[60] Fullerene Adducts with Improved Electron Acceptor **Properties**

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The synthesis of C_{60} -based dyads in which the C_{60} core is covalently attached to a strong electron acceptor moiety such as quinones, TCNQ or DCNQI derivatives, has been carried out by 1,3-dipolar cycloaddition of "in situ" generated azomethyne ylides or nitrile oxides to C_{60} . As expected, the obtained pyrrolidino [3', 4': 1, 2] [60] fullerenes exhibit reduction potentials of the C₆₀ framework which are cathodically shifted in comparison with the parent C_{60} . In contrast, isoxazolo[4',5':1,2][60]fullerenes show reduction waves for the fullerene core that are anodically shifted in comparison with the parent C_{60} , which indicates that they are remarkably stronger acceptors than C_{60} . The electron acceptor organic addend also undergoes an anodic shift due to the electronic interaction with the C_{60} molecular geometry of pyrrolidinofullerenes has been calculated at the semiempirical PM3 level and reveals a highly distorted geometry for the acceptor moiety in compound **13**, and a most stable conformation in which both dicyanomethylene units are far away from the C₆₀ surface.

Introduction

[60]Fullerene exhibits a remarkable electron acceptor character that has been skillfully used for the preparation of a wide variety of different electroactive systems by the covalent attachment to electron donor molecules.¹ Wudl et al. proposed that C_{60} can be chemically modified with organic groups while retaining its unique electronic properties.² However, despite the correctness of this statement, it is well known that most of the [60]fullerene derivatives present poorer electron acceptor properties than the parent C_{60} as a consequence of the saturation of a double bond of the C_{60} framework that raises the LUMO energy.³ Therefore, the design and synthesis of new organofullerenes showing better electron acceptor abilities than the parent C₆₀ are very appealing tasks in the search of applications to materials science^{1,4} and biochemistry.5

Within the past few years, several attempts have been carried out by different groups directed at the synthesis of stronger acceptors than the parent C₆₀.¹ Basically, the strategies followed for increasing the electron acceptor character in fullerene derivatives have been mainly focused on (i) the presence of electronegative atoms directly linked to the C_{60} core (1,⁶ 2^7), (ii) electron acceptor groups $(3, {}^{8}4^{9})$, (iii) periconjugative effect (5, 6), ${}^{10-12}$ (iv) pyrrolidinium salts (7),¹³ and (v) the presence of hetero-

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atoms as constituents of the fullerene framework (heterofullerenes) (8)14 (Chart 1).

On the other hand, only a few examples are known in which the C_{60} framework is covalently attached to an electron acceptor unit.¹ In light of a possible electron transfer from the photoexcited fullerene to the adjacent strong electron acceptor, we have recently reported dyad 9.15 In this system, formation of the fullerene triplet excited-state rather than an intramolecular electrontransfer was observed,¹⁶ which can be accounted for by the inability of C_{60} to form stable cationic species.^{17,18} However, modulation of the electronic properties of C₆₀ derivatives showing enhanced acceptor abilities over C₆₀

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Chart 1. Selected Examples of Modified Fullerenes Exhibiting Higher Electron Affinity Than the Parent C60



is still a demanding goal in fullerene chemistry with potential applications in charge-transfer and lightinduced electron-transfer processes.

In this work we present the synthesis of pyrrolidino-[3',4':1,2][60]fullerenes (**12–15**, **22**, **25**) and isoxazolo-[4',5':1,2][60]fullerenes (**17**, **19**, **33**) endowed with strong electron acceptor moieties. We have investigated, by cyclic voltammetry measurements, the influence of the organic addends as well as the nature of the heterocycle fused to the C₆₀ unit on the electron acceptor properties. In addition, theoretical calculations at the semiempirical PM3 level have been used to predict the molecular geometry in pyrrolidino[3',4':1,2][60]fullerenes.

Results and Discussion

Synthesis. A wide variety of modified fullerenes have been prepared by cycloaddition reactions to [60]fullerene. Among them, Diels–Alder¹⁹ and 1,3-dipolar²⁰ cycloadditions have played a very important role.

In a previous communication we reported the facile formation of pyrrolidino[3',4':1,2][60]fullerenes endowed with strong electron acceptors derived from the wellknown tetracyano-*p*-quinodimethane (TCNQ) and dicyano-*p*-quinonediimine (DCNQI).²¹ We describe herein the preparation of isoxazolino[4',5':1,2][60]fullerenes bearing strong electron acceptor organic addends. Although a number of papers dealing with the synthesis²² and further chemical transformations of isoxazolo[4'5':1,2][60]-

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fullerenes²³ have been reported during the past few years, the enhanced electron accepting properties, related to the parent C_{60} , have only recently been reported.²⁴

The target pyrrolidino[3',4':1,2][60]fullerenes (12, 13) were synthesized from the recently reported 2-formyl-9,10-anthraquinone (10).²⁵ Thus, reaction of sarcosine (Nmethylglycine) and aldehyde **10** in the presence of C_{60} affords cycloadduct 12 resulting from the addition of the "in situ" generated azomethine ylide to C₆₀ by following Prato's procedure.²⁶ Further reaction of **12** with Lehnert's reagent (malononitrile, titanium tetrachloride, pyridine)²⁷ leads to 11,11,12,12-tetracyanoanthraquinodimethane (TCAQ) derivative **13** in moderate yield.²¹ Alternatively, fulleropyrrolidine 13 was also obtained from commercially available 2-hydroxymethylanthraquinone by reaction with Lehnert's reagent, oxidation, and further reaction of **11** with C_{60} and sarcosine (**11**: C_{60} /sarcosine 1:1:5) affording compound 13 in 20% yield (40% based on recovered C_{60}). This procedure seemed to be more appropriate than the former one from 12, which requires a much longer reaction time (13 days) as well as a much larger stoichiometric ratio of reactants (12/CH₂(CN)₂/ TiCl₄/pyr 1:95:95:190) (Scheme 1).

9,10-Dicyanoanthraquinonediimine (DCAQI) **14** was prepared from compound **12** in low yield (4%) by reaction with bis(trimethylsilyl)carbodiimide (BTC) in the pres-

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^{(27) (}a) Lehnert, W. *Tetrahedron Lett.* **1970**, 4723. (b) Lehnert, W. *Synthesis* **1974**, 667.

Scheme 1



ence of titanium tetrachloride according to Hünig's procedure.²⁸ Monocondensated compound **15** was also obtained together with **14** in 5% yield as a mixture of constitutional isomers according to the ¹H NMR data.²¹

We have also carried out the synthesis of fulleropyrrolidines endowed with other stronger electron-acceptor quinones such as 1,4-benzo and 1,4-naphthoquinones (**22**, **25**). By following the azomethine ylides approach, we prepared,²⁹ simultaneously with Iyoda et al.,³⁰ pyrrolidino[3',4':1,2][60]fullerene derivative **22** bearing a *p*benzoquinone addend. The synthetic procedure is depicted in Scheme 2. Compound **25** bearing a naphthoquinone moiety was prepared in two steps from 23^{31} which in turn was prepared in three steps from commercially available *p*-benzoquinone. Further oxidation of **23** with PCC leads to 6-formyl-1,4-naphthoquinone in quantitative yield, which reacts with sarcosine and C₆₀ to form novel cycloadduct **25** in 22% yield (42% based on consumed C₆₀).

Compounds **22** and **25** show in the ¹H NMR spectra typical signals for the pyrrolidine ring as two doublets at δ 4.34 (J= 9.3 Hz) and 4.96 (J= 9.3 Hz), and a singlet at δ 5.32 for **22** and two doublets at δ 4.37 (J= 9.6 Hz) and 5.06 (J= 9.6 Hz) and a singlet at δ 5.13 for **25**. The ¹³C NMR spectrum of **25** reveals the presence of 59 signals which indicates a lack of symmetry in the molecule.

Novel isoxazolo[4',5':1,2][60]fullerenes (**17**, **19**) have been prepared by 1,3-dipolar cycloaddition of the in situ

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i) NCS, py

ÓН

31

ii) C₆₀, Et₃N

ÒН

32

generated nitrile oxides to C_{60} . Thus, the precursor oximes 16 and 18 were obtained from the respective aldehydes 10 and 11 by reaction with hydroxilamine hydrochloride. Further chlorination of 16 and 18 with N-chlorosuccinimide (NCS) and subsequent dehydrochlorination of the formed hydroximoyl chlorides yield the respective nitrile oxides which undergo a [3+2] cycloaddition reaction with C₆₀ to afford compounds 17 and 19 in 19% and 16% yield, respectively. It is worth mentioning that compound 19 was obtained together with the compounds resulting from the partial and total hydrolysis of the dicyanomethylene groups. Thus, in addition to 19, compound 17 was obtained from the reaction mixture in 11% yield as well as the monocondensated compounds (20) resulting from the hydrolysis of only one dicyanomethylene group, which was obtained as a mixture of constitutional isomers in a very low yield (4%).

NH2OH-HCI

EtOH/H₂O

ĠН

30

The isoxazolofullerenes prepared (**17**, **19**) were thermally stable brown solids, which is in agreement with the thermal gravimetric analysis previously reported for related structures.^{23a} The spectroscopic data are in accord with the proposed structures. Thus, the ¹³C NMR spectra

reveal a C_s symmetry which confirms a [6,6] ring junction of the organic addend to the C_{60} core (see Experimental Section).

33

In addition to isoxazolofullerenes (17, 19), we have also carried out the synthesis of the novel 3'[2(p-benzoquinonyl)]isoxazolo[4',5':1,2][60]fullerene (33) which requires a multistep synthetic procedure (Scheme 3). A first approach was followed from 2,5-dimethoxybenzaldehyde (26) by transformation into the respective oxime (27) which reacted with NCS and C₆₀ in the presence of pyridine and triethylamine to afford 3'[2(1,4-dimethoxyphenyl)]isoxazolo[4',5':1,2][60]fullerene (28) in 32% yield. Further reaction of 28 with boron tribromide in chloroform should yield the expected hydroquinone derivative according to previously related examples.³² However, reaction of **28** with BBr₃ afforded **29** as the only product. Therefore, we followed an alternative synthetic route by preparing the formylhydroquinone (30) in the first synthetic step, followed by transformation into the oxime (31) and subsequent reaction with NCS and C₆₀ leading to

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32 in low yield (8%) (Scheme 3). Hydroquinone **32** was further oxidized by reaction with dichlorodicyano-*p*-benzoquinone (DDQ) to afford **33** in good yield (88%).

All of the organofullerenes synthesized showed the presence of a weak absorption band at around 426 nm in the UV-vis spectra which is a typical feature of most 1,2-dihydrofullerenes.

Electrochemistry. The compounds reported in this work are composed of two electroactive moieties (C_{60} and quinones, TCNQ or DCNQI derivatives). Therefore, we have studied their electrochemical properties by cyclic voltammetric (CV) measurements in solution at room temperature, using tetrabutylammonium perchlorate as supporting electrolyte and a glassy carbon as reference electrode (see Experimental Section).

The CV data of the prepared compounds are collected in Table 1 along with C_{60} and *p*-benzoquinone, 6-methylnaphthoquinone, and TCAQ for comparison purposes.

All of the pyrrolidino[3'4':1,2][60]fullerenes (12, 13, 14, 22, 25) and the isoxazolo[4',5':1,2][60]fullerenes (17, 19, **33**) show three or four quasireversible reduction waves for the fullerene moiety, similarly to that found for the parent C₆₀. In addition, another quasireversible reduction wave(s) is observed corresponding to the reduction of the electroactive organic addend. Interestingly, a remarkable difference is found between the reduction potentials corresponding to the fullerene moiety in pyrrolidinofullerenes and isoxazolofullerenes. Thus, pyrrolidinofullerenes show reduction waves shifted to more negative potentials than the parent C₆₀ due to the saturation of a double bond in the C₆₀ cage which raises the LUMO energy.³³ This cathodic shift is the standard behavior found in most of 1,2-dihydrofullerenes.³ In contrast, isoxazolofullerenes exhibit reduction potentials which are anodically shifted (70-110 mV) in comparison with the parent C_{60} , which indicates that they are stronger electron acceptors than C₆₀. This finding can be accounted for by the presence of the oxygen atom directly linked to the C_{60} cage as well as by the electronic effect of the electron accepting organic addend covalently attached to the isoxazole ring.

The organic addends present in the studied organofullerenes show the presence of two quasireversible reduction waves for the quinone moiety, which appear remarkably shifted to more positive values than the respective unsubstituted quinones (Table 1). The observed shifts are stronger in the isoxazolofullerenes, which confirms the higher electron affinity of these systems related to the analogous pyrrolidinofullerenes.

As shown in Table 1, substitution on the *p*-benzoquinone ring has a striking influence on the redox behavior. The presence of one (**25**) or two (**12**, **17**) benzene rings fused to the *p*-benzoquinone moiety cathodically shifts the first reduction potential of the organic addend and, in a lesser extent, of the C_{60} core. It is worth mentioning that the first reduction wave of the naphthoquinone moiety in **25** appears together with the first reduction wave on the C_{60} core giving rise to a broad reduction wave involving two electrons.

The first reduction potential of the *p*-benzoquinone moiety appears very close to that of the C_{60} unit. We have previously reported by using density functional theory

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(DFT) calculations that in Diels–Alder cycloadducts the LUMO of the *p*-benzoquinone ring lies slightly below, in energy, than the LUMO of the C_{60} unit,³² thus confirming the CV findings (Table 1).

Compounds bearing the TCAQ fragment show the presence of only one reduction wave involving two electrons for the organic addend moiety.³⁴ This behavior is in agreement with that expected for other tetracyano*p*-quinodemethane (TCNQ) derivatives,³⁵ and it has been previously rationalized by using theoretical calculations at semiempirical and ab initio levels.³⁶ In contrast, organofullerene bearing the DCNQI fragment (**14**) exhibits two reduction potentials for the organic addend, similarly to the above quinones. The strong electron acceptor character of the cyanoimino moieties, similar to the dicyanomethylene group, is responsible for the potential values found for this compound.^{21,35}

Both the C_{60} cage and the organic addend in these systems are expected to behave as excellent electron acceptors in which, depending upon the nature of the organic addend, it is possible to address the attachment of the first electron in the reduction process either to the C_{60} cage or to the organic addend.

Theoretical Calculations. The molecular geometries or pyrrolidinofullerenes **25** and **13** were determined by theoretical calculations at the semiempirical PM3 level.³⁷ Depending upon the orientation of the oxygen atoms, two rotational isomers are possible for **25** (Figure 1). A difference of only 0.7 kcal/mol was found between them, which suggests that both isomers are present in solution, thus supporting the broad signals found for the aromatic protons in the ¹H NMR spectrum at room temperature. These signals are well defined when the ¹H NMR spectrum was recorded at 60 °C, which indicates the presence of an equilibrium between both isomers that is accelerated at high temperature.

The bond length predicted between C1 and C2 (1.588 Å) is similar to that found by X-ray analysis for other pentagonal fused rings to C_{60} such as triazolino[4',5':1,2]-[60]fullerenes (1.574 Å)³⁸ and isoxazolo[4',5':1,2][60]-fullerenes (1.576 Å),^{22c} being shorter than that found for methanofullerenes,³⁹ benzocyclobutene structures (1.645 Å),⁴⁰ or Diels–Alder cycloadducts (1.62 Å).⁴¹

Organofullerene **13** presents a geometry in which the TCAQ fragment is severely distorted from planarity due to the strong steric interactions between the cyano groups and the CH units in adjacent peri positions. To avoid

⁽³⁴⁾ The single-wave reduction involving two electrons for the parent TCAQ has been previously confirmed by coulometric analysis. See: Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, *107*, 556.

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⁽⁴¹⁾ Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. J. Am. Chem. Soc. **1993**, 115, 4919.

. <u></u>	Compound	E _{red} ^{subst}	E ¹ red	E ² _{red}	E ³ red	E ⁴ red
	C ₆₀		-0.60	-1.00	-1.52	-2.04
33		-0.34 -0.98 (2e ⁻)	-0.49	-0.98 (2e ⁻)	-1.56	
17		-0.92 (2e ⁻) -1.38	-0.51	-0.92 (2e ⁻)	-1.55	
19		-0.33 (2e ⁻)	-0.53	-0.99	-1.53	-1.92
22		-0.40 -0.91	-0.65	-1.07	-1.67	-1.95
25		-0.70 (br, 2e ⁻) -1.27	-0.70 (br, 2e ⁻)	-1.06	-1.70	-2.17
12	Me N	-0.95 -1.40	-0.64	-1.05	-1.68	
13		-0.38 (2e ⁻)	-0.65	-1.06	-1.67	_
14		-0.32 -0.98	-0.64	-1.07	-1.78	_
<i>p</i> -Benzoquinone		-0.50* -1.00*				_
6-Methylnaphthoquinone		-0.82 -1.24		_		—
	TCAQ	-0.58 (2e ⁻)	_			_

 Table 1. Redox Potentials of Novel Organofullerenes^a

^a V vs SCE; GCE as working electrode; 0.1 mmol/dm³ NBu₄⁺ClO₄⁻; Toluene/MeCN (5:1); 200 mV/s. *Halfwave potential.

these interactions the TCNQ central ring and the dicyanomethylene units are folded in opposite directions. The TCAQ moiety therefore adopts a butterfly-type structure, similar to that observed for the parent TCAQ from X-ray data, ⁴² and theoretical calculations, ⁴³ in which the lateral

aromatic rings preserve their planarity, with the central ring in a boat conformation.

The presence of the fulleropyrrolidine fragment covalently attached to the TCAQ moiety gives rise to two possible isomers depending upon the orientation of the

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Figure 1. Favored geometries calculated by semiempirical PM3 method for compounds **25** and **13**.

two dicyanomethylene units (up and down). Theoretical calculations predict that conformation B, with the dicyanomethylene unit pointing upward, is 2.1 kcal/mol more stable than A (Figure 1).

In agreement with the above data, the distance predicted for the C1–C2 bond (1.584 Å) resulted to be similar to that found for other organofullerenes endowed with a fused pentagonal ring.^{22c,38}

Summary and Conclusions

We have described the synthesis of novel organofullerenes in which the C_{60} core is covalently attached to strong electron acceptor moieties such as quinones and TCNQ and DCNQI derivatives. The synthesis has been carried out by formation of the respective formylsubstituted electron acceptors and subsequent 1,3-dipolar cycloaddition of the in situ generated azomethyne ylides and nitrile oxides, respectively, to C_{60} .

The molecular geometry of compounds **25** and **13** was calculated from semiempirical PM3 calculations and reveals the presence of two favorable isomers and a highly distorted electron acceptor moiety with a butterfly-type structure for **13**, in full agreement with previously reported data for the parent acceptor molecule by X-ray diffraction and theoretical calculations.

Pyrrolidino[3',4':1,2][60]fullerenes (**12**, **13**, **14**, **22**, **25**) exhibit reduction potential values for the C_{60} moiety which are cathodically shifted related to the parent C_{60} (40–100 mV). In contrast, isoxazolo[4',5':1,2][60]fullerenes (**17**, **19**, **33**) present a remarkable anodic shift in comparison with the parent C_{60} (70–110 mV). These findings clearly indicate that these systems are stronger electron acceptors than C_{60} , which has been accounted for by the electronic effects of both oxygen atom and electron accepting organic addends covalently linked to the C_{60}

moiety. In addition, the striking electron acceptor behavior of the organic substituents makes these systems truly electron sponges that are able to accept up to eight electrons in solution.

This remarkable electron acceptor character of the systems now reported is of interest for further applications in the preparation of optoelectronic devices. Work is in progress directed to the preparation of blends with conjugated semiconducting polymers in the search of photovoltaic applications.

Experimental Section

General Details. Mass spectra were recorded operating at 30 kV by using a bombardment of Cs⁺ ions and 2-NPOE or 3-NBA as matrix. Cyclic voltammetry measurements were performed using a glassy carbon electrode as indicator electrode in voltammetric studies (1×10^{-5} M solutions of the compound in toluene/acetonitrile 5:1, 0.1 M Bu₄NClO₄ as the supporting electrolyte, platinum working as counter electrode, SCE as reference electrode at 20 °C). All chromatography was performed using Merck silica gel (70–230 mesh). All reagents were used as purchased unless otherwise stated. All solvents were dried according to standard procedures. Calculations were performed using the semiempirical PM3 method.

Formyl Derivatives 11, 24. *General Procedure.* To a solution of the corresponding hydroxymethyl derivative (1 equiv) in methylene dichloride, piridinium chlorochromate (1.5 equiv) was added. After 12 h with stirring, the solvent was removed under reduced pressure and the solid residue was purified by column chromatography over silica gel using hexane/ethyl acetate 3:1 as eluent.

6-Formyl-1,4-naphthoquinone (24). 99% yield; mp 153 °C (dec); IR (KBr) ν/cm^{-1} 1700, 1675, 1605, 1315, 1195, 1155, 1055, 845; ¹H NMR (300 MHz, Acetone- d_6) δ 7.09 (s, 2H), 8.27 (m, 2H), 8.60 (m, 1H), 10.20 (s, 1H); MS m/z (%) 186 (M⁺, 100), 157 (44), 129 (23), 103 (46), 75 (93), 63 (12), 51 (40). Anal. Calcd for C₁₁H₆O₃: C, 70.96; H, 3.23. Found: C, 70.66; H, 3.65.

2-Formyl-9,10-bis(dicyanomethylene)anthracene (11). 72% yield; mp 273 °C (dec); IR (KBr) ν/cm^{-1} 2240, 1705, 1565, 1280, 1225, 835, 775, 700; ¹H NMR (300 MHz, CDCl₃) δ 7.80 (m, 2H), 8.24 (dd, 1H, J = 8.1 and 1.5 Hz), 8.28 (m, 2H), 8.43 (d, 1H, J = 8.1 Hz), 8.73 (d, 1H, J = 1.5 Hz), 10.17 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 112.6, 127.7, 127.8, 127.9, 128.3, 128.5, 129.7, 130.0, 131.2, 132.3, 132.9, 132.9, 134.7, 138.1, 158.9, 189.1. Anal. Calcd for C₂₁H₁₀N₄O: C, 75.90; H, 2.41; N, 16.87. Found: C, 75.87; H, 2.47; N, 16.61.

N-Methyl-2'[6(1,4-naphthoquinonyl)]pyrrolidino-[3',4':1,2][60]fullerene (25). To a solution of C₆₀ (100 mg, 0.14 mmol) in 40 mL of toluene, 6-formyl-1,4naphthoquinone 24 (26 mg, 0.14 mmol) and N-methylglycine (62 mg, 0.69 mmol) were added. After refluxing for 18 h, the solvent was removed under reduced pressure and the solid residue obtained was purified by column chromatography over silica gel, using cyclohexane/toluene to elute the nonreacted C₆₀ and toluene/ethyl acetate to elute the monoadduct. Further purification was accomplished by washing the solid three times with hexane/ methanol. 22% yield (42% based on consumed C₆₀); FTIR (KBr) v/cm⁻¹ 1667, 1601, 1300, 1044, 842, 526; ¹H NMR (300 MHz, CDCl₃, 60 °C) δ 2.84 (s, 3H), 4.36 (d, 1H, J =9.6 Hz), 5.06 (d, 1H, J = 9.6 Hz), 5.13 (s, 1H), 6.98 (s, 2H), 8.18 (d, 1H, J = 8.4 Hz), 8.31 (broad d, 1H), 8.53 (s,

1H);¹³C NMR (75 MHz, CDCl₃/CS₂) δ 40.10, 68.98, 69.89, 82.69, 82.89, 126.96, 127.32, 131.78, 131.93, 134.24, 134.43, 135.55, 136.05, 136.29, 137.24, 138.12, 139.00, 139.43, 140.05, 140.18, 140.21, 141.54, 141.64, 141.75, 141.82, 141.94, 141.98 (2C), 142.07, 142.11, 142.16 (2C), 142.47, 142.55 (2C), 142.66, 142.97, 143.08, 144.02 (2C), 144.24, 144.35, 144.39, 144.65, 145.13 (2C), 145.22 (2C), 145.31 (2C), 145.42, 145.51, 145.61 (2C), 145.89 (2C), 146.00, 146.07 (2C), 146.17 (2C), 146.24 (2C), 147.23, 147.27, 151.71, 152.36, 153.42, 155.64, 184.46, 184.66; MS *m*/*z* (%) 934 (M⁺, 26), 720 (C₆₀, 100); UV−vis (CHCl₃) λ_{max} /nm 250, 268, 304, 316, 422, 690.

N-Methyl-2'[2(9,10-bis(dicyanomethylene)anthracenyl)]pyrrolidino[3',4':1,2]-[60]fullerene (13). Method A. To a solution of N-methyl-2'[2(9,10-anthraquinonyl)]pyrrolidino-[3',4':1,2][60]fullerene **12** (53 mg, 0.054 mmol) and malononitrile (9 mg, 0.14 mmol) in 50 mL of dry methylene dichloride at room temperature and under argon atmosphere, titanium tetrachloride (0.14 mmol, 0.14 mL of a 1 M solution in CH₂Cl₂) and dry pyridine (0.022 mL, 0.27 mmol) were added dropwise with a syringe. The reaction was monitored by tlc, and new portions of malononitrile (90 mg, 1.4 mmol), TiCl₄ (1.4 mmol, 1.4 mL of a 1 M solution in CH₂Cl₂), and dry pyridine (0.22 mL, 2.7 mmol) were added every 24 or 48 h. After 13 days, no evolution is observed (final stoichoimetry relation **12**/malononitrile/TiCl₄/py 1:95:95: 190). The solvent was removed under reduced pressure, and the obtained residue was chromatographed over silica gel using toluene/chloroform as eluent. Further purification was accomplished by washing the solid three times with hexane/methanol. 19% yield.

Method B. A solution of 2-formyl-9,10-bis(dicyanomethylene)anthracene 11 (50 mg, 0.15 mmol), C_{60} (108 mg, 0.15 mmol), and N-methylglycine (67 mg, 0.76 mmol) in 70 mL of toluene was refluxed for 24 h. The solid obtained by evaporation to dryness was purified on a silica gel column using toluene/chloroform as eluent. Further purification was accomplished by washing the solid three times with hexane/methanol. 20% yield (40% based on consumed C₆₀); FTIR (KBr) ν/cm^{-1} 2224, 1553, 1463, 1261, 1031, 803, 767, 527; ¹H NMR (300 MHz, CDCl₃) δ 2.88 (s, 3H), 4.33 (d, 1H, J = 9.6 Hz), 5.06 (d, 1H, J = 9.6 Hz), 5.12 (s, 1H), 7.77 (dd, 2H, J = 5.7 and 3.3 Hz), 8.29 (m, 4H), 8.78 (broad m, 1H);13C NMR (75 MHz, CDCl₃) δ 40.28, 69.17, 70.00, 77.25, 83.27, 112.94, 112.95, 112.98, 113.05, 127.77 (2C), 127.82 (2C), 130.12, 130.14, 132.60 (2C), 132.65 (2C), 133.27, 133.33, 136.07, 136.34, 140.36, 140.42, 141.19, 141.60, 141.65, 141.82, 142.04, 142.14, 142.21, 142.23, 142.27, 142.30, 142.60 (2C), 142.68, 142.70 (2C), 142.82, 143.12, 143.20, 143.43, 144.29, 144.52, 144.57, 145.17 (2C), 145.30, 145.39, 145.45, 145.50, 145.55, 145.63, 145.66, 145.70, 145.97, 146.03 (2C), 146.05, 146.19, 146.22 (2C), 146.24, 146.29, 146.31, 146.34, 146.40, 147.26, 147.37, 147.53, 152.21, 153.45, 155.67, 159.61; MS m/z (%) 1079 (M⁺, 17), 720 (C₆₀, 100); UV-vis (CHCl₃) λ_{max} /nm 258, 286, 314, 430, 698.

Reaction of N-Methyl-2'[2(9,10-anthraquinonyl)]pyrrolidino[3',4':1,2][60]-fullerene (12) with BTC. To a solution of **12** (130 mg, 0.13 mmol) in 50 mL of dry chloroform under argon atmosphere, titanium tetrachloride (0.14 mmol, 0.14 mL of a 1 M solution in CH₂Cl₂) followed by bis(trimethylsilyl)carbodiimide (BTC) (1.4 mL, 6.6 mmol) were added dropwise with a syringe. The mixture was refluxed and monitored by tlc. New portions of TiCl₄ (0.14 mmol, 0.14 mL of a 1 M solution in CH₂-Cl₂) and BTC (1.4 mL, 6.6 mmol) were added after 24 and 48 h. After 5 days, the solvent was removed under reduced pressure and the brown solid obtained was chromatographed on a silica gel column, using cyclohexane/chloroform 1:1 as eluent. The monocondensated product was eluted in first place (**15**, 6.2 mg) followed by the dicondensated one (**14**, 5.6 mg).

N-Methyl-2'[2(9,10-dicyaniminoanthracenyl)]pyrrolidino[3',4':1,2][60]fullerene (14). 4% yield; FTIR (KBr) ν/cm^{-1} 2169, 1465, 1334, 1225, 789, 766, 527; ¹H NMR (300 MHz, CDCl₃) δ 2.86 (s, 3H), 4.36 (d, 1H, J =9.6 Hz), 5.07 (d, 1H, J = 9.6 Hz), 5.17 (s, 1H), 7.53 (dd, 2H, J = 5.7 y 3.3 Hz), 7.71 (dd, 2H, J = 5.7 and 3.3 Hz), 7.90 (broad m, 2H), 8.42 (broad m, 1H); MS m/z (%) 1031 (M⁺, 28), 720 (C₆₀, 100); UV-vis (CHCl₃) λ_{max} /nm 258, 298, 358, 430, 698.

N-Methyl-2'[2(9-cyanimino-10-oxoanthracenyl)]pyrrolidino[3',4':1,2][60]-fullerene and *N*-Methyl-2'-[2(10-cyanimino-9-oxoanthracenyl)]pyrrolidino-[3',4': 1,2][60]fullerene (15). 5% yield (isomeric mixture); FTIR (KBr) ν/cm^{-1} 2162, 1674, 1646, 1558, 1329, 1008, 804, 791, 527; ¹H NMR (300 MHz, CDCl₃) δ 2.84 (s), 2.87 (s), 4.35 (d), 4.38 (d), 5.05 (d), 5.08 (d), 5.17 (s), 5.18 (s), 7.54 (dd, J = 6.0 and 3.3 Hz), 7.72 (dd, J = 6.0 and 3.3 Hz), 7.86 (broad m), 8.43 (broad m); MS m/z (%) 1008 (M⁺+1, 19), 720 (C₆₀, 100); UV-vis (CHCl₃) λ_{max}/nm 254, 298, 358, 428, 698.

Synthesis of Oximes. *General Procedure.* To a solution of the corresponding aldehyde (1 eq) in ethanol at 70 °C, a solution of hydroxylamine hydrochloride in water (2.5 equiv for **27** and 28 equiv for **31**, **16**, and **18**) was added. The mixture was kept at 70 °C for a variable period of time and then diluted with 100 mL of water. The workup procedure was different in any case.

2,5-Dimethoxybenzaldehyde Oxime (27). Reaction time: 2 h. The reaction mixture was extracted three times with chloroform. The organic extracts were dried over MgSO₄ and evaporated to dryness, giving **27** in a 94% yield; mp 103–104 °C; FTIR (KBr) ν/cm^{-1} 3242, 2908, 1655, 1578, 1504, 1460, 1279, 1234, 1040, 972, 743; ¹H NMR (300 MHz, CDCl₃) δ 3.80 (s, 3H), 3.83 (s, 3H), 6.86 (d, 1H, J = 9.2 Hz), 6.93 (dd, 1H, J = 9.2 and 3.1 Hz), 7.26 (d, 1H, J = 3.1 Hz), 8.26 (broad s, 1H), 8.48 (s, 1H); ¹³C NMR (300 MHz, DMSO- d_6) δ 55.42, 56.28, 109.74, 113.30, 116.44, 121.61, 143.39, 151.31, 153.16; MS m/z (%) 181 (M⁺, 81), 149 (100), 121 (39).

2,5-Dihydroxybenzaldehyde Oxime (31). Reaction time: 1 h 30 min. After extracting the mixture three times with chloroform, the organic extracts were dried over MgSO₄ and evaporated to dryness, obtaining a solid residue that was purified by column chromatography over silica gel using hexane/ethyl acetate as eluent. 76% yield; mp 129–131 °C; FTIR (KBr) ν/cm^{-1} 3277, 2924, 1638, 1506, 1360, 1283, 1260, 1005, 961, 822, 785, 677; ¹H NMR (300 MHz, CDCl₃) δ 6.64 (dd, 1H, J = 8.8 and 2.9 Hz), 6.69 (d, 1H, J = 8.8 Hz), 6.88 (d, 1H, J = 2.9 Hz), 8.22 (s, 1H), 8.93 (s, 1H), 9.38 (s, 1H), 11.24 (s, 1H); ¹³C NMR (75 MHz, DMSO- d_6) δ 112.9, 116.9, 117.9, 118.6, 147.2, 148.8, 149.9; MS m/z (%) 153 (M⁺, 100), 135 (77), 107 (37).

9,10-Anthraquinone-2-carbaldoxime (16). Reaction time: 1 h. The product precipitated in the medium and it was filtrated and washed with ethanol. 97% yield; mp 241–243 °C (dec); FTIR (KBr) ν/cm^{-1} 3381, 1668, 1587, 1340, 1286, 982, 723, 710, 638; ¹H NMR (300 MHz,

DMSO- d_6) δ 7.93 (m, 2H), 8.10 (dd, 1H, J = 8.1 and 1.5 Hz), 8.20 (m, 3H), 8.38 (m, 2H), 11.86 (s, 1H); ¹³C NMR (75 MHz, DMSO- d_6) δ 124.47, 126.74, 126.77, 127.40, 131.36, 132.91, 132.97, 133.04, 133.39, 134.51, 134.62, 138.75, 147.17, 181.96, 182.21; MS m/z (%) 251 (M⁺, 61), 233 (100), 205 (86), 177 (74).

2-Formyl-9,10-bis(dicyanomethylene)anthraquinone Oxime (18). Reaction time: 30 min. After extracting the reaction mixture three times with chloroform, the organic extracts were dried over MgSO₄ and evaporated to dryness, giving rise to a solid residue that was purified by column chromatography over silica gel using hexane/ethyl acetate 3:1 as eluent. 52% yield; mp 208-210 °C (dec); FTIR (KBr) v/cm⁻¹ 3392, 2923, 2226, 1670, 1587, 1560, 1285, 980, 941, 775, 710, 608; ¹H NMR (300 MHz, DMSO- d_6) δ 7.87 (m, 2H), 8.01 (dd, 1H, J = 8.2 and 1.7 Hz), 8.34 (m, 4H), 8.59 (d, 1H, J = 1.4 Hz), 11.16 (s, 1H); ¹³C NMR (75 MHz, DMSO- d_6) δ 115.10, 115.20, 115.28, 126.20, 129.12, 129.18, 129.68, 131.50, 132.19, 132.25, 132.32, 132.84, 133.72, 133.78, 138.55, 148.36, 161.53, 161.77; MS m/z (%) 347 (M⁺, 6), 329 (41), 304 (100).

Reaction of Oximes with C₆₀. *General Procedure.* To a solution of *N*-chlorosuccinimide (NCS, 50 mg, 0.2 mmol) and dry pyridine (0.1 mL) in 5 mL of dry chloroform, the corresponding oxime (0.2 mmol) was added in one portion at 25 °C. The chlorination was usually over in ca. 10 min. A solution of C₆₀ (180 mg, 0.25 mmol) in 15 mL of ODCB was added, and the temperature raised to 40–50 °C. Triethylamine (21 mg, 0.21 mmol) in 3 mL of dry CHCl₃ was added dropwise. After a variable period of time at the same temperature, the solvent was removed under reduced pressure and the solid residue thus obtained was purified by column chromatography over silica gel using a different eluent in any case.

3'[2(9,10-Anthraquinonyl)]isoxazolo[4',5':1,2][60]fullerene (17). Reaction time: 16 h. Eluent used in column chromatography: toluene. 19% yield (90% based on consumed C₆₀); FTIR (KBr) v/cm⁻¹ 2920, 1673, 1589, 1323, 1278, 1255, 929, 865, 711, 526; ¹H NMR (300 MHz, CDCl₃/CS₂ 1/1) δ 7.85 (m, 2H), 8.34 (m, 2H), 8.51 (d, 1H, J = 8.4 Hz), 8.69 (dd, 1H, J = 8.4 and 1.8 Hz), 9.23 (d, 1H, J = 1.8 Hz); ¹³C NMR (75 MHz, CDCl₃/CS₂ 1/1) δ 77.21, 78.12, 127.09, 127.17, 127.19 (2C), 127.86, 133.13, 133.20, 133.71 (2C), 134.03, 134.06, 134.13, 134.50, 136.51, 137.09, 140.18, 140.31, 141.60, 141.82, 142.07, 142.11, 142.28, 142.68, 142.69, 142.81, 143.67, 143.70, 143.88, 144.20, 144.43, 144.95, 145.08, 145.13, 145.27, 145.61, 145.78, 145.82, 146.09, 146.11, 146.22, 147.08, 147.60, 181.42, 181.51; MS m/z (%) 970 (M⁺+1, 100); UV-vis (CHCl₃) λ_{max}/nm 256, 290, 318, 426, 458, 684.

Reaction of 2-Carbaldoxime-9,10-bis(dicyanomethylene)anthraquinone (18) with C₆₀. After stirring at 40–50 °C for 22 h, the solid residue was purified using cyclohexane/toluene 1:1 as eluent, recovering unreacted C₆₀, 3'[6(1,4-anthraquinonyl)]isoxazolo[4',5':1,2]-[60]fullerene (17, 11%), 3'[2(9-dicyanomethylene-10oxoanthracenyl)]isoxazolo[4',5':1,2][60]fullerene and 3'[2(10-dicyanomethylene-9-oxoanthracenyl)]isoxazolo-[4',5':1,2][60]fullerene as isomers mixture (**20**, 4%) and 3'[2(9,10-bis(dicyanomethylene)anthracenyl)]isoxazolo-[4',5':1,2][60]fullerene (**19**, 16%).

3'[2(9,10-bis(Dicyanomethylene)anthracenyl)]isoxazolo[4',5':1,2][60]fullerene (19). FTIR (KBr) ν/cm⁻¹ 2923, 2226, 1718, 1676, 1559, 1277, 860, 770, 694, 527; ¹H NMR (300 MHz, CDCl₃) δ 7.79 (m, 2H), 8.29 (m, 2H), 8.44 (d, 1H, J = 8.3 Hz), 8.66 (dd, 1H, J 8.3 and 1.7 Hz), 9.14 (d, 1H, J = 1.7 Hz); ¹³C NMR (75 MHz, CDCl₃/CS₂ 1/1) δ 77.21, 98.36, 112.13, 112.36, 112.41, 112.44, 127.02, 127.50, 127.58, 128.00, 129.79, 130.00, 131.02, 131.05, 131.33, 131.75, 132.38, 132.42 (2C), 133.51, 135.34, 136.52, 136.55, 137.35, 140.23, 140.62, 141.66, 141.78, 142.12, 142.32, 142.76, 142.79, 142.86, 143.10, 143.31, 143.87, 144.23, 144.33, 145.01, 145.07, 145.12, 145.16, 145.71, 145.86, 145.89, 146.14, 146.18, 146.30, 147.16, 151.43, 158.27, 158.48; MS *m*/*z* (%) 1066 (M⁺+1, 45) 1070 (M⁺+3, 100); UV-vis (CHCl₃) λ_{max} /nm 256, 276, 318, 426, 684.

3'[2(9-Dicyanomethylene-10-oxoanthracenyl)]isoxazolo[4',5':1,2][60]fullerene and 3'[2(10-Dicyanomethylene-9-oxoanthracenyl)]isoxazolo[4',5':1,2]-[60]fullerene (20). Isomeric mixture; FTIR (KBr) ν/cm^{-1} 2922, 2221, 1732, 1672, 1578, 1455, 1280, 1120, 750, 699, 526; ¹H NMR (300 MHz, CDCl₃) δ 9.23 (d, J = 1.7 Hz), 9.20 (d, J = 1.5 Hz), 8.66 (m), 8.50 (m), 8.34 (m), 7.81 (m); MS m/z (%) 1018 (M⁺+1, 58), 1020 (M⁺+3, 100); UV-vis (CHCl₃) λ_{max} /nm 258, 286, 318, 426, 684.

3'[**2**(**1**,**4**-**Benzohydroquinonyl**)]**isoxazolo**[**4**',**5**':**1**,**2**]-**[60]fullerene (32).** Reaction time: 1 h 30 min. Eluent used in column chromatography: toluene/ethyl acetate. 8% yield (48% based on consumed C₆₀); FTIR (KBr) ν/cm^{-1} 3384, 2923, 1703, 1662, 1460, 1203, 1103, 847, 786, 527; ¹H NMR (300 MHz, CDCl₃) δ 4.80 (broad s, 1H), 6.96 (dd, 1H, J = 9.2 and 2.9 Hz), 7.16 (d, 1H, J = 9.2 Hz), 8.10 (d, 1H, J = 2.9 Hz), 9.81 (s, 1H); MS m/z (%) 872 (M⁺+1, 100); MS m/z (%) 872 (M⁺+1, 100); UV-vis (CHCl₃) $\lambda_{\text{max}}/\text{nm}$ 256, 318, 424, 686.

3'[**2**(**1**,**4**-**Dimethoxyphenyl**)]**isoxazolo**[**4**',**5**':**1**,**2**][**60**]**fullerene (28).** Reaction time: 2 h. Eluent used in column chromatography: toluene. 32% yield (71% based on consumed C₆₀); FTIR (KBr) ν/cm^{-1} 2922, 1628, 1498, 1421, 1268, 1218, 1043, 804, 575, 527; ¹H NMR (300 MHz, CDCl₃) δ 3.77 (s, 3H), 3.84 (s, 3H), 6.97 (d, 1H, J= 9.0 Hz), 7.04 (dd, 1H, J= 9.0 and 2.9 Hz), 7.22 (d, 1H, J= 2.9 Hz); MS m/z (%) 900 (M⁺+1, 100); UV–vis (CHCl₃) λ_{max}/nm 258, 318, 426, 488, 682.

3'[2(1-Hydroxy-4-methoxyphenyl)]isoxazolo[4',5': 1,2][60]fullerene (29). To a solution of compound 28 (55 mg, 0.076 mmol) in dry chloroform, BBr₃ (0.38 mmol, 0.38 mL of a 1 M solution in CH_2Cl_2) was added dropwise under argon at room temperature. After 2 h 30 min with stirring, the mixture was washed three times with water, the organic layer was dried over MgSO₄, and the solvent removed under reduced pressure. The solid residue thus obtained was purified by column chromatography over silica gel using toluene as eluent obtaining 29 with quantitative yield; FTIR (KBr) ν/cm^{-1} 3444, 2920, 1489, 1459, 1379, 1285, 1261, 1223, 1097, 1035, 802, 564, 526; ¹H NMR (300 MHz, CDCl₃) δ 3.61 (s, 3H), 7.04 (dd, 1H, J = 9.0 and 2.9 Hz), 7.21 (d, 1H, J = 9.0 Hz), 8.20 (d, 1H, J = 2.9 Hz), 9.85 (s, 1H); ¹³C NMR (75 MHz, CDCl₃/ CS_2 1/1) δ 55.39, 78.32, 98.45, 102.91, 112.16, 112.33, 113.63, 118.63, 118.67, 118.91, 136.60, 137.29, 139.76, 140.36, 141.45, 141.78, 142.23, 142.27, 142.42, 142.46, 142.86, 142.96, 143.98, 144.33, 144.42, 144.51, 145.09, 145.20, 145.27, 145.52, 145.72, 145.92, 145.96, 146.19, 146.28, 146.40, 147.27, 147.71, 152.21, 152.37, 152.50; MS m/z (%) 886 (M⁺+1, 100); UV-vis (CHCl₃) λ_{max}/nm 254, 282, 320, 426, 458, 678.

3'[2(1,4-Benzoquinonyl)]isoxazolo[4',5':1,2][60]fullerene (33). A solution of **32** (44 mg, 0.051 mmol) and DDQ (32 mg, 0.14 mmol) in 50 mL of dry chloroform was stirred at room temperature for 4 h 30 min. The solvent was removed under reduced pressure, and the solid residue thus obtained was chromatographed over silica gel using toluene as eluent. 88% yield; FTIR (KBr) ν/cm^{-1} 2921, 1659, 1384, 1280, 751, 526; ¹H NMR (300 MHz, CDCl₃) δ 6.96 (dd, 1H, J = 10.3 and 2.6 Hz), 7.02 (d, 1H, J = 10.3 Hz), 7.42 (d, 1H, J = 2.6 Hz); MS m/z (%) 870 (M⁺+1, 100); UV-vis (CHCl₃) $\lambda_{\text{max}}/\text{nm}$ 256, 318, 424, 684.

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Supporting Information Available: Cyclic voltammograms for compounds **13**, **19**, and **25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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