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A ready access to unprecedented *N*-anilinopyrazolino[60]fullerenes

Juan L. Delgado, Pilar de la Cruz, Vicente López-Arza and Fernando Langa*

Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, 45071 Toledo, Spain

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Abstract—A simple and efficient method for the preparation of new synthons based on versatile amino-functionalize pyrazoline[60]fullerene is described. These intermediates are useful in the preparation of new derivatives for applications in materials science. Finally, electrochemical studies of the newly prepared compounds have been performed in solvents with different polarities.
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The chemical derivatization of fullerenes continues to be the focus of research aimed at finding useful applications of fullerene derivatives in biological and materials science.[1] Amongst the applications of functionalized fullerenes, those based on their electrochemical[2] and photophysical properties[3] are currently the most avidly investigated. Functionalized fullerenes can potentially be prepared using a wide range of synthetic reactions. The most popular approaches to the modification of fullerene C_{60} are the Bingel–Hirch reaction and the Prato–Maggini reaction, which lead to methanofullerenes (**A**) or pyrrolidino[60]fullerenes (**B**), respectively (Fig. 1).[4]

We have developed the 1,3-dipolar cycloaddition reaction of nitrile imines, prepared in situ from hydrazones, to afford pyrazolino[60]fullerenes (**C**).[5] This procedure has several advantages: (1) hydrazones are easily available in one step from aldehydes with almost quantitative yields, (2) the cycloadducts are obtained in good yields, (3) the formation of stereoisomers does not occur—in contrast to other methods of functionalization—and, most importantly, (4) unlike other fullerene derivatives, pyrazolino[60]fullerenes present similar reduction potentials to the parent C_{60}, which has proven to be an excellent three-dimensional electron acceptor.[6]

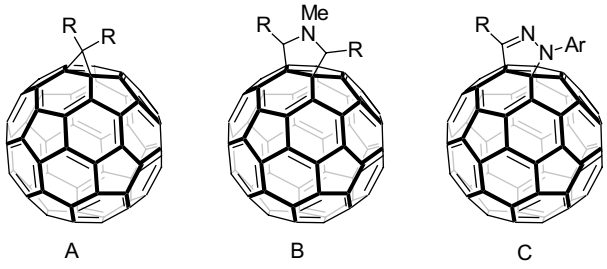

Figure 1.

Consequently, pyrazolino[60]fullerenes are excellent candidates for the preparation of donor-C_{60} dyads for photoinduced electron transfer.[7] One drawback of this method of functionalization is that, although the reaction is general for any kind of aldehyde (C-side of the final pyrazolino[60]fullerene), in terms of the N-side the route is limited by the availability of the starting hydrazine to form the hydrazone. Despite the fact that *N*-phenyl or *N*-*p*-methoxyphenyl pyrazolino[60]fullerenes have been prepared, the best results have been obtained from *p*-nitrophenyl hydrazones.[8] It is therefore desirable to find a procedure that would allow the preparation of pyrazolino[60]fullerenes with substitution in the N-side of the pyrazoline ring. This would open the gate to introduce a range of desirable moieties on the N-side of the pyrazolino[60]fullerene system. In particular, an amino-functionalized fullerene would be a convenient synthon to prepare other derivatives with the appropriate functionalities for a given application.[9] In this paper we describe the synthesis and electrochemical properties of new *N*-anilinopyrazolino[60]fullerenes **2a**–**e** and their chemical modification by acylation reactions.

The strategy employed for the preparation of the target compounds **2a**–**e**, **3** and **4** starts from *N*-*p*-nitrophenylpyrazolino[60]fullerene derivatives **1a**–**e**[10] and is depicted in Scheme 1. Fullerene derivative **1c**[11] was

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* Corresponding author. Tel.: +34-92-5268-843; fax: +34-925-268-840; e-mail: fernando.lpuente@uclm.es

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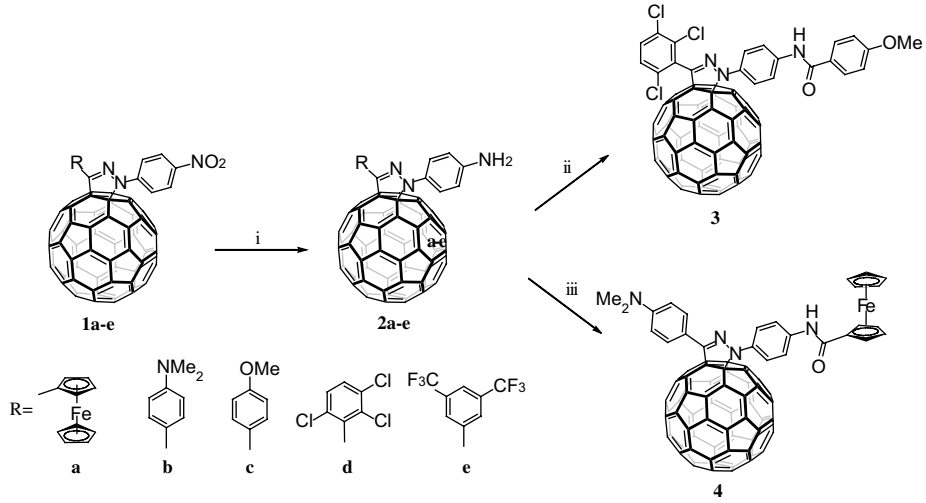

Scheme 1. Reagents and conditions: (i) Sn, HCl, $CHCl_3$, 2 h, reflux; (ii) 4-MeO–C_6H_4–COCl, CH_2Cl_2, 4 h, room temperature; (iii) Fc-COCl, CH_2Cl_2, 24 h, room temperature.

prepared in 43% yield from the corresponding hydrazone according to the procedure described previously for other pyrazolino[60]fullerenes.[12]

The reduction of **1a**–**e** (50 mg) was performed with tin (2 g) and concd HCl (25 mL) in chloroform (20 mL) for 2 h at reflux and alkanilization with concd NaOH.[13] The reactions gave, after work up and purification by column chromatography, compounds **2a**–**e** in 72–88% yield.

Amino derivatives **2a**–**e** were characterized by UV–vis, FT-IR, and ^1H and ^{13}C NMR.[14] The structures of all new compounds were also confirmed by their MALDI-TOF mass spectra, which showed the expected molecular ion peaks in each case.

The electrochemical properties of cycloadducts **2a**–**e** were studied by cyclic voltammetry (CV) at room temperature in *o*-dichlorobenzene/acetonitrile (4:1) and *o*-dichlorobenzene/dichloromethane (4:1) as solvents. The CV data of the new series of amino derivatives are collected in Table 1 along with those of C_{60}.

The prepared compounds exhibited amphoteric redox behavior. All compounds showed the presence of three quasi-reversible reduction waves (see Fig. 2, left), resembling the trend found for C_{60}.[15] Interestingly, amino derivatives **2a**–**e** show different electrochemical behavior in the solvents studied in comparison to C_{60}. In the less polar mixture (ODCB/dichloromethane), compounds **2a**–**e** show reduction potentials that are shifted to more positive values than the parent C_{60} (i.e., an improved electron affinity). Nevertheless, in the most polar solvent mixture (ODCB/acetonitrile), the reduc-

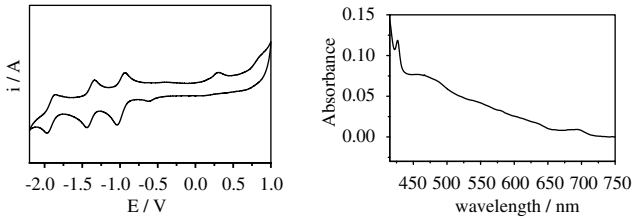

Figure 2. Left: cyclic voltammetry of compound **2d** in ODCD/acetonitrile (4:1); right: UV–vis spectrum of compound **2d** in CH_2Cl_2.

Table 1. $E_{1/2}$ values measured as the average of the anodic and cathodic peak potentials (CV) of compounds **2a**–**e** and C_{60} at room temperature[a]

Compound	Solvent					
	ODCB/acetonitrile 4/1					ODCB/CH_2Cl_2 4/1
	E^1_{red}	E^2_{red}	E^3_{red}	E^1_{ox}	E^2_{ox}	E^1_{red}
C_{60}	−0.94	−1.36	−1.84	—	—	−0.94
2a	−1.01	−1.41	−1.91	0.13[c]	0.39[b]	−0.91
2b	−1.00	−1.40	−1.90	0.16	0.32[b]	−0.88
2c	−1.00	−1.39	−1.90	0.37[b]	0.57[b]	−0.89
2d	−0.98	−1.39	−1.91	0.30[b]	—	−0.89
2e	−1.00	−1.40	−1.89	0.32[b]	—	−0.89

[a] Experimental conditions: V versus $Ag/AgNO_3$; GCE as working electrode; 0.1 M TBAP; scan rate: 100 mV/s.
[b] Irreversible.
[c] Reversible, corresponding to the ferrocene addend.

tion potentials are slightly shifted to more negative values compared to C_{60}. A possible explanation for this observation is related to an electronic interaction between the aniline group and the fullerene cage, which is a good acceptor, in the ground state;[16] such an interaction should be stabilized in more polar solvents, although this question requires a more in-depth study. As confirmation of this interaction, in the UV–vis spectra of these compounds, a weak broad band is observed between 440 and 520 nm (Fig. 2, right). Further electrochemical investigations in other solvents need to be undertaken to confirm this explanation.

On the oxidation side, an irreversible wave at around 0.3–0.4 V is observed in all cases and this can be assigned to oxidation of the amino group. In compound **2a** an additional reversible wave is seen at 0.13 V, and this corresponds to oxidation of the ferrocene moiety. In compound **2b**, the *N*,*N*-dimethylamino group is oxidized at 0.16 V.

As an example of further functionalization, we used amino-fulleropyrazolines **2b** and the newly synthesized derivative **2d** to prepare the amide derivatives **3** and **4**. These compounds were prepared in 82% (**3**) and 78% (**4**) yield by reaction with the corresponding acid chloride (Scheme 1). The new compounds **3** and **4** were fully characterized.[17] Derivative **4**, in which two different donors (*N*,*N*-dimethylanilino and ferrocene) are linked to the C_{60} cage through a pyrazoline ring spacer, is particularly interesting from the photophysical point of view and its electrochemical and photophysical properties are currently under investigation.

In conclusion, we have described a simple and efficient method for the preparation of new synthons based on versatile amino-functionalized fullerenepyrazolines. The electrochemical properties of the new amino derivatives have been studied in solvents of different polarity. Finally, simple condensation reactions of these intermediates produce new derivatives that are useful for applications in material science.

Acknowledgements

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10. The synthesis of **1a** and **1b** has been described previously: Espíldora, E.; Delgado, J. L.; de la Cruz, P.; de la Hoz, A.; López-Arza, V.; Langa, F. *Tetrahedron* **2002**, *58*, 5821–5826, The synthetic procedure for **1d** and **1e** will be described elsewhere.
11. Selected spectroscopic data for **1c**: ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 3H), 7.07 (d, $J = 8.9$ Hz, 2H), 8.19 (d, $J = 8.9$ Hz, 2H), 8.26 (d, $J = 9.4$ Hz, 2H), 8.33 (d, $J = 9.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.8, 114.6, 119.4, 124.0, 125.5, 130.8, 136.2, 137.1, 139.5, 142.3, 142.5, 143.4, 144.2, 144.5, 144.7, 145.4, 145.7, 146.0, 146.2, 146.5, 148.2, 149.9, 144.3, 144.8, 145.1, 145.2, 145.4, 145.7, 145.8, 145.8, 143.2, 147.2, 147.7; MS *m*/*z* 989.2, 720.1.
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14. Selected spectroscopic data for **2a**–**e**. **2a**: FT-IR (KBr) ν (cm^{-1}) 3421, 1501, 1107, 815, 723, 533; ^{1}H NMR ($CDCl_3$) δ 3.72 (br s, 2H), 4.23 (s, 5H), 4.52 (t, $J = 1.8$ Hz, 2H), 5.27 (d, $J = 1.8$ Hz, 2H), 6.78 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 68.6, 70.3, 84.0, 93.4, 105.0, 106.4, 115.8, 124.1, 126.9, 135.8, 138.9, 141.8, 142.7, 142.9, 143.2, 144.4, 144.7, 145.4, 145.7, 146.0, 146.2, 147.2, 147.6, 156.6; UV–vis (CH_2Cl_2) λ_{max} (nm) ($\log\varepsilon$) 256 (5.3), 312 (4.9), 426 (3.8), 466 (3.3), 687 (3.0); MS *m*/*z* 1037.1, 720.1. **2b**: FT-IR (KBr) ν (cm^{-1}) 3442, 1504, 1194, 810, 526; ^{1}H NMR ($CDCl_3$) δ 3.04 (s, 6H), 3.72 (br s, 2H), 6.77 (d, $J = 8.8$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 7.67 (d, $J = 8.8$ Hz, 2H), 8.21 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 40.6, 112.1, 115.8, 120.3, 127.0, 130.0, 136.0, 136.5, 137.1, 139.8, 140.1, 141.7, 142.2, 142.4, 142.8, 143.1, 143.8, 144.4, 144.6, 144.2, 145.2, 145.3, 145.7, 145.9, 146.1, 146.3, 146.4, 146.9, 147.1, 147.6, 150.8; UV–vis (CH_2Cl_2) λ_{max} (nm) ($\log\varepsilon$) 258 (5.0), 315 (4.6), 425 (3.7), 699 (2.5); MS *m*/*z* 972.2, 720.1. **2c**: FT-IR (KBr) ν (cm^{-1}) 3370, 1600, 1500, 1250, 1170, 825, 525; ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H), 3.92 (br s, 2H), 6.79 (d, $J = 8.8$ Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 2H), 7.80 (d, $J = 8.8$ Hz, 2H), 8.10 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 56.0, 114.4, 115.9, 125.3, 127.2, 130.4, 136.1, 136.7, 136.8, 140.1, 140.4, 142.0, 142.3, 143.0, 143.3, 144.5, 144.9, 145.3, 145.4, 145.6, 145.9, 146.1, 146.3, 145.6, 145.9, 146.1, 146.3, 146.5, 146.6, 146.7, 147.4, 147.8; UV–vis (CH_2Cl_2) λ_{max} (nm) ($\log\varepsilon$) 258 (5.0), 314 (4.6), 426 (3.4), 691 (2.2); MS *m*/*z* 959.1, 720.1. **2d**: FT-IR (KBr) ν (cm^{-1}) 3462, 3421, 3355, 1624, 1516, 1173, 723, 528; ^{1}H NMR ($CDCl_3$) δ 3.75 (br s, 2H), 6.79 (d,

$J = 8.8$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 69.8, 92.6, 115.7, 116.0, 126.9, 127.2, 129.1, 132.1, 132.7, 135.6, 135.8, 136.3, 136.5, 140.0, 140.5, 141.8, 142.0, 142.2, 142.3, 142.7, 143.2, 144.2, 144.3, 144.8, 145.1, 145.2, 145.4, 145.7, 145.8, 145.8, 146.2, 147.2, 147.7; UV–vis (CH_2Cl_2) λ_{max} (nm) ($\log \varepsilon$) 263 (5.3), 314 (5.0), 427 (3.6), 466 (3.5), 693 (2.7); MS m/z 1033.0, 720.1. **2e**: FT-IR (KBr) ν (cm^{-1}) 3375, 1619, 1501, 1276, 1158, 1132, 810, 697, 528; ^{1}H NMR ($CDCl_3$) δ 3.79 (br s, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.88 (s, 1H), 8.84 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 80.2, 93.7, 115.7, 116.1, 120.6, 122.0, 126.1, 127.5, 127.7, 128.2, 131.2, 131.8, 132.5, 133.2, 134.8, 135.1, 136.0, 137.9, 138.9, 140.1, 141.9, 142.2, 142.3, 142.9, 142.9, 143.2, 144.3, 144.4, 145.0, 145.1, 145.3, 145.3, 145.5, 145.6, 145.7, 145.8, 146.0, 146.3, 146.4, 147.3, 147.7; UV–vis (CH_2Cl_2) λ_{max} (nm) ($\log \varepsilon$) 256 (5.2), 317 (4.9), 425 (3.7), 686 (2.5); MS m/z 1064.1, 720.1.

15. A weak peak at around 0.6 V (see Fig. 2) is observed after the first oxidation of the amino group. It does not appear in the first sweep, when starting at 0 V and going first to negative potentials.
16. For a recent review on electronic interactions between donors and [60]fullerene, see: Echegoyen, L.; Herranz, M. A. In *Fullerene Electrochemistry*; Guldi, D. M., Martín, N., Eds.; *Fullerenes: From Synthesis to Optoelectronic Properties*; Kluwer, 2002. Chapter 9.
17. Selected spectroscopic data for **3**: ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H), 3.90 (s, 3H), 7.00 (d, $J = 8.8$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 7.77–7.88 (m, 8H), 8.31 (d, $J = 8.8$ Hz, 2H); MS m/z 1165.1, 720.1. **4**: ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 6H), 4.28 (s, 5H), 4.43 (s, 2H), 4.78 (s, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 7.42 (br s, 1H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.93 (d, $J = 8.8$ Hz, 2H), 8.22 (d, $J = 8.8$ Hz, 2H); MS m/z 1184.1, 720.1.