample cone voltage: 30, 70, 100, 130 V. Source temp.: 100°C. − Electrochemical measurements: Versastat PAR EG & G potentiostat with analytical electrochemical software (Mod. 250). These measurements were made in a double-wall cell (Metrohm EA 876−20). A glassy carbon working electrode (Metrohm 6.0804.010) was used after being polished with alumina (0.3 μ) for 1 min, and as counterelectrode a platinum wire was used. A saturated calomel solution, used as reference electrode, was separated from the solution by a solution of tetrabutylammonium perchlorate, which was used as supporting electrolyte, in toluene/acetonitrile (4:1) as solvent. The samples were purged with argon prior to measurement.

General Procedure: A mixture of the corresponding pyrrolidino[3′,4′:1,2][60]fullerene (0.04 mmol), 2,4-dinitrochlorobenzene (0.18 mmol), potassium carbonate (0.23 mmol) and tetrabutylammonium bromide (0.11 mmol) was homogenised in an ultrasonic bath for 10 min and heated in a preheated sand bath at 150°C for the corresponding time. Then the mixture was cooled to room temperature and washed with carbon disulfide. The solvent was evaporated under reduced pressure and the crude product was purified by gravitatory chromatography [SiO_2, hexane/toluene (1:2) and hexane/toluene (1:4)] to give the reaction product and the starting material.

***N*-(2,4-Dinitrophenyl)-2-(4-methoxyphenyl)pyrrolidino[3′,4′:1,2][60]fullerene (2a):** Reaction time 8 h. Yield: 21%. − ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ = 3.73 (s, 3 H), 4.87 (d, 1 H, J = 10.0 Hz), 5.52 (d, 1 H, J = 10.0 Hz), 6.21 (s, 1 H), 6.84 (d, 2 H, J = 8.7 Hz), 7.59 (d, 1 H, J = 8.8 Hz), 7.62 (d, 2 H, J = 8.7 Hz), 8.34 (dd, 1 H, J = 8.8, 2.5 Hz), 8.84 (d, 1 H, J = 2.5 Hz). − MS (FAB); m/z: 1036 [MH^{+}]. − FT IR (KBr): $\tilde{\nu}$ = 2665, 2360, 2338, 1653, 1558, 1540, 1507, 1437, 1364, 729, 523. cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 255, 327, 430 nm.

***N*-(2,4-Dinitrophenyl)-2-phenylpyrrolidino[3′,4′:1,2][60]fullerene (2b):** Reaction time 8 h. Yield: 25%. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 4.92 (d, 1 H, J = 9.8 Hz), 5.56 (d, 1 H, J = 9.8 Hz), 6.30 (s, 1 H), 7.30−7.37 (m, 3 H), 7.61 (d, 2 H, J = 9.5 Hz), 7.74 (d, 1 H, J = 9.0 Hz), 8.37 (dd, 1 H, J = 9.0, 2.7 Hz), 8.88 (d, 1 H, J = 2.7 Hz). − Electrospray MS; m/z: 1006 [MH^{+}], 839, 720 [C_{60}]. − FT IR (KBr): $\tilde{\nu}$ = 2930, 2850, 1629, 1535, 1423, 1050, 903, 728, 526, 462 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 272, 310, 432 nm.

***N*-(2,4-Dinitrophenyl)-2-(4-nitrophenyl)pyrrolidino[3′,4′:1,2][60]fullerene (2c):** Reaction time 12 h. Yield: 19%. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 4.92 (d, 1 H, J = 10.0 Hz), 5.56 (d, 1 H, J = 10.0 Hz), 6.40 (s, 1 H), 7.98 (d, 2 H, J = 8.8 Hz), 7.70 (d, 1 H, J = 9.0 Hz), 8.24 (d, 2 H, J = 8.8 Hz), 8.40 (dd, 1 H, J = 9.0, 2.7 Hz), 8.89 (d, 1 H, J = 2.7 Hz). −MS (FAB); m/z: 1051 [MH^{+}]. − FT IR (KBr): $\tilde{\nu}$ = 2940, 2821, 1736, 1629, 1530, 1454, 1310, 1050, 875, 754, 616, 530, 462 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 267, 313, 430 nm.

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