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## Spin-labeled fulleropyrrolidines

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### Abstract

We describe the synthesis and properties of a series of fulleropyrrolidines bearing stable nitroxide free radical moieties covalently linked to the [60]fullerene cage. The nitroxide electron spin functions as a weakly interacting probe for the investigation of radical anions and paramagnetic excited states of functionalized fullerenes. Electron transfer processes, spin coupling in polyradical adducts, and interactions between radical and fullerene excited triplet unpaired electrons have been studied through electron paramagnetic resonance. Photogenerated quartet and quintet high spin species, obtained from the spin coupling of the fullerene triplet with the nitroxide spins, have been observed for the first time at room temperature. *To cite this article: C. Corvaja et al., C. R. Chimie 9 (2006).*

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### 1. Introduction

Although extensively studied in the last decade, the fullerenes continue to be a promising challenge in current chemical research. After a first phase characterized by theoretical, physical and physicochemical studies, a well-established ‘organic chemistry of the fullerenes’ developed in a very rapid progression to the point that, currently, a wide variety of functionalized fullerenes are available through simple and accessible synthetic routes [1]. Among the several derivatives, those containing covalently linked TEMPO moieties (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) have been studied by means of

EPR spectroscopy (standard and time-resolved) to elucidate and understand the peculiar characteristics of important species such as fullerene anions or triplet excited states. These species are connected with relevant fullerene features, such as optical limiting properties, ferromagnetism, singlet oxygen sensitization. Here we review our most significant achievements in the field of nitroxide-labeled fullerenes that were synthesized by means of the addition to [60]fullerene of azomethine ylides.

### 2. Synthesis

Among the many reactions that were successfully developed, the 1,3-dipolar cycloaddition of azomethine ylides, introduced in 1993 [2], provides a valuable synthetic procedure that is used by many for the preparation of functionalized fullerenes for applications in materials science and for the study of fundamental physicochem-

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ical properties of the fullerene spheroid. The azomethine ylide cycloaddition was employed to prepare the spin-labeled fulleropyrrolidines discussed in this work whose structure is presented in Fig. 1 and Figs. 7 and 8 (vide infra). Derivatives 1–3 have the TEMPO moiety spiro-linked (1 and 2) or linked (3) to position 2 of the pyrrolidine ring. Derivative 1 was prepared by condensing *N*-methylglycine, 2,2,6,6-tetramethyl-4-piperidone-1-oxyl and [60]fullerene [3], whereas for derivative 2, 4-amino-4-carboxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TOAC) and *para*formaldehyde were used along with [60]fullerene [3]. Fulleropyrrolidine 3 was synthesized starting from 4-formyl-TEMPO, *N*-methylglycine and [60]fullerene [3]. Fulleropyrrolidine 3 was synthesized starting from 4-formyl-TEMPO, *N*-methylglycine and [60]fullerene [3]. *N*-acylated derivative 4 was obtained by allowing *N*-H fulleropyrrolidine to react with 4-carboxy-TEMPO in the presence of 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide (EDC) and *N*-hydroxybenzotriazole (HOBt) as coupling agents [3]. Derivatives 5 and 6 are donor–acceptor dyads in which a nitroxide spin-labeling has been introduced to study the photoinduced electron transfer from the ferrocene to the fuller-

ene. They were synthesized by condensing the corresponding *N*-alkylferrocenyl glycine with 2,2,6,6-tetramethyl-4-piperidone and [60]fullerene, followed by oxidation with 4-chloroperbenzoic acid [4]. Bis-fulleropyrrolidines 7–11 and binitroxide 12 are interesting examples of biradicals. A standard bis-addition protocol to [60]fullerene was used to prepare biradicals 7–11 in which two 2,2,5,5-tetramethylpyrrolidine-1-oxyl moieties were placed at precise distance and mutual orientation on the fullerene sphere [5,6]. TOAC and 4-formyl-TEMPO were employed to synthesize biradical 12 [7].

### 3. Radical anions

[60]Fullerene has a low reduction potential ( $-0.94$  V vs.  $\text{Fc}^+/\text{Fc}$  in 3:1 toluene/ $\text{CH}_3\text{CN}$  at  $-45$  °C) [8] and therefore it can be reduced to its radical mono-anion by several reducing agents or by electrolysis [9]. Due to the extensive delocalization of the negative charge over many carbon atoms, the anion is quite stable in the absence of oxygen.

The magnetic nuclei of [60]fullerene that produce hyperfine splittings in the EPR spectra of its anion are the  $^{13}\text{C}$  atoms in their isotopic natural abundance. In functionalized fullerenes, the magnetic nuclei could be also those of the addends which, however, present very small hyperfine couplings. Therefore, because of the many non-equivalent  $^{13}\text{C}$  atoms that could be potentially present, the  $^{13}\text{C}$  hyperfine structure analysis does not give unequivocal results about the electron spin distribution in fullerene anions. We discover that the addition of a nitroxide group to [60]fullerene was a useful way to overcome the above-mentioned problems, thus allowing to map the anion charge distribution through its interactions with the nitroxide unpaired spin density.

Fullerene-nitroxide anions of pyrrolidines 1–4 were prepared by reduction with Na or K in 2-methyltetrahydrofuran [3]. Before reduction, all nitroxides gave EPR spectra made of a triplet of lines of equal intensity due to  $^{14}\text{N}$  hyperfine interaction. The isotropic hyperfine constant ( $a_{\text{N}} = 15.35$  Gauss) and the  $g$  factor ( $g = 2.0061$ ) were typical of nitroxide radicals in apolar solvent (Fig. 2). Further splitting, by the methyl and methylene protons of the piperidine ring, were resolved only for some of the mentioned derivatives.

After metal reduction, an additional 1:1:1 triplet was recorded, with  $g = 2.0030$  and  $a_{\text{N}} = 7.65$  Gauss (Fig. 3) that was attributed to a biradical anion species where the unpaired electrons are located on the fullerene and nitroxide moieties, respectively. An  $a_{\text{N}}/2$  nitrogen hyperfine splitting has been observed (within experimental errors).

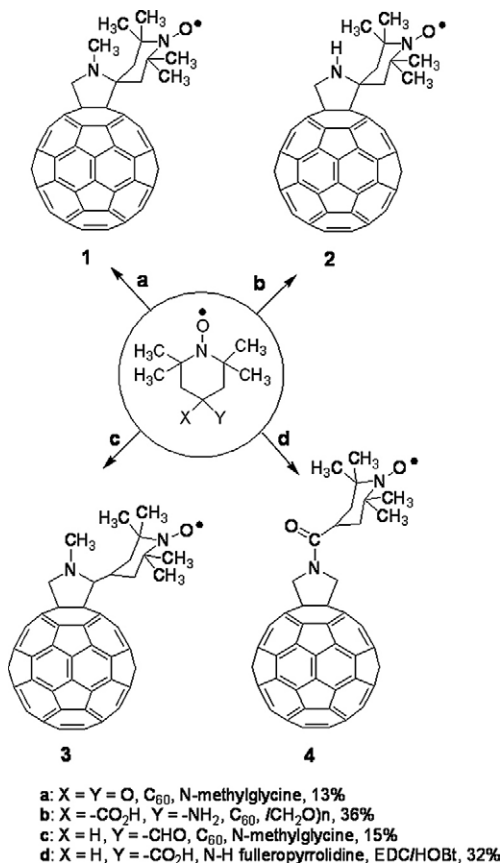


Fig. 1. Fullerene-mononitroxides considered in this work.

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