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[60]Fullerene-Based Electron Acceptors with Tetracyano-*p*-quinodimethane (TCNQ) and Dicyano-*p*-quinonediimine (DCNQI) Derivatives

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Abstract: *The first TCNQ and DCNQI derivatives of [60]fullerene are reported. Cyclic voltammetry indicates that the attachment of the first electron in the reduction process takes place in the organic addend.* © 1997 Elsevier Science Ltd. All rights reserved.

[60]Fullerene exhibits a reasonably high electron affinity and several attempts have been carried out in order to form electrically conducting salts and charge transfer complexes (CTCs) by reaction with electron donor molecules.[1] However, most of the complexes thus formed appeared to be electrically insulating due to the weak electron acceptor behaviour of [60]fullerene.[2] Consequently, the search for novel organofullerenes showing better acceptor abilities than the parent C_{60} is still a demanding goal in the fullerene chemistry.[3]

Only a few examples have been reported in which the presence of electronegative atoms [4] or strong electronwithdrawing groups[5] directly attached to the C_{60} core lead to slightly better reduction potentials, related to the unsubstituted [60]fullerene. Alternatively, the periconjugative effect[6] has also been used to form quinone-type methanofullerenes showing better acceptor properties than C_{60}.[7]

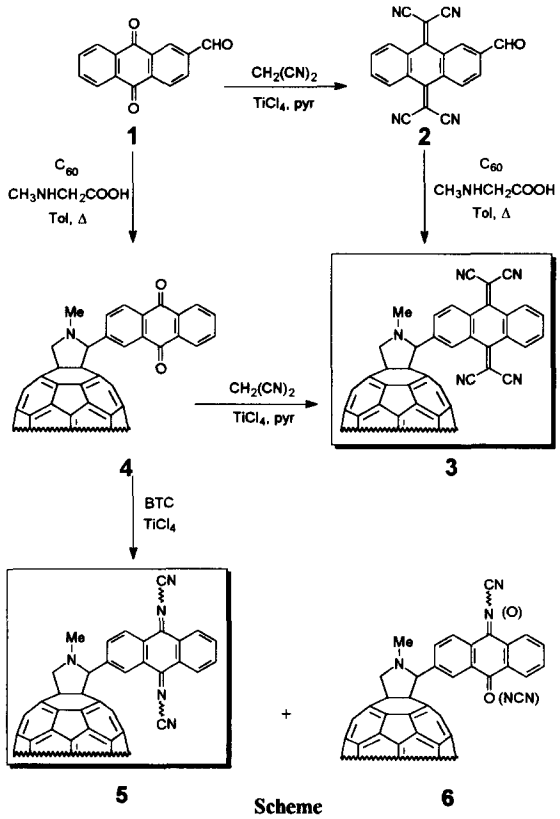
In this communication we describe a different approach in which the C_{60} cage is covalently linked to a strong electron acceptor moiety derived from the well-known acceptors tetracyano-*p*-quinodimethane (TCNQ)[8] and dicyano-*p*-quinonediimine (DCNQI)[9] as precursors for novel C_{60}-based *organic metals*.

Recently, we have reported the first CT-complexes of covalently bound [60]fullerene-tetrathiafulvalene (TTF) systems with strong electron acceptor molecules showing an electrically semiconducting behaviour.[10]

The target molecules (**3**, **5**) were prepared from the novel 2-formyl-9,10-anthraquinone (**1**)[11] which, in turn, can be easily obtained by oxidation of the commercially available 2-hydroxymethyl-9,10-anthraquinone. Aldehyde **1** was a suitable precursor for the covalent attachment to the C_{60} core. In fact, the addition of azomethine ylides, obtained from sarcosine (*N*-methylglycine) and the appropriate aldehyde, to [60]fullerene is among the most suitable procedures for the functionalization of the [60]fullerene.[12] Thus, from compound **1** two alternative routes can be followed for the preparation of the fulleropyrrolidine containing the 11,11,12,12-tetracyanoanthraquinodimethane (TCAQ) moiety as is depicted in the Scheme. Although both synthetic routes lead to compound **3** in similar yields, formation of 2-formyl-TCAQ by using

Lehnert's reagent [13] and further treatment with C_{60} and sarcosine (**2**: C_{60}: sarcosine; 1: 1: 5) affords compound **3**[14] in 20% yield (40% based on recovered C_{60}) after refluxing in toluene for 24 h. Formation of **3** from the fulleropyrrolidine containing the anthraquinone moiety (**4**)[11] obtained from **1** by following the standard procedure[12] (Scheme), requires a much longer reaction time (13 days) and also a much larger stoichiometric ratio of reactives (**4**: $CH_2(CN)_2$: $TiCl_4$: pyr; 1: 95: 95: 190).

Fulleropyrrolidine bearing the 9,10-dicyanoanthraquinonediimine (DCAQI) (**5**)[14] was obtained, in low yield (4%), from compound **4** by reaction with *bis*(trimethylsilyl)carbodiimide (BTC) in the presence of titanium tetrachloride following Hünig's procedure[9] using a large amount of BTC (**4**: BTC: $TiCl_4$; 1: 150: 30) after refluxing in CH_2Cl_2 for 5 days (Scheme). This DCNQI derivative (**5**) was obtained together with the monocondensate compound (**6**) which was obtained in 5% yield as a mixture of constitutional isomers according to the ^1H NMR data. It is interesting to note that the alternative route to **5** from **1** by reaction of the formyl protected compound with BTC afforded a mixture of mono and dicondensed compounds together with compound **1** which proved impossible to separate by using different stationary phases (silica-gel, neutral silica-gel or florisil) due to the hydrolysis of the cyanoimino group during the flash chromatography process.



5 **Scheme** 6

The spectroscopic data of the novel C_{60}-based acceptors (**3** and **5**) are in agreement with the proposed structures. Thus, both compounds showed a typical weak absorption band at around 430 nm in the UV-vis spectrum, similar to that of most dihydrofullerenes. The ^1H NMR spectra showed, in addition to the aromatic signals, the presence of the pyrrolidine protons at δ 4.33 and 5.06 as doublets (J= 9.6 Hz; geminal hydrogens) and δ 5.12 (CH) for the TCAQ derivative (**3**) and d 4.36 and 5.07 (doublets, J= 9.6 Hz) and δ 5.17 (CH) for the DCAQI derivative (**5**), in agreement with related derivatives. The ^{13}C NMR spectrum of compound **3** shows, in addition to the N-Me group at δ 40.3, the signals at δ 69.2, 70.0, 77.3 and 83.3 for the sp^3 carbons of the pyrrolidine ring and those at the 6,6-ring junction of the C_{60} cage. The observation of 45 other signals, including four signals near to δ 112 of the cyano groups, shows the lack of symmetry in these compounds (**3**, **5**). The positive liquid secondary ion mass spectra (LSIMS) in NBA matrix showed the molecular ions for **3** and **5** at *m/z* 1079 and 1031 respectively.

Table: Reduction potentials of organofullerenes **3** and **5**.[a]

Compound	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E_{red} (addend)
3	-0.65	-1.06	-1.67	-	-0.38 ($2e^-$)
5	-0.64	-1.07	-1.78	-	-0.32; -0.98
C_{60}	-0.60	-1.00	-1.52	-2.04	-
TCAQ	-	-	-	-	-0.58 ($2e^-$)
DCAQI	-	-	-	-	-0.35; -0.74

[a] All potentials in V *vs* SCE; Toluene:MeCN (5:1); 0.1 M Bu_4NClO_4; scan rate: 0.2 Vs^{-1}.

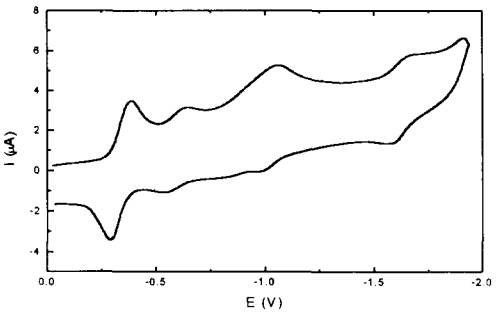


Figure. Cyclic voltammogram of **3** at 200 $mV \cdot s^{-1}$.

The cyclic voltammograms of compounds **3** and **5** show, in addition to the first three one-electron quasireversible reduction waves corresponding to the reduction steps of the fullerene moiety (Figure), the presence of the reduction wave of the organic addends which appear as a reversible two-electron reduction wave for the TCAQ moiety in **3**, and two one-electron reduction waves for the DCAQI fragment in compound **5**, in agreement with the behaviour observed for the unsubstituted TCAQ[15] and DCAQI[16] (Table).

The first reduction potentials for these fulleropyrrolidines is remarkably shifted to less negative values related to the parent C_{60}, showing both organic addends (TCAQ and DCAQI) a slightly better acceptor ability than the parent unsubstituted molecules TCAQ and DCAQI due, probably, to the proximity of the electronwithdrawing C_{60} core. Consequently, these novel [60]fullerene-based electron acceptors are suitable precursors for the preparation of intermolecular CT-complexes by reaction with strong electron donor molecules.[17]

In summary, we have carried out the first synthesis of organofullerenes bearing TCNQ and DCNQI derivatives leading to molecules which can accept up to eight electrons in solution. Work is in progress to prepare CT-complexes and other fulleropyrrolidines covalently attached to the parent TCNQ and DCNQI molecules which behave as stronger electron acceptors, in order to prepare C_{60}-based electrically conducting CT-complexes with potential applications in molecular electronics.

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REFERENCES AND NOTES

1. Saito, G; Teramoto, T.; Otsuka, A.; Sugita, Y.; Ban, T.; Kusunoki, M.; Sakaguchi, K. *Synth. Met* **1994**, *64*, 359.
2. See for example: Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. *J. Chem. Soc., Chem. Commun.* **1992**, 1764.
3. Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359.
4. Zhou, F.; Van Berkel, G. J.; Donovan, B. T.; *J. Am. Chem. Soc.* **1994**, *116*, 5485.
5. Keshavarz, K.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371.
6. Wudl, F.; Suzuki, T.; Prato, M.; *Synth. Met.* **1993**, *59*, 296; Eiermann, M.; Haddon, R. C.; Knight, B.; Chan Li, Q.; Maggini, M.; Martín, N.; Ohno, T.; Prato, M.; Suzuki, T.; Wudl, F. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1591.
7. Ohno, T.; Martín, N.; Knight, B.; Wudl, F.; Suzuki, T.; Yu, H. *J. Org. Chem.* **1996**, *61*, 1306.
8. Acker, D. S.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Melby, L. R.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1960**, *82*, 6408; Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.
9. Aumüller, A.; Hünig, S. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 47.
10. Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, J.; Orduna, J. *Tetrahedron Lett.* **1996**, *37*, 5979.
11. The synthesis of 2-formyl-9,10-anthraquinone and fulleropyrrolidine **4** will be described elsewhere.
12. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
13. Lehnert, W. *Tetrahedron Lett.* **1970**, 4723; Lehnert, W. *Synthesis* **1974**, 667.
14. Selected spectroscopic data for compounds **3**: FTIR (KBr, cm^{-1}): 2224, 1553, 1463, 1261, 1031, 803, 767, 527. ^1H NMR ($CDCl_3$): 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 (m, 2H), 8.29 (m, 4H), 8.78 (br m, 1H). ^{13}C NMR ($CDCl_3$): 159.61, 155.67, 153.45, 152.11, 147.37, 147,26, 146.30, 146.22, 146.14, 145.97, 145.55, 145.47, 145.42, 145.37, 145.30, 145.17, 144.76, 144.44, 144.23, 143.23, 143.11, 143.03, 142.73, 142.60, 142.52, 142.19, 142.13, 142.06, 141.96, 141.73, 141.53, 140.34, 140.26, 136.24, 133.17, 132.56, 132.50, 130.05, 127.85, 127.74, 127.67, 113.05, 112.98, 112.95, 112.94, 83.27, 77.25, 70.00, 69.17, 40.28. MS *m/z*: 1079 (M^+), 720. UV-vis ($CHCl_3$): 430, 698 nm. **5**: FTIR (KBr, cm^{-1}): 2169, 1465, 1334, 1225, 789, 766, 527. ^1H NMR ($CDCl_3$): 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 (m, 2H), 7.71 (m, 1H), 7.90 (br m, 2H), 8.42 (m, 2H). MS *m/z*: 1031 (M^+), 720. UV-vis ($CHCl_3$): 430, 698 nm.
15. Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618; Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, *107*, 556.
16. Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1986**, 142.
17. Mukai, T.; Suzuki, T.; Yamashita, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2433.

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