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Synthesis of New C_{60}-Donor Dyads by Reaction of Pyrazolylhydrazones with [60]Fullerene under Microwave Irradiation.

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Abstract: *A facile synthesis of a series of pyrazolo[4',5'][60]fullerenes from pyrazolyl hydrazones under microwave irradiation is described. Evidence of intramolecular charge transfer interaction is shown.*

The design of novel organic molecules containing electron donor (D) and electron acceptor (A) moieties constitutes a promising field due to the interesting optical and electronic properties that they can display.[1] D-σ-A structures are the base for the development of molecular electronic devices and they can also be used for the synthesis of artificial photosynthetic systems. It is well known that [60]fullerene is a good electron acceptor and some [60]fullerene derivatives show charge-transfer (CT) interactions. The design of this type of compound is an intriguing research subject.

Although remarkable photoinduced electron-transfer phenomena have been studied[2] and some intermolecular CT complexes of [60] and [70]fullerene have been reported,[3] the first direct observation of an intramolecular CT interaction was recently made by fusing a pyrazoline ring to C_{60}.[4] Two facts were claimed as proof of CT in these compounds: the low-field shift increase for the *ortho* protons, in particular, those for a *N*-phenyl group ($\Delta\delta = 0.79$) with respect to the corresponding pyrazoline and the observation of a band at around 470 nm, which shows a shift to longer wavelength with increasing solvent polarizability, in the corresponding UV spectrum. Interestingly, no CT interaction was shown to take place with a C-phenyl group.

In this context, it was of interest to study the influence of the introduction of a π-donor heterocycle as well as different substituted *N*-aryl groups in the proximity of the C_{60} cage in order to get a better insight into this possible CT phenomenon.

In this communication, we report the preparation of several 1-aryl-3-(1-phenylpyrazol-4-yl)-pyrazolo[4',5':1,2][60]fullerene adducts **2**. These compounds were synthesised by two different methods (Scheme 1)

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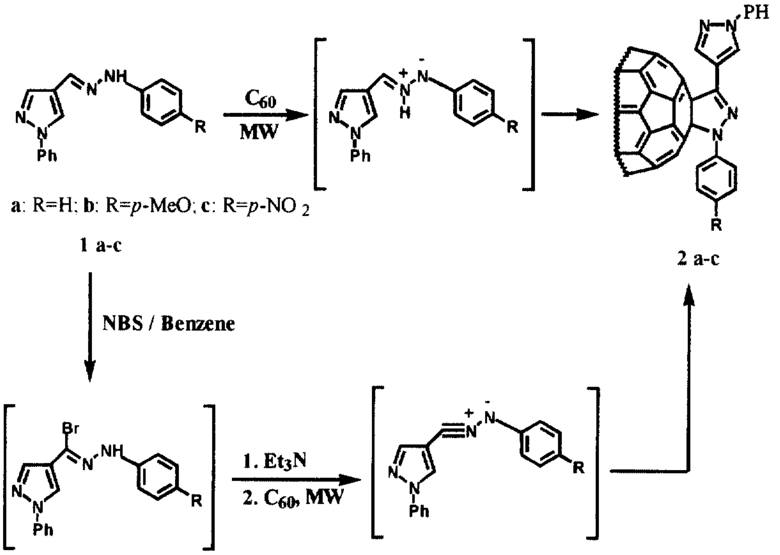
We have shown that bipyrazoles can be obtained from pyrazolyl hydrazones under microwave irradiation,[5] by [3+2] cycloaddition with alkenes, after an efficient hydrazone-azomethine imine tautomerization. The reaction does not proceed under classical heating. According to this procedure, when hydrazones **1a-c** were reacted with C_{60} in *o*-dichlorobenzene or trichlorobenzene as solvent under microwave irradiation, adduct **2a** was formed in 6 % yield,[6] while only traces of **2b** were detected and **2c** was not formed at all.



Scheme 1

As an alternative route, we used nitrile imines as dipoles.[5] Previously,[4,7] 2-pyrazoline rings fused to C_{60} were prepared by cycloaddition to nitrile imines generated *in situ* from the corresponding N-chlorobenzylidene derivatives. We describe a simpler procedure for the preparation of pyrazolofullerenes; nitrile imines were generated *in situ* from the corresponding hydrazone **1a-c** and NBS in the presence of Et_3N and reacted with C_{60} under microwave irradiation (Scheme 1)

Table 1. Preparation of **2a-c** under Microwave Irradiation

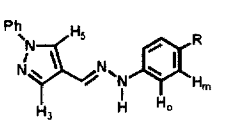
	Reaction Conditions	Yield (%)[a]
2a	Benzene, 30 min, 105 W	38 (55)[b]
2b	Benzene, 30 min, 105 W	24 (33)[b]
2c	Benzene, 5 min, 210 W	20 (43)[b]

[a]Isolated product. Yields are not optimised. [b]Considering recovered C_{60}

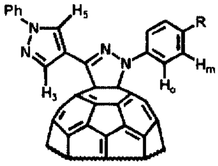
The target molecules **2a-c** were obtained from the corresponding hydrazones **1a-c**[8] which can be easily prepared by condensation of 4-formyl-1-phenylpyrazole[9] with phenylhydrazine. In a typical experiment, hydrazone **1** (55 mg, 0.21 mmol), and NBS (38 mg, 0.21 mmol) in benzene (45 mL) were stirred for 15 m; afterwards Et_3N (21 mg, 0.21 mmol) and C_{60} (50 mg, 0.07 mmol) were added. The mixture was irradiated in a focused microwave reactor [10] (for power irradiation and time, see table 1) and the crude reaction was purified by flash chromatography on silica gel.

The structures of compounds **2a-c** were determined by spectroscopic analysis (FAB-MS, IR, NMR and UV-Vis)[11] which showed the characteristic data of 6,6-bond addition products. FAB-MS spectra exhibited the corresponding M^+H ion peak (m/z) 981 for **2a**, 1011 for **2b** and 1026 for **2c**. The UV-Vis spectra showed the typical weak absorption at 430 nm indicating that cycloaddition had take place on the 6,6-bond of C_{60}.

Table 2. Selected ^{1}H-NMR data for compounds **1** and **2**



1 a-c



2 a-c

	H_3	H_5	H_o Ph-N	H_m Ph-N
1a (R= H)	7.95	8.11	7.67	7.25
1b (R=*p*-MeO)	7.93	8.09	7.01	6.83
1c (R=*p*-NO_2)	8.03	8.22	7.10	8.20
2a (R= H)	8.54 (+0.59)[a]	8.71 (+0.60)[a]	7.95 (+0.90)[a]	7.34 (+0.09)[a]
2b (R=*p*-MeO)	8.53 (+0-60)[a]	8.71 (+0.62)[a]	7.81 (+0.80)[a]	7.02 (+0.19)[a]
2c (R=*p*-NO_2)	8.55 (+0.52)[a]	8.73 (+0.51)[a]	8.28 (+1.18)[a]	8.36 (+0.16)[a]

[a] In brackets: shift increments respecting to the corresponding hydrazone **1**

It has been reported that the magnitude of the low field shift in the donor unit when fused to C_{60} provides direct information for CT interactions between the donors and the [60]fullerene.[12] Interestingly, in compounds **2a-c**, H_3 and H_5 in the pyrazole ring (see table 2) are shifted by 0.51-0.62 ppm and H_o-Ph-N by 0.80-1.18 ppm, with respect to the corresponding hydrazone (selected ^{1}H-NMR data of compounds **1a-c** and **2a-c** are depicted in Table 2). Considering previous results, intramolecular CT interactions from the *N*-phenyl and *C*-pyrazolyl groups are possible. Much lower shifts (or none) have been found in 3-pyrazol-5-yl)-pyrazolo[4',5':1,2][60]fullerene or 2-(pyrazol-4-yl)-pyrrolidine[3',4':1,2][60]fullerene.[13]

The UV-Vis spectra of these compounds are similar to those described for other pyrazolo[4',5':1,2][60]fullerenes[4] with a band at around 460 nm which is shifted towards longer wavelength with increasing solvent polarizability. In our opinion, in order to assert the existence of an intramolecular CT interaction and to show which group is responsible for the interaction, the N- or C-substituent or the nitrogen lone pair, it will be necessary to prepare new derivatives and to find new spectroscopic evidence for the interaction. Work is in progress in our laboratory to get a deeper insight into the behaviour of these compounds in CT processes.

ACKNOWLEDGEMENTS:

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8. Selected data for hydrazones **1a-c**: **1a** m.p.170-171°C (from ethanol); FTIR (KBr, cm^{-1}): 3299, 1938, 1845, 1719, 1623, 1601, 1563, 1501; ^1H-NMR ($CDCl_3$) δ (ppm): 11.95 (s, 1H), 8.11 (s, 1H), 7.95 (s, 1H), 7.68 (d, *J*=8.0 Hz, 2H), 7.67 (s, 1H), 7.44 (t, *J*=8.0 Hz, 2H), 7.25 (m, 3H), 7.05 (d, *J*=8.0 Hz, 2H), 6.83 (t, *J*=8.0 Hz, 1H). **1b** m.p. 148-149 °C (from ethanol); FTIR (KBr, cm^{-1}): 3304, 2838, 1864, 1617, 1596, 1548, 1518, 1503; ^1H-NMR ($CDCl_3$) δ (ppm): 8.09 (s, 1H), 7.93 (s, 1H), 7.67 (d, *J*=8.0 Hz, 2H), 7.63 (s, 1H), 7.43 (t, *J*=8.0 Hz, 2H), 7.31 (s, 1H), 7.25 (t, *J*= 8.0 Hz, 1H), 7.01 (d, *J*=9.0 Hz, 2H), 6.83 (d, *J*=9.0 Hz, 2H), 3.78 (s, 3H). **1c** m.p. 232-234 °C (from ethanol); FTIR (KBr, cm^{-1}): 3253, 1621, 1613, 1597, 1560, 1497, 1317, 1276; ^1H-NMR ($CDCl_3$) δ (ppm): 8.22 (s, 1H), 8.20 (d, *J*=9.1 Hz, 2H), 8.03 (s, 1H), 7.94 (s, 1H), 7.83 (s, 1H), 7.74 (d, *J*=8.1 Hz, 2H), 7.50 (dd, *J*=8.1 Hz, J=7.7 Hz, 2H), 7.37 (t, *J*=7.7 Hz, 1H), 7.10 (d, *J*=9.1Hz, 2H).
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11. Selected spectroscopic data for cycladducts **2a-c: 2a** FTIR (KBr, cm^{-1}): 1661, 1653, 1647, 1637, 1628, 1624, 1100, 952, 805, 750, 526, 473; ^1H-NMR ($CDCl_3$): 8.71 (s, 1H), 8.54 (s, 1H), 7.95 (d, *J*=8 Hz, 2H), 7.74 (d, *J*=7.6 Hz, 2H), 7.49 (m, 5H), 7.36 (t, *J*=7.6 Hz, 1H); FAB-MS (MH^+) m/z: 981; UV-Vis (C_6H_{12}): 255, 310, 425, 488. **2b** FTIR (KBr, cm^{-1}): 1662, 1634, 1558, 1541, 1506, 1458, 754, 526; ^1H-NMR ($CDCl_3$): 8.71 (s, 1H), 8.53 (s, 1H), 7.81 (d, *J*=8.9 Hz, 2H), 7.73 (d, *J*=7.8 Hz, 2H), 7.49 (dd, *J*=7.3 Hz, *J*=7.8 Hz, 2H), 7.35 (t, *J*=7.3 Hz, 1H), 7.02 (d, *J*=8.9 Hz, 2H), 3.86 (s, 3H);FAB-MS (MH^+) m/z: 1011; UV-Vis (C_6H_{12}): 255, 313, 421, 488. **2c** FTIR (KBr, cm^{-1}): 1903, 1588, 1546, 1496, 1428, 1112, 754, 526; ^1H-NMR ($CDCl_3$): 8.73 (s, 1H), 8.55 (s, 1H), 8.36 (d, *J*=9.3 Hz, 2H), 8.28 (d, *J*=9.3 Hz, 2H), 7.75 (d, *J*=8.2 Hz, 2H), 7.51 (dd, *J*=7.3 Hz, *J*=8.2 Hz, 2H), 7.39 (t, *J*=7.3 Hz, 1H); FAB-MS (MH^+) m/z: 1026; UV-Vis (C_6H_{12}): 257, 328, 424, 488.
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