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Relation between charge transfer and solvent polarity in fullerene derivatives: NMR studies†

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In this paper, we show that solvent-dependent NMR studies can be used as an indication of charge transfer processes in the ground state in isoxazolino- and pyrazolinofullerenes. NMR studies have several advantages over other techniques, not only can the occurrence of the CT process be detected but the power of NMR spectroscopy in structural determination can be used to indicate the group responsible for the CT process in [60]fullerene-based materials.

Introduction

The increasing interest in efficient procedures to harvest solar energy as an alternative to fossil fuels has led to intensive research in the field of photoinduced electron transfer[1] and the possibility of using such charge separation in molecular information storage has been suggested.[2] These kinds of molecules have a donor unit (D) and an acceptor unit (A) that are either spatially close but not covalently bonded (intermolecular) or are linked by covalent bonds (intramolecular). In this field, molecular optical and electronic devices using fullerenes are of interest because of their unique electrochemical and photophysical behaviour as both acceptors and as sensitizers[3] and there are several reports on the participation of fullerenes in photoinduced electron transfer processes.[4]

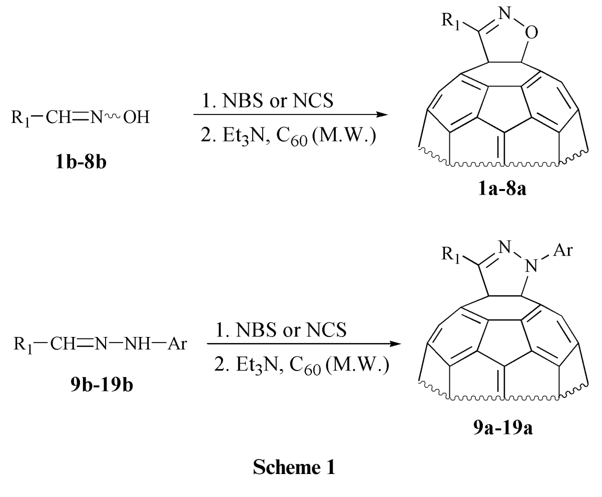
In recent years, as a consequence of the development of different synthetic approaches for the preparation of C_{60} derivatives,[5] various donor–spacer–fullerene systems (D–spacer–C_{60}) have been prepared and porphyrin,[6] amine,[7] polycondensed aromatic,[8] transition metal complex,[9] carotenoid,[10] ferrocene,[11] phthalocyanine[12] tetrathiafulvalene (TTF)[13] and arylvinylene[14] derivatives have been reported. In some cases, intramolecular photoinduced charge separation has been observed.

Although remarkable photoinduced electron-transfer phenomena have been studied[15] and some intermolecular charge transfer (CT) complexes of [60] and [70]fullerene have been reported,[16] the first direct observation of an intramolecular CT interaction in the ground state was described for a system containing a pyrazoline ring fused to C_{60}.[17] Two facts were put forward as proof of CT in these compounds: (i) the low-field shift increases for the *ortho* protons, particularly those of the *N*-phenyl group, with respect to the corresponding pyrazoline and (ii) the observation of a CT band in the UV spectrum at around 470 nm, which shows a bathochromic shift with increasing solvent polarizability. In other examples of this type of phenomenon,[18–20] weak bands between 450 and 520 nm have been ascribed to weak electronic interactions between donor and acceptor moieties. Cyclic voltammetry (CV) measurements have also been quoted as evidence for intramolecular charge-transfer between the donor and C_{60}.[21]

We have recently described the synthesis of isoxazolino- and pyrazolino[60]fullerenes by 1,3-dipolar cycloaddition of nitrile oxides[22] and imines,[23] respectively, under microwave irradiation (Scheme 1). The dipolar species were prepared *in situ* from the corresponding oximes and hydrazones. We thought that these species would be particularly suitable to show CT phenomena due to the possible combination of a good donor and a spacer, like an isoxazole or a pyrazole ring with an electronegative heteroatom directly attached to the C_{60} ring — a structural unit that may increase the acceptor properties of fullerene. Indeed, these compounds showed improved electron affinity with respect to C_{60}, as deduced by cyclic voltammetry (CV).

The UV-vis spectra of these materials show a broad band that is red-shifted with increasing solvent polarity, suggesting the formation of a weak charge transfer in the ground state.[17] This band was not observed in derivatives bearing electron-withdrawing substituents.

In this paper we would like to show that solvent-dependent NMR spectroscopy is a useful tool to indicate the occurrence of CT phenomena in the ground state in fullerene derivatives. With this aim in mind, we studied the ^1H NMR spectra of the isoxazolino- and pyrazolino[60]fullerenes **1**–**19a**, which are



Scheme 1

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†Electronic supplementary information (ESI) available: Table S1: chemical shifts (ppm) in C_6D_6 ($E_T^N = 0.111$), $CDCl_3$ ($E_T^N = 0.259$), and CD_2Cl_2 ($E_T^N = 0.309$). See http://www.rsc.org/suppdata/jm/b2/b203112b/

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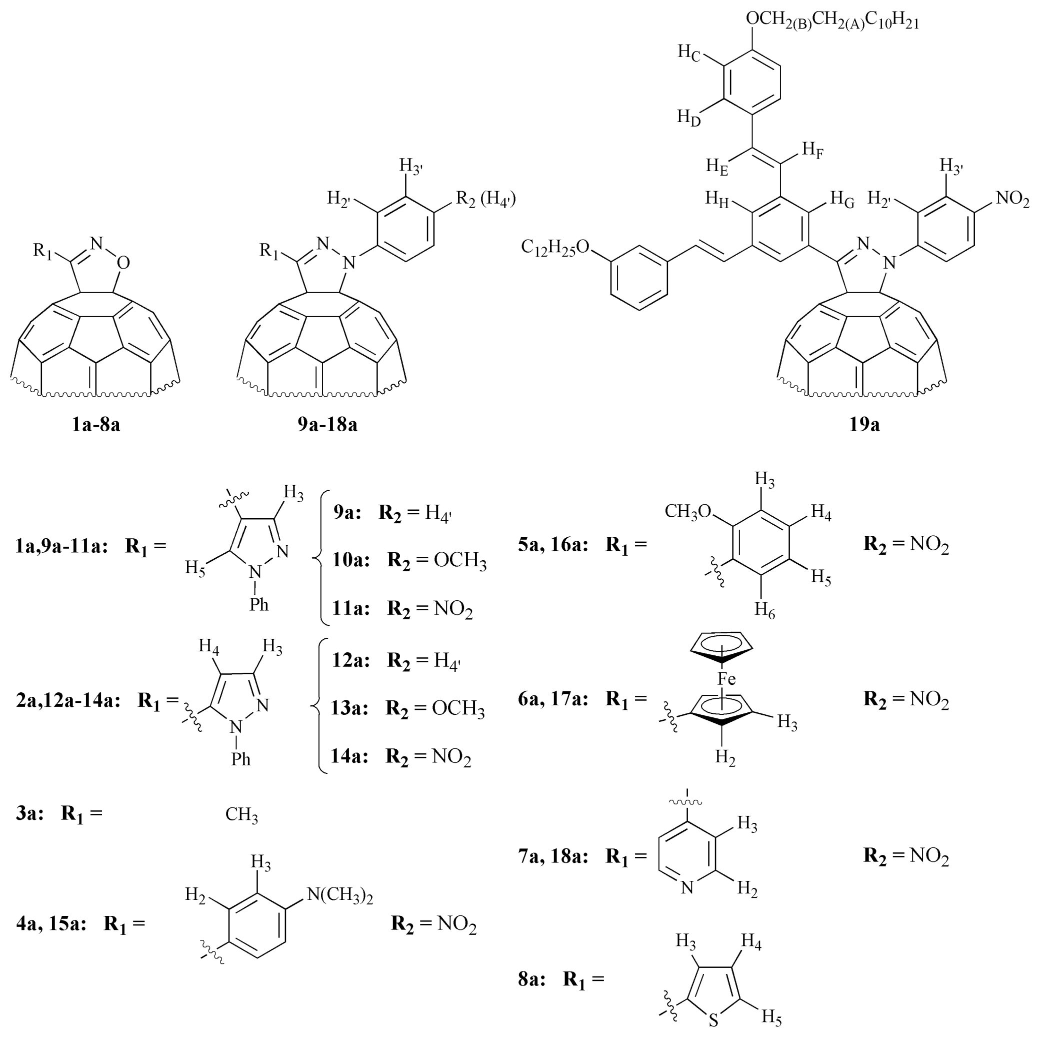

Chart 1

collected in Chart 1. Finally, the NMR results are compared with the information afforded by UV-vis spectrophotometry.

Results and discussion

It has been known since the early days of fullerene research that the C_{60} cage experiences strong ring-current anisotropy effects and that paramagnetic ring currents in the pentagons deshield protons located above them and mild diamagnetic currents supported by hexagons weakly shield the protons located above their centre.[5] On the other hand, as described above, it has been suggested that the magnitude of the low-field shift in the donor unit, when fused to C_{60}, provides direct information regarding the CT interactions between donors and [60]fullerene.[17] In 1,3-diaryl substituted pyrazolinofullerenes the low-field shifts for the *ortho* protons ($\Delta\delta = 0.79$ ppm) in the *N*-aryl group, in comparison to the corresponding pyrazoline, were indicative of a charge transfer process. Interestingly, deshielding of the *C*-phenyl group was not observed and, consequently, it was suggested that the charge transfer interaction did not take place in the *C*-aryl group.

We have compared the NMR spectra of cycloadducts **1**–**19a** with those of the corresponding oximes and hydrazones **1**–**19b**; these data, along with the chemical shift differences, are collected in Tables 1 and 2. Strong deshielding effects are observed for the *ortho* protons of the *N*-aryl group in most of the pyrazolinofullerenes with respect to the corresponding hydrazones: **9**, $\Delta\delta = 0.89$ ppm, **10**, $\Delta\delta = 0.80$ ppm, **11**, $\Delta\delta = 1.18$ ppm, **12**, $\Delta\delta = 0.58$ ppm, **14**, $\Delta\delta = 0.68$ ppm, **15**, $\Delta\delta = 1.20$ ppm, **16**, $\Delta\delta = 1.14$ ppm, **17**, $\Delta\delta = 1.18$ ppm, **18**, $\Delta\delta = 1.07$ ppm and **19** $\Delta\delta = 1.12$ ppm. However, it is interesting to note that strong deshielding effects are also observed for the *C*-substituent in both pyrazolines and

Table 1 Chemical shift differences (ppm) between cycloadducts (*a*) and oximes (*b*). Solvent, $CDCl_3$

Compd.		C-Substituent *a*	*b*	Difference[a]
1	H_3	8.74	8.63	0.11
	H_5	8.52	8.01	**0.51**
2	H_3	7.84	7.68	0.16
	H_4	7.04	6.81	0.23
3	Me	2.75	1.83	**0.92**
4	NCH_3	3.04	2.98	0.06
	H_2	8.14	7.43	**0.71**
	H_3	6.82	6.67	0.15
5	OCH_3	3.82	3.88	−0.06
	H_3	7.05	6.93	0.12
	H_4	7.56	7.37	0.19
	H_5	7.13	6.97	0.16
	H_6	7.67	7.67	0
6	$H_{Cp'}$	4.18	4.21	−0.03
	H_2	5.21	4.51	**0.70**
	H_3	4.53	4.35	0.18
7	H_2	8.79	8.64	0.15
	H_3	8.12	7.51	**0.61**
8	H_3	8.05	7.55	**0.50**
	H_4	7.17	7.08	0.09
	H_5	7.55	7.38	0.17

[a]Difference *a*–*b*. [b]Differences > 0.50 are indicated in bold.

Table 2 Chemical shift differences (ppm) between cycloadducts (a) and hydrazones (b). Solvent, $CDCl_3$

	C-Substituent				N-Substituent			
Compd.		*a*	*b*	Difference[a]		*a*	*b*	Difference[a]
9	H_3	8.54	7.95	**0.59**	$H_{2'}$	7.95	7.06	**0.89**
	H_5	8.71	8.11	**0.60**	$H_{3'}$	7.49	7.25	0.24
					$H_{4'}$	7.36	6.84	**0.52**
10	H_3	8.53	7.93	**0.60**	$H_{2'}$	7.81	7.01	**0.80**
	H_5	8.7	8.09	**0.61**	$H_{3'}$	7.02	6.83	0.19
11	H_3	8.55	7.94	**0.61**	$H_{2'}$	8.28	7.1	**1.18**
	H_5	8.73	8.22	**0.51**	$H_{3'}$	8.36	8.2	0.16
12	H_3	7.76	7.63	0.13	$H_{2'}$	7.51	6.93	**0.58**
	H_4	7.05	6.85	0.20	$H_{3'}$	7.3	7.25	0.05
					$H_{4'}$	7.14	6.91	0.23
13	H_3	7.8	7.63	0.17	$H_{2'}$	7.35	6.93	0.42
	H_4	7.05	6.7	0.35	$H_{3'}$	6.84	6.79	0.05
14	H_3	7.86	7.72	0.14	$H_{2'}$	7.66	6.98	**0.68**
	H_4	7.14	6.89	0.25	$H_{3'}$	8.18	8.16	0.02
15	NCH_3	3.06	3.02	0.04	$H_{2'}$	8.26	7.06	**1.20**
	H_2	8.16	7.56	**0.60**	$H_{3'}$	8.33	8.16	0.17
	H_3	6.82	6.71	0.11				
16	OCH_3	3.8	3.88	−0.08	$H_{2'}$	8.25	7.11	**1.14**
	H_3	7.06	6.92	0.14	$H_{3'}$	8.32	8.18	0.14
	H_4	7.51	7.36	0.15				
	H_5	7.14	7.02	0.12				
	H_6	7.68	7.99	−0.31				
17	H_{cp}	4.23	4.2	0.03	$H_{2'}$	8.21	7.03	**1.18**
	H_2	5.28	4.4	**0.88**	$H_{3'}$	8.33	8.17	0.16
	H_3	4.59	4.62	−0.03				
18	H_2	8.81	8.66	0.15	$H_{2'}$	8.26	7.19	**1.07**
	H_3	8.21	7.55	**0.66**	$H_{3'}$	8.37	8.23	0.14
19	H_A	1.8	1.80	−0.01	$H_{2'}$	8.29	7.17	**1.12**
	H_B	3.98	3.99	−0.01	$H_{3'}$	8.36	8.22	0.14
	H_C	6.90	6.92	−0.02				
	H_D	7.45	7.49	−0.04				
	H_E	7.07	7.09	−0.02				
	H_F	7.07	7.09	−0.02				
	H_G	8.20	7.64	**0.56**				
	H_H	7.71	7.62	0.09				

[a]Difference *a*–*b* [b]Differences > 0.50 are indicated in bold.

isoxazolines: **1**, $\Delta\delta = 0.51$ ppm, **3**, $\Delta\delta = 0.92$ ppm, **4**, $\Delta\delta = 0.71$ ppm, **6**, $\Delta\delta = 0.70$ ppm, **7**, $\Delta\delta = 0.61$ ppm, **8**, $\Delta\delta = 0.50$ ppm, **9**, $\Delta\delta = 0.59$ ppm and 0.60 ppm, **10**, $\Delta\delta = 0.60$ ppm and 0.61 ppm, **11**, $\Delta\delta = 0.61$ ppm and 0.51 ppm, **15**, $\Delta\delta = 0.60$ ppm, **17**, $\Delta\delta = 0.88$ ppm, **18**, $\Delta\delta = 0.66$ ppm, **19**, $\Delta\delta = 0.56$ ppm.

Comparison of the 4- and 5-pyrazolyl-substituted derivatives **1**, **9**, **10**, **11** and **2**, **12**, **13**, **14**, respectively, shows that significant deshielding does not occur in 5-substituted pyrazolinofullerenes and, as a consequence, a CT process should not take place in these derivatives according to the previously mentioned hypothesis.

^{13}C NMR spectroscopy is more sensitive to electronic density, as is the predominant paramagnetic shielding term σ^{para}, and anisotropic effects are therefore minimized in comparison to ^1H NMR spectroscopy.[24] For this reason we studied the ^{13}C NMR spectra of compounds **9**–**14a,b** in order to confirm that the deshielding effects are produced by a charge transfer process rather than by anisotropic effects. Representative signals from the ^{13}C NMR spectra of compounds **9a**–**14a** and the corresponding hydrazones **9**–**14b** are collected in Table 3.

Comparison of the ^{13}C NMR spectra of compounds **9a**–**11a** (4-pyrazolyl-substituted derivatives) with those of the corresponding hydrazones **9b**–**11b** (Table 3) shows a strong deshielding (up to 11.8 ppm) of the *ortho-C* in the pyrazoline *N*-aryl group. On the other side of the molecule there is no evidence of significant deshielding in the pyrazole ring, indicating that the

Table 3 ^{13}C NMR data for compounds **9a**–**14a** and **9b**–**14b** in $CDCl_3$[a]

	C-*i*	C-*o*	C-*m*	C-*p*	C-3	C-4	C-5	C-1′	C-2′	C-3′	C-4′	C=N
9a	—	117.9	128.1	125.6	140.8	—	123.5	—	**124.6**	127.8	122.5	
9b	140.1	119.3	129.7	127.0	139.7	114.2	124.6	129.9	112.9	129.5	120.2	144.9
10a	—	119.6	129.8	127.3	140.9	117.1	126.0	—	**126.7**	114.8	158.0	
10b	140.2	119.4	129.8	127.0	139.2	115.1	124.6	139.4	115.1[b]	114.4[b]	152.3	139.4
11a	—	119.7[b]	129.9	126.6	142.5	—	127.7	—	**119.4**[b]	125.6	—	
11b	134.8	118.4	129.6	126.8	139.2	120.3	126.6	137.9	110.9	126.2	129.6	150.6
12a	—	126.4	129.5[b]	128.5	140.5	110.1	—	—	**123.5**	129.4[b]	125.3	
12b	138.9	125.9	129.5[b]	129.5[b]	140.8	105.4	139.8	126.3	113.0	129.5[b]	120.4	144.1
13a	137.7	126.4	129.5	128.5	140.5	110.0	136.3	129.7	**126.0**	114.6	157.8	
13b	139.5	125.9	129.5	128.5	140.5	105.1	—	125.3	114.2	115.0	154.4	138.2
14a	—	125.4	128.8	127.6	140.7	110.6	—	—	**119.6**	126.5	129.1	
14b	131.7	126.0[b]	129.6	128.8	140.8	106.6	139.2[c]	138.2[c]	112.1	126.5[b]	129.1	149.0

[a]Signals with deshieldings > 8 are indicated in bold. [b]Assignment of these signals can be interchanged. [c]Assignment of these signals can be interchanged.

charge transfer, if it exists, should arise from the *N*-aryl ring and not from the *C*-substituent — as suggested by the ^{1}H NMR data.

In compounds **12a**–**14a** (5-pyrazolyl-substituted derivatives), similar deshielding of the *ortho-C* of the pyrazoline *N*-aryl (up to 11.8 ppm) is observed along with a deshielding of the pyrazole C-4 (up to 5 ppm), as compared to the corresponding hydrazones (**12b**–**14b**), suggesting that the CT process should arise from both the *N*-aryl ring and the pyrazole ring. *This result is opposite to that inferred by the* ^{1}*H NMR spectra and suggests that the strong deshielding in the* ^{1}*H NMR spectra is due mainly to the anisotropy of the fullerene cage.*

In summary, we do not consider the deshielding effect in the ^{1}H NMR spectra to constitute conclusive proof of the CT process on the basis that several methods (^{13}C NMR spectra, UV spectroscopy, steady-state fluorescence spectroscopy and transient absorption spectra) indicate that charge transfer is produced more efficiently in the 5-pyrazolyl derivatives than in the 4-pyrazolyl derivatives.[23b] This situation is in contrast to that suggested by ^{1}H NMR spectroscopy alone and, as such, the deshielding of the signals corresponding to protons closest to the C_{60} cage could well be a consequence of the strong anisotropic effect of the fullerene. Other examples in which the close proximity of the substituent to the C_{60} cage results in deshielding of the corresponding signals in the NMR spectra have been described recently.[25]

Solvent effect on ^{1}H NMR spectra

The electronic structure of chromophores was investigated by studying the evolution of the ^{1}H NMR spectra with solvent polarity.[26] Polar compounds orientate and/or polarize surrounding solvent molecules, thus creating an electric reaction field. For polar molecules in polar solvents, significant reaction fields can be attained and these, in turn, can polarize the solute molecules. The magnitude of this effect is related to the polarizability of the molecule and has been used to study the effect of solvent polarity on ground-state structure as support for NLO properties.[27]

We believe that this effect could be used as an indication of the charge transfer process from the organic addend to the C_{60} unit in a similar way to the UV-vis spectra, but with the advantages inherent in ^{1}H NMR spectroscopy in terms of structural determination. We recorded the ^{1}H NMR spectra of isoxazolinofullerenes **1a**–**8a** and pyrazolinofullerenes **9a**–**19a** in solvents of different polarizability and compared the spectra with those of the starting oxides **1b**–**8b** and hydrazones **9b**–**19b** obtained in the same solvents. Plots were produced of chemical shifts for a given proton *versus* solvent polarizability (expressed as E_T^N values — a semi empirical parameter of solvent polarity) for cycloadducts and the corresponding oximes or hydrazones. A higher slope of the plot for the cycloadducts should be indicative of a higher polarizability for the system and thus a more favourable situation for the occurrence of the charge transfer process. This CT process can be related to the magnitude of the deshielding and also the position that experiences greater deshielding. Moreover, anisotropic effects are minimized by comparison of the chemical shifts in various solvents. We used benzene-d$_6$, chloroform-d$_1$ and dichloromethane-d$_2$ as the solvents because the low solubility of the C_{60} derivatives precludes the use of a wider range of solvents.

The evolution of chemical shifts of cycloadducts **1a**–**19a** and the corresponding oximes and hydrazones **1b**–**19b**, respectively, with the solvent polarity was assessed for the pyrazole and the pyrazoline *N*-phenyl group. Results are presented in Table S1 (see ESI†) together with the E_T^N values. As an example, the linear plots of cycloadducts **1a**, **2a**, **10a** and **12a**, the corresponding oximes **1b** and **2b** and hydrazones **10b** and **12b** are represented in Figs. 1 and 2.

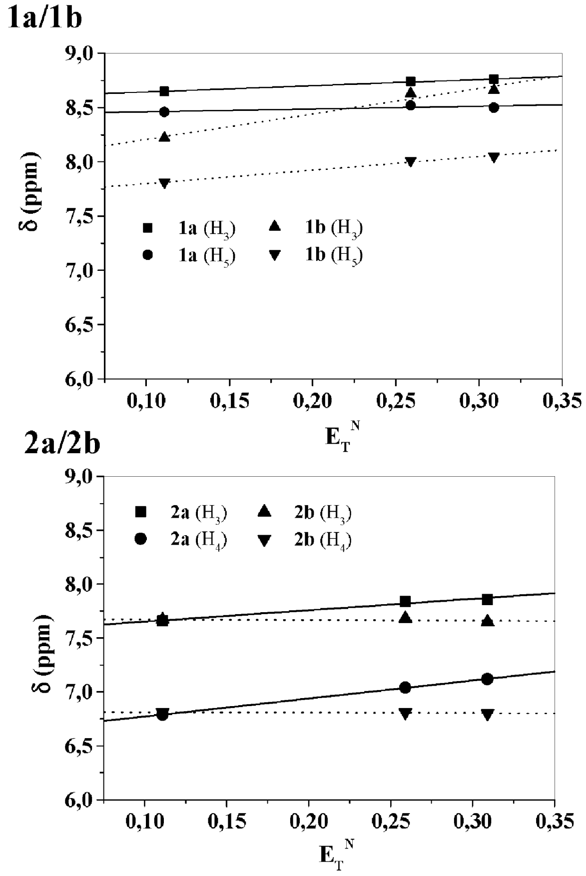

Fig. 1 Evolution of chemical shifts in cycloadducts **1a** and **2a** and oximes **1b** and **2b**.

Comparison of the slopes of the linear plots for the hydrazones and cycloadducts leads to interesting conclusions regarding the nature of the compounds, the substitution and, in particular, the influence of the fullerene cage.

In order to clarify the results we have divided the analysis into the two types of groups connected to the pyrazoline ring: the *C*-substituent and the *N*-substituent.

C-substituent

The *C*-substituent can be polarized as shown by the resonance structures represented in Fig. 3. The polar structures should be favoured in polar solvents and, as a consequence, the *ortho* and *para* protons should be deshielded when a phenyl substituent is present.

In compounds **1**, **2**, and **9**–**14**, which contain a pyrazolyl substituent, charge transfer is not observed in the 4-pyrazolyl derivatives (**1a**, **9a**–**11a**) as the slopes of the *C*-substituent hydrogens (H_3 and H_5) in the cycloadducts are lower than the corresponding slopes for the oxime **1b** and hydrazones **9b**–**11b**. In contrast, in the 5-pyrazolyl derivatives (**2**, **12**–**14**) the charge transfer should be observed as the slopes (for H_3 and H_4) in the cycloadducts (**2a**, **12a**–**14a**) are higher than in the oxime **2b** and hydrazones **12b**–**14b**. The deshielding effect and the higher slopes in the cycloadducts are especially evident in protons close to the donor part of the molecule. A higher slope is observed for H_4, which is closest to the pyrazoline and isoxazoline rings, in relation to H_3 and consequently the charge transfer process should be produced from the pyrazoline and isoxazoline rings. This situation is in complete agreement with previous results obtained by UV-vis and fluorescence spectroscopy, where the charge transfer was believed to be produced from the lone pair of the heteroatom directly attached to the fullerene moiety.

Similarly, charge transfer should be produced in isoxazolines

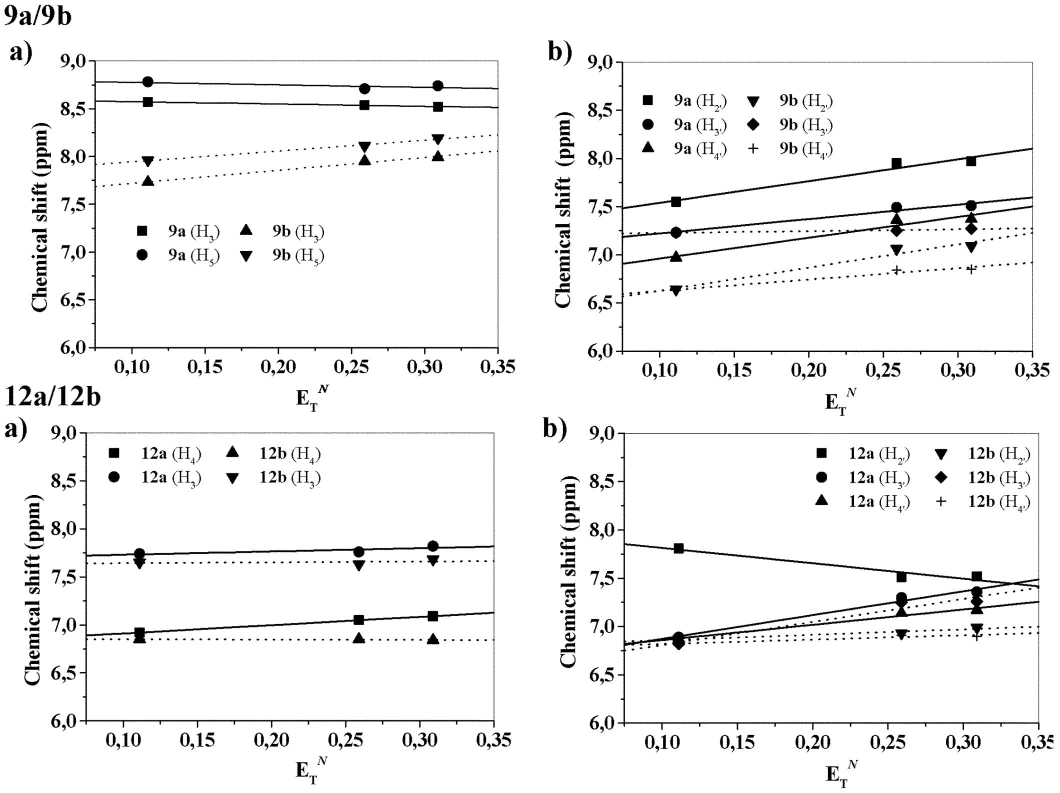

Fig. 2 Evolution of chemical shifts in cycloadducts **9a** and **12a** and hydrazones **9b** and **12b** (a) C-substituent, (b) *N*-substituent.

3a and **5a** and pyrazoline **16a**, but not in isoxazoline **7a** or pyrazoline **18a** — both of which contain a π-deficient heterocycle as the substituent.

A different situation is observed in compounds with a strong donating group, as exemplified by **4** and **15**, which both contain a *p*-*N*,*N*-dimethyl group, **6** and **17**, which incorporate a ferrocenyl group, and the thienyl-containing compound **8**. In all cases higher slopes are observed in the cycloadduct, a fact that indicates the occurrence of a charge transfer process. However, the higher slope is observed in H_3 (closest to the *N*,*N*-dimethylamino group) in **4a** and **15a**, H_3 in **6a** and **17a**, and H_5 (closest to the sulfur atom) in **8a**. It can therefore be concluded that the charge transfer is produced from the substituent, *i.e.* from the dimethylamino group in **4a** and **15a**, the sulfur atom in **8a** and the cyclopentadienyl ring in **6a** and **17a**.

The dendrimeric structure **19** gives rise to a small increase in the slope in the cycloadduct in H_G. Consequently, a small charge transfer should be produced and, once again, this originates from the pyrazoline ring.

One final question arises — why is charge transfer observed in 5-pyrazolyl-substituted isoxazolines and pyrazolines but not in the isomeric 4-substituted derivatives? (see Table S1 in the ESI† and Figs. 1 and 2). The use of ^{13}C NMR spectroscopy can shed light on this question. The extent of conjugation between the pyrazole and phenyl rings in phenyl-substituted pyrazoles can be deduced from the difference $\delta_{m\text{-C}} - \delta_{o\text{-C}}$.[28] In 4-substituted pyrazoles, conjugation between the pyrazole ring and the phenyl group is extensive, as indicated by the difference $\delta_{m\text{-C}} - \delta_{o\text{-C}} = 10.2$ ppm in **19a**, **10a** and **11a**, and by the PM3-calculated dihedral angles phenyl–pyrazole (9.76°) and isoxazoline–pyrazole (32.02°). In these cases the electron density of the π-excedent pyrazole ring is directed towards the phenyl group and not to the isoxazoline or pyrazoline ring. The high electron density at the phenyl group is demonstrated by the strong shielding of the *o*-C, as indicated by the low chemical shift for this signal (δ = 117.9 ppm, 119.6 ppm and 119.7 ppm, respectively). However, in 5-substituted pyrazoles the conjugation of the pyrazole ring with the phenyl group is hindered, as indicated by the difference $\delta_{m\text{-C}} - \delta_{o\text{-C}} = 3.1$ ppm in **12a** and 3.4 in **13a** and the calculated dihedral angles phenyl–pyrazole (88.09°) and isoxazoline–pyrazole (11.98°). The higher chemical shift of the *o*-C (δ = 126.4 ppm, 126.4 ppm and 125.4 ppm, respectively) confirms that the electron density is not directed toward the phenyl group. In this case, the electron density of the π-excessive pyrazole ring should be directed towards the isoxazoline ring, thus favouring the charge transfer process towards the fullerene moiety.

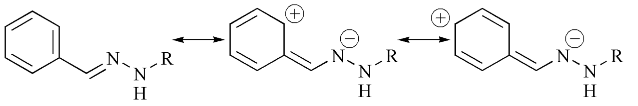

Fig. 3 Resonance structures for aromatic hydrazones (C-substituent).

N-substituent

The nature of the *N*-substituent in pyrazolinofullerenes has a marked influence on the charge transfer process and, consequently, on the slopes of the plots.

The presence of an electron-withdrawing group in the *N*-substituent produces an increase in the slopes for the protons of the *C*-substituent in both the hydrazones and cycloadducts. The effect is particularly marked in the latter compounds and indicates a higher polarization when this kind of substituent is introduced. The nature of the *N*-substituent allows the ele- ctronic density of the cycloadduct and thus the charge transfer process to be modulated. According to the values observed for the slopes, the following order for the intensity of the CT process can be deduced: pyrazoline *N*-*p*-methoxyphenyl < pyrazoline *N*-phenyl < pyrazoline *N*-*p*-nitrophenyl < isoxazoline (for comparisons see Table S1,† slopes for H_3 and H_4 in compounds **13a**, **12a**, **14a** and **2a**).

In terms of the *N*-substituent, both hydrazones and cycloadducts show high slopes. The slope for $H_{2'}$ (the proton *ortho* to the nitrogen) is always higher in the hydrazone, while for $H_{3'}$ (the proton *meta* to the nitrogen) the slope is always higher in the cycloadduct — particularly when a *p*-nitro-substituent is present. This trend again shows that the change in the polarity of the cycloadduct in relation to the hydrazone must be related to the fullerene moiety. The variation of the slopes, *i.e.* higher slopes for *meta* ($H_{3'}$) and *para* ($H_{4'}$) protons in the cycloadducts and *ortho* ($H_{2'}$) protons in the hydrazones, shows once again that the charge density is directed toward the pyrazoline ring in the cycloadducts. This situation is in complete agreement with the hypothesis of charge transfer from the heteroatom in isoxazolino- and pyrazolinofullerenes. Comparison of the slopes in $H_{2'}$ and $H_{3'}$ (see for instance Table S1,† compounds **9a**, **10a** and **11a**) shows than charge transfer from the *N*-substituent to the pyrazoline ring and, consequently, the C_{60} should adhere to the following trend $R_2 = OCH_3 > R_2 = H > R_2 = NO_2$.

It should be noted that the higher slopes observed for the chemical shift changes with solvent polarity should be a consequence of the polarization of the molecule through a charge transfer process and not due to the anisotropy of the C_{60} cage. This situation is evidenced by those cases where a strong donor is attached to the pyrazoline ring and the higher slopes are found for the hydrogen atoms closest to the donor and not for those hydrogens closest to the C_{60} cage (see for example **4a**, **5a**, **6a**, **8a**, **15a**, **16a** and **17a** in Table S1†).

Finally, a comparison of these results with the information afforded by UV-vis studies should be made in order to validate the results presented here. UV-vis spectra of isoxazolino[60]fullerenes **1a**–**8a**[22*a*] show a broad band in the region 440–650 nm and this is attributed to the formation of CT complexes.[18–20] Pyrazolino[60]fullerenes **9a**–**14a** also show a weak band in the same region and this is stronger in dyads with an electron-donating substituent on the nitrogen atom of the pyrazoline ring.[23*b*] Nevertheless, only qualitative information is afforded by UV-vis spectra in terms of the CT process and this technique can not shed any light on the atoms (or groups) that are involved in the process. On the other hand, solvent effects on the NMR spectra not only give semi-qualitative information regarding the CT process (by comparison of the slopes in the plots of chemical shifts *vs.* polarity of solvent) but can also identify the group (or groups) from which the CT process originates (by comparison of the slopes between different hydrogen atoms). In other words, a weak interaction can present a weak band in a UV-vis spectrum that can be overlooked, but the same interaction can be detected as a positive slope in the plot of chemical shift *vs.* the polarity parameter and this slope can easily be measured. Boyd *et al.* have also noted the higher sensitivity of NMR techniques in comparison to UV-vis in porphyrin–fullerene systems.[29]

Conclusions

In conclusion, we have shown that solvent-dependent NMR studies can be used as an indication of charge transfer processes in the ground state in isoxazolino- and pyrazolinofullerenes. By recording the ^1H NMR spectra in solvents with different polarizability and by comparing of the slopes of cycloadducts and the corresponding oximes and hydrazones, a number of conclusions can be drawn regarding the CT process.

The effect of solvent polarizability on the chemical shifts of the *C*-substituent has been used to show the occurrence of the CT process. The position giving rise to the higher slope has been used to indicate the position of the charge transfer process — either from the isoxazoline and pyrazoline ring or from the *C*-substituent.

The *N*-substituent has a strong influence on the electronic properties of pyrazolinofullerenes and, as a result, the nature of this substituent can be used to modulate the CT process.

Despite the fact that UV-vis is a more sensitive technique and solubility problems are less of an issue, NMR studies have several advantages; not only can the occurrence of the CT process be detected but the power of NMR spectroscopy in structural determination can be used to indicate the group responsible for the CT process.

These results open up new possibilities in the chemistry of C_{60} due to the simplicity of the method and the possibility of using the technique as a useful and predictive tool to elucidate the properties of these C_{60}-based materials.

Experimental Section

Compounds **1a** and **2a** were prepared as described in ref. 22*a*; Compounds **3a**, **4a**, and **6a**–**8a** were prepared as described in ref. 22*b*; Compound **5a** was prepared as described in ref. 22*c*; Compounds **9a**–**14a** were prepared as described in refs. 23*a* and 23*b*; Compound **16a** was prepared as described in ref. 22*c*; Compound **19a** was prepared as described in ref. 23*c*; The synthesis of compounds **15a**, **17a** and **18a** will be described elsewhere.

^1H NMR and ^{13}C NMR spectra were recorded on Varian Mercury 200 and Varian Unity 300 spectrometers. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane. Theoretical calculations were performed with the program Hyperchem 5.1 using the semiempirical PM3 method and complete (RHF) geometry optimization. The Polak–Riviere conjugated-gradient algorithm was employed and all calculations converged successfully and had gradients less than 0.1. Input structures were generated by molecular mechanics procedures using the MM+ force field as implemented in Hyperchem.

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