Pergamon

Tetrahedron Letters 40 (1999) 4889–4892

TETRAHEDRON
LETTERS

Electroactive 3'-(*N*-Phenylpyrazolyl)isoxazoline[4',5':1,2][60]Fullerene Dyads

Pilar de la Cruz,[a] Eva Espíldora,[a] José J. García,[a] Antonio de la Hoz,[b*]
Fernando Langa,[a*] Nazario Martín,[c*] and Luis Sánchez[c]

[a] *Departamento Q. Orgánica, Facultad de CC del Medio Ambiente, Universidad de Castilla-La Mancha, 45071, Toledo, Spain*[1]
[b] *Departamento de Q. Orgánica, Facultad de CC Químicas, Universidad de Castilla-La Mancha, 13071, Ciudad Real, Spain*
[c] *Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain*

Received 25 March 1999; accepted 6 May 1999

Abstract: Novel C_{60}-fused isoxazolines have been synthesized by using 1,3-dipolar cycloadditions of pyrazole nitrile oxides, generated *in situ*, to C_{60} under thermal or focused microwave irradiation. The cyclic voltammetry measurements show a strong donor pyrazole ring and a better acceptor ability of the fullerene moiety compared to pristine C_{60}. The UV-Vis and ^{1}H NMR spectra suggest a weak CT interaction in the ground state. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Fullerenes; Cycloadditions; Cyclic Voltammetry; Microwave Heating; Isoxazole, Pyrazole

The design and synthesis of novel modified fullerenes exhibiting better electron-acceptor properties than the parent [60]fullerene is currently an active research field due to their potential applications as in optoelectronic devices.[1] Organofullerenes show, in general, reduction potential values which are cathodically shifted in comparison to C_{60},[2] and only a limited number of examples with less negative potentials than C_{60} have been reported.[3] The presence of electronegative atoms,[4] periconjugative effects[5] or ammonium salts[6] have been successfully used in the preparation of stronger acceptors than C_{60}.

Recently, we have described the synthesis of several 1-aryl-3-(1-phenylpyrazol-4-yl)-pyrazolo[4',5':1,2][60]fullerene adducts by 1,3-dipolar cycloaddition of the corresponding nitrile imines generated *in situ* from the corresponding hydrazones and NBS in the presence of Et_3N and reacted with C_{60} under microwave irradiation.[7] The target molecules showed an interesting low field shift in their ^{1}H-NMR spectra with respect to the corresponding hydrazone. Considering previous results [8] and that the magnitude of the low field shift in the donor unit when linked to C_{60} provides direct information for CT interactions between the donor moiety and the [60]fullerene,[9] it was of interest to study a possible intramolecular CT interaction from the *N*-phenyl and *C*-pyrazolyl groups to C_{60} in the ground state.

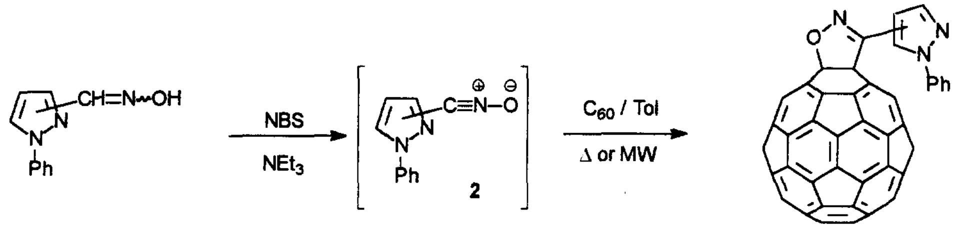
In this context and in order to get a deeper insight into the behaviour of this kind of C_{60}-donor dyad, we report herein the preparation of dyads **3** and **4**, in which a donor pyrazole unit is covalently attached to the strong isoxazolinefullerene acceptor. We have used the corresponding nitrile oxides **2** as precursors for adducts **3-4**. Although the most common way to generate nitrile oxides use hydroxymoyl chlorides as starting materials, in our case the oxime was treated with NBS in the presence of Et_3N and reacted *in situ* with C_{60} under

---

[1] E-mail: flanga@amb-to.uclm.es

PII: S0040-4039(99)00904-1

microwave irradiation.[10] Under these conditions, adducts **3-4** were obtained in 22% in both cases after isolation by flash chromatography (silica gel, toluene). Longer reaction times afforded greater amounts of bisadducts. The same reactions were carried out under thermal conditions and similar yields were obtained (**3**: 14 %; **4**: 17%). A significative accelerating effect (10 minutes *vs* 24 hours) occurs under microwave irradiation without significant improvement in yield[11] or change in selectivity.[12] The structures of the novel compounds were supported by their spectroscopic data (UV-Vis, FTIR, ^{1}H-NMR and FAB mass spectra).[13] In the ^{1}H-NMR spectra, the signals of the pyrazole hydrogens appeared at δ 8.52 (H_3) and 8.73 (H_5) for compound **3** and δ 7.04 (H_4) and 7.84 (H_3) for compound **4**. For dyad **3** these values show a remarkable low field shift related to the corresponding starting oxime [δ 8.03 (H_3) and 8.64 (H_5) for **1a** and δ 6.76 (H_4) and 7.66 (H_3) for **1b**]. Although these findings could be accounted for by the theoretically predicted (PM3) shorter distance of proton H-3 to the pentagonal ring of the C_{60} surface in comparison to dyad **4**, (**3**: 2.46 Å; **4**: 2.66 Å), a specific donor/acceptor interaction can not be ruled out.



1a: 4-formyl(N-phenyl)pyrazole oxime
1b: 5-formyl(N-phenyl)pyrazole oxime

3: 4-(N-Phenyl)pyrazolyl
4: 5-(N-Phenyl)pyrazolyl

Scheme

On the basis of ^{1}H NMR and UV-Vis studies, an intramolecular CT-interaction between a benzene ring and C_{60} has been previously reported by Yoshida *et al.*[9] In our case, in addition to similar NMR observations, a weak CT band at around 460 nm which is bathochromically shifted with increasing solvent polarizability[14] is observed in the UV-Vis spectra [**3**: cyclohexane (n=1.4262) 455 nm; dichloromethane (n=1.4242) 455 nm; CS_2 (n=1.6275) 460 nm; **4**: cyclohexane 458 nm; dichloromethane 458 nm; CS_2 463 nm]. The same trend is also observed for the band at around 690 nm. The typical weak peak for the [6,6] ring junction of 1,2-dihydrofullerenes is also observed at 425 nm.

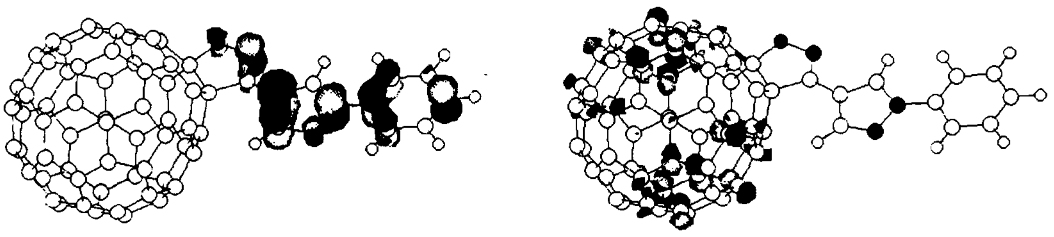


Figure 1. PM3 calculated frontier orbitals (left: HOMO, right: LUMO) of **3**.

Theoretical calculations confirm the lowest energy of the LUMO in **3** (HOMO: -9.17 eV, LUMO: -2.91 eV) and **4** (HOMO: -9.40 eV, LUMO: -3.00 eV) related to pristine C_{60} (HOMO: -9.48 eV, LUMO: -2.88 eV). In these compounds, the HOMO is located on the organic addend and the LUMO spreads on the C_{60} core

(Figure 1). The calculated distance between the closest C-atom of the pyrazole ring to the C_{60} surface was found to be 3.29 Å in dyads **3**; this distance is shorter than the sum of the Van der Waals radii for C-C interaction (3.40 Å).[15] These data suggest that a weak electronic interaction could take place between both moieties.

To support the strong donor character observed for the pyrazole ring, the redox properties of the novel compounds were determined by cyclic voltammetry measurements at room temperature (Table). Compounds **3** and **4** show a quasi-reversible electrochemical behaviour with four one-electron reduction waves corresponding to the reduction of the [60]fullerene moiety and the organic addend. Interestingly, the reduction potential values show an anodic shift (70 mV for **3** and 50 mV for **4**) in comparison to the parent C_{60}. Therefore, these new isoxazoline-fused organofullerenes present a better acceptor ability than unsubstituted C_{60}. This effect could be reasonably attributed to the combined effect of the electronegativity of the oxygen atom linked to the C_{60} core and, in a less extent, to the electron-deficient character of C-3 of the isoxazoline ring. In this regard, it is important to note that although isoxazoline[4',5':1,2][60]fullerene are well known species,[16] their electrochemical properties have been scarcely studied by CV and only one isoxazolinefullerene bearing an ester group was electrochemically characterized [17] showing a first reduction potential close to that of pristine C_{60}.

Table. Redox Potentials of Compounds **1a**,**b**, **3**, **4** and C_{60}.

Compound[a]	E^1_{red}	E^2_{red}	E^3_{red}	$E_{red}^{org.\ addend}$	E_{ox}
1a	—	—	–	—	0.37
1b	—	—	–	—	0.37
3	-0.52	-0.92	-1.42	-1.73	0.38
4	-0.54	-0.93	-1.40	-1.64	0.31
C_{60}	-0.59	-0.99	-1.48	—	—

[a] Experimental Conditions: V *vs* SCE; GCE as working electrode; $Bu_4N^+ClO_4^-$ 0.1 M as supporting electrolyte; ODCB:MeCN (4:1) as solvent; scan rate 200 mV/s.

An irreversible oxidation wave, at around 0.35 V, corresponding to the oxidation of the pyrazole moiety, is also observed (Figure 2). This oxidation potential of the *N*-phenylpyrazole unit is quite remarkable being lower than that observed for *N,N*-dimethylaniline[18] which forms intermolecular CT-complexes in solution with C_{60} showing low equilibrium constants.[19] Therefore, organofullerenes **3** and **4** could behave like C_{60}-σ-donor dyads in which a certain electronic interaction can take place to some extent.

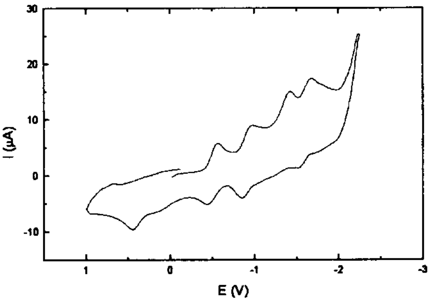


Figure 2. Cyclic voltammogram of compound **4** at 200 mV/s

In summary, we have prepared novel isoxazoline-fused [60]fullerene derivatives by using 1,3-dipolar cycloadditions of nitrile oxides to [60]fullerene under thermal and focused microwave irradiation. The resulting compounds show an enhanced acceptor ability in comparison to the parent C_{60}. The electrochemical measurements show an oxidation wave at low positive values which indicates the presence of a strong electron-donor *N*-phenylpyrazole unit. The UV-Vis and ^{1}H NMR spectroscopic data could support a weak donor-acceptor interaction in the ground state. These systems are promising candidates for further photophysical studies. Work is in progress in that way.

Acknowledgments. Financial support from DGESIC (Projects PB97-0429 and PB95-0428-CO2) and Iberdrola is gratefully acknowledged. One of us (E.E.) thanks the Junta de Comunidades de Castilla-La Mancha for a fellowship.

References and Notes

[1] Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. Chem. Rev. 1998, 98, 2527-2548.

[2] Echegoyen, L.E.; Echegoyen, L. Acc. Chem. Res. 1998, 31, 593-601.

[3] Illescas, B.; Martín, N.; Sánchez, L.; Pérez, I, Herranz, M.A.; González, S.; Ortí E.; Viruela, P.M.; Viruela, R. C_{60}-Based Electron Acceptor Organofullerenes in "*Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*"; Kadish, K. M.; Ruoff, R. S. Eds.; Vol. 6 (August 1998), pp. 1127-1145.

[4] Hummelen, J.C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. Science, 1995, 269, 1554-1556.

[5] Knight, B.; Martín, N.; Ohno, T.; Ortí, E.; Rovira, C.; Veciana, J.; Vidal-Gancedo, J.; Viruela, P.M.; Viruela, R.; Wudl, F. J. Am. Chem. Soc. 1997, 119, 9871-9882 and references cited therein.

[6] da Ros, T.; Prato, M.; Carano, M.; Ceroni, P.; Paolucci, F.; Roffia, F. J. Am. Chem. Soc. 1998, 120, 11645-11648.

[7] de la Cruz, P.; Díaz-Ortiz, A.; García, J.J.; Gómez-Escalonilla, M.J.; de la Hoz, A.; Langa, F. Tetrahedron Lett. 1998, 40, 1587-1590.

[8] Talukdar, S.; Pradhan, P.; Banerji, A. Full. Sci. & Techn. 1997, 5, 547.

[9] Matsubara, Y.; Tada, H.; Nagase, S.; Yoshida, Z. J. Org. Chem. 1995, 60, 5372-5373.

[10] Oxime **1** (13 mg, 0.07 mmol), NBS (13 mg, 0.07 mmol) in benzene (45 mL) were stirred for 15m; afterwards Et_3N (7 mg, 0.07 mmol) and C_{60} (50 mg, 0.07 mmol) were added. The mixture was irradiated in a focused microwave reactor (Maxidigest MX350, from Prolabo) at 210 W for 10 min.

[11] de la Cruz, P.; de la Hoz, A.; Langa, F.; Illescas, B.; Martín, N. Tetrahedron 1997, 53, 2599-2608.

[12] Langa, F.; de la Cruz, P.; de la Hoz, A.; Diez-Barra, E.; Diaz-Ortiz, A. Contemporary Org. Synth. 1997, 373-386.

[13] Selected spectroscopic data. **3:** 22 % yield (55 % yield based on recovered C_{60}); ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 8.73 (s, 1H), 8.52 (s, 1H), 7.74 (d, 2H, J=8.0 Hz), 7.51 (dd, 2H, J=7.3 Hz, J=8.0 Hz), 7.37 (t, 1H, J=7.3 Hz); FAB-MS m/z: 906 (MH$^+$), 720 (C_{60}); IRFT (KBr) ν: 2932, 1652, 1646, 1635, 1627, 1464, 1458, 1376, 803, 587 cm^{-1}; UV-Vis (C_6H_{12}) λ_{max} (log ε) 317 (6.30), 425 (5.06), 455 (4.85), 684 (4.11) nm. **4:** 22 % yield (65 % yield based on recovered C_{60}); ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.84 (d, 1H, J=2.0 Hz), 7.65 (d, 2H, J=6.2 Hz), 7.51 (m, 3H), 7.04 (d, 1H, J=2.0 Hz); FAB-MS m/z: 906 (MH$^+$), 720 (C_{60}); IR-FT (KBr) ν: 1514, 1498, 1385, 1330, 1103, 759, 852, 769, 526 cm^{-1}. UV-Vis (C_6H_{12}) λ_{max} (log ε) 317 (6.56), 426 (5.29), 458 (5.18), 675 (4.25), 685 (4.34) nm

[14] The polarizability of a solvent is connected with the index of refraction (n) according to the equation of Lorenz-Lorentz. Reichardt Ch, "Solvents and Solvents Effects in Organic Chemistry", VCH, Weinheim, 1990.

[15] Bondi, A. J. Phys. Chem. 1964, 64, 441-451.

[16] a) Meier, M.S.; Poplawska, M. J. Org. Chem. 1993, 58, 4524-4525; b) Irngartinger, H.; Köhler, C-M.; Huber-Patz, U.; Krästchmer, W. Chem. Ber. 1994, 127, 581-584; c) Irngartinger, H.; Weber, A. Tetrahedron Lett. 1996, 37, 4137-4140; d) Ohno, M.; Yashiro, A.; Eguchi, S. Synlett 1996, 815-816; e) Irngartinger, H.; Weber, A.; Escher, T. Liebigs Ann. 1996, 1845-1850; f) Irngartinger, H.; Weber, A. Tetrahedron Lett. 1997, 38, 2075-2076; g) Da Ros, T.; Prato, M.; Novello, F.; Maggini, M.; de Amici, M.; de Micheli, C. Chem. Commun. 1997, 59-60.

[17] Meier, M.S.; Poplawska, M. Tetrahedron 1996, 52, 5043-5052.

[18] Williams, R.M.; Zwier, J.M.; Verhoeven, J.W. J. Am. Chem. Soc. 1995, 117, 4093-4097.

[19] Seshadri, R.; D'souza, F.; Krishnan, V.; Rao, C.N.R. Chem. Lett. 1993, 217-218.