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ESR Detection of the Regioisomers Due to Addition of Methoxy and Methylthio Radicals to Fullerene C_{70}

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Photolysis of alkyl peroxides (ROOR) and disulfides (RSSR) generates, respectively, alkoxy ($RO^\bullet$) and alkylthio ($RS^\bullet$) radicals which add, in appropriate conditions, to one of the 30 double bonds of the sphere of fullerene C_{60} yielding, respectively, the radical adducts $RO\text{-}C_{60}^\bullet$ and $RS\text{-}C_{60}^\bullet$. These adducts were detected by ESR spectroscopy in steady-state conditions.[1]

Fullerene C_{70} has an ellipsoidal shape so that five different positions (corresponding to the carbons labeled as A−E) are available for addition.[2] As a consequence, five possible regioismers ($X\text{-}C_{70}^\bullet$) can be, in principle, expected when a radical $X^\bullet$ reacts with C_{70}. In the initial ESR experiments, when carbon-centered radicals $X^\bullet$ were employed, only three such adducts were observed;[2] subsequent investigations showed that, in some cases, a fourth regioisomer could also be detected.[3,4] So far, however, ESR signals corresponding to all the five possible species have not been published.[5]

In keeping with this behavior we report here the ESR observation of three regioisomers of the $MeS\text{-}C_{70}^\bullet$ adduct obtained by photolyzing dimethyl disulfide (MeSSMe) in the presence of C_{70}. Each regioisomer exhibits a spectrum which comprises a 1:3:3:1 quartet, due to the coupling of the unpaired electron with the three equivalent hydrogens of the CH_3S group (Figure 1). The corresponding hyperfine splitting constants (a_H) are similar, but not identical, to that reported[1] for the $MeS\text{-}C_{60}^\bullet$ radical; their values, and the corresponding *g* factors, are collected in Table 1.

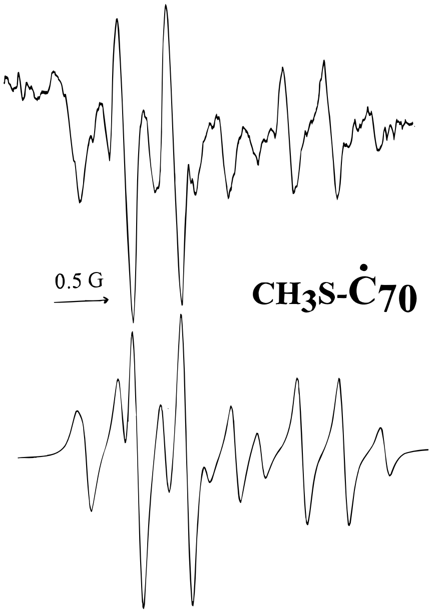

Figure 1. Experimental (top) and computer-simulated (bottom) ESR spectra of the three regioisomers due to the addition of the $MeS^\bullet$ radical to C_{70}. The temperature of the experiment is −20 °C, and the line width of the computed traces is 85 mG for all the three species.

Table 1. ESR parameters of the $MeX\text{-}C_{60}^\bullet$ and $MeX\text{-}C_{70}^\bullet$ radical adducts (X = S, O)

radical	relative proportion (%)	*g* factor	a_{Me} (G)
$MeS\text{-}C_{60}^\bullet$	100	2.00237	0.38
$MeS\text{-}C_{70}^\bullet$	26	2.00082	0.39
	53	2.00177	0.47
	21	2.00188	0.41
$MeO\text{-}C_{60}^\bullet$	100	2.00233	
$MeO\text{-}C_{70}^\bullet$	10	2.00172	
	5	2.00193	
	50	2.00216	
	18	2.00231	
	17	2.00245	

Photolysis of di-*tert*-butyl peroxide (*t*-BuOOBu-*t*) in the presence of C_{70} also yields an ESR spectrum due to a few isomeric $t\text{-}BuO\text{-}C_{70}^\bullet$ adducts, but the large number of overlapping lines prevented a reliable spectral analysis to be achieved. This is because each regioisomer is expected to exhibit a 10-line multiplet spectrum, owing to the coupling of the unpaired electron with the nine equivalent hydrogens of the three methyl groups.[1] Recently, however, we found[6] that photolysis of dimethoxy disulfide (MeOSSOMe) generates the $MeO^\bullet$ radical which adds to the sphere of fullerene C_{60} yielding the $MeO\text{-}C_{60}^\bullet$ adduct. The corresponding ESR spectrum appears as a single line since the a_H splitting, due to the three hydrogens of the methoxy group, is too small to be resolved.[7] It is thus conceivable to expect that each regioisomer of the $MeO\text{-}C_{70}^\bullet$ radical adducts would also exhibit a single line ESR spectrum. Indeed photolysis of MeOSSOMe in the presence of C_{70} affords a spectrum (Figure 2) displaying five lines of different intensity. Variation of the temperature of the experiment in the range 25−80 °C causes the relative proportions of these signals to change in a noticeable manner. This proves that none of the observed lines belongs to a manifold spectrum, since the quartet splitting due to the coupling with the three methoxy hydrogens should always display a 1:3:3:1 intensity ratio. As a consequence each line must correspond, as predicted, to the whole spectrum of a single regioisomer (Table 1). Furthermore, in order to obtain an acceptable computer simulation (reported underneath in Figure 2) it was necessary to use a different line width for each of the five signals (range 75−125 mG), a feature indicating that there are unresolved fine structures due to the coupling of the unpaired

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[1] Cremonini, M. A.; Lunazzi, L.; Placucci, G.; Krusic, P. J. *J. Org.Chem.* **1993**, *58*, 4735.

[2] Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Chem. Soc., Chem. Commun.* **1992**, 1259.

[3] Morton, J. R.; Negri, F.; Preston, K. F. *Chem. Phys. Lett.* **1994**, *218*, 467.

[4] Borghi, R.; Lunazzi, L.; Placucci, G.; Krusic, P. J.; Dixon, D. P.; Knight, L. B., Jr. *J. Chem. Phys.* **1994**, *98*, 5295.

[5] Recently we succeeded in carrying out a particular experiment which revealed five ESR spectra for the five adducts expected for the addition of the radical $CF_3^\bullet$ to C_{70}. See: Borghi, R.; Lunazzi, L.; Placucci, G.; Krusic, P. J.; Dixon, D. A.; Matsuzawa, N; Ata, M. *J. Am. Chem. Soc.* **1996**, in press.

[6] Borghi, R.; Lunazzi, L.; Placucci, G.; Cerioni, G.; Plumitallo, A. *J. Org.Chem.* **1996**, *61*, 3327.

[7] We proved[6] that the splittings due to the hydrogens bonded to carbons in the α-position to the oxygen atom is always negligible in the $RO\text{-}C_{60}^\bullet$ radical adducts, contrary to the case of the corresponding splittings in the $RS\text{-}C_{60}^\bullet$ analogs.[1,6] On the other hand the splitting due to the hydrogens bonded to the *β*-carbons of the $RO\text{-}C_{60}^\bullet$ adducts is relatively large,[1,6] thus explaining the complex spectral appearance of the $t\text{-}BuO\text{-}C_{70}^\bullet$ ESR spectrum.

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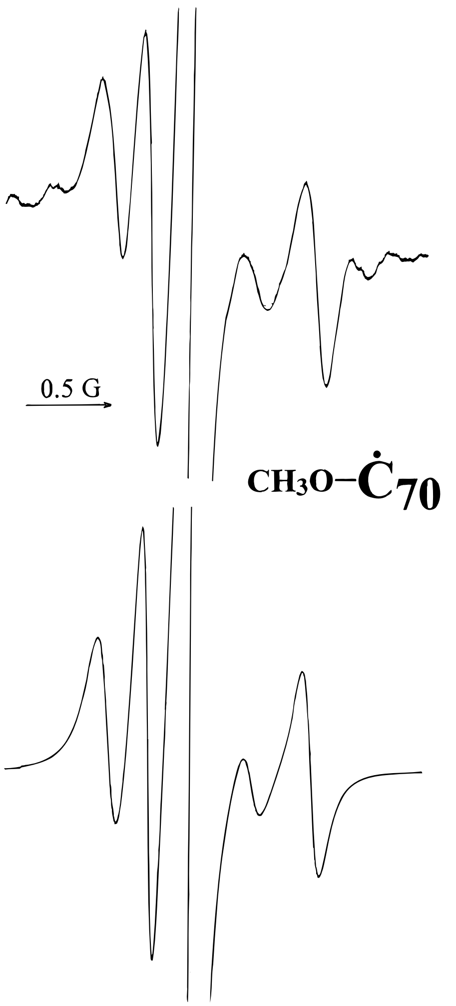

Figure 2. Experimental (top) and computer-simulated (bottom) ESR spectra of the five regioisomers due to the addition of the MeO$^•$ radical to C_{70} (the most intense, central line has been recorded off scale for convenience). The temperature of the experiment is +70 °C, and the line width of the computed traces varies in the range of 75−125 mG (see text).

electron with the hydrogens of the MeO moiety which, as expected, is not precisely the same for all five regioisomers. The existence of such hidden fine structures is thus revealed by the different line widths. In the case of the MeS-$C_{70}^•$ adducts (where the fine structures could be resolved) the a_H values turned out, in fact, to be slightly different (Table 1) in each of the three regioisomers, and contrary to the case of MeO-$C_{70}^•$, each MeS-$C_{70}^•$ spectrum exhibits, as a consequence, the same line width (85 mG).

The MeO-$C_{70}^•$ radical adducts thus represent an unusual example where all the five expected regioisomers can be detected by ESR spectroscopy.[8] It is worth outlining that the relative amount of one such adduct is indeed very small (about 5%); this might explain how radicals less reactive than MeO$^•$ toward C_{70} failed to produce a detectable amount of the fifth regioisomer. A picture showing the structures of the regioisomers due to the addition of MeO$^•$ into positions A−E of C_{70} is displayed in Figure 3.

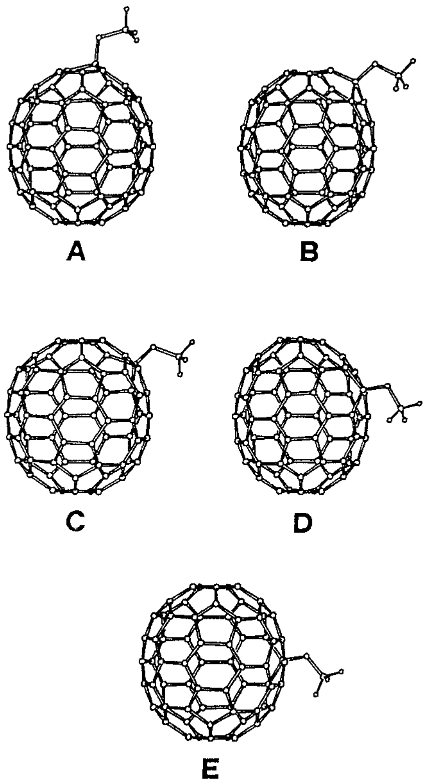

Figure 3. Pictures of the five regioisomers of MeO-$C_{70}^•$, displaying the sites of addition of the MeO substituent into positions A, B, C, D, and E of the ellipsoid of C_{70}.

The assignment of the structures of Figure 3 to the observed ESR signals is however a quite difficult task, even for the MeO-$C_{70}^•$ adducts where all the five possible species are available. In the case of carbon-centered radicals (R$^•$) we had suggested a possible criterion, on the basis of symmetry, persistence, and spin density distribution, by which the assignment of the R-$C_{70}^•$ isomers could be attempted.[4,5] When dealing with carbon-centered radicals R$^•$ adding to C_{70} we found that the *g* factors of the R-$C_{70}^•$ adducts essentially depend on the position of the substituent R upon the ellipsoid rather than on the nature of the substituent itself. Thus the *g* factors of these R-$C_{70}^•$ isomers increase according to sequence B, D, C, E, A, with the *g* factors of E and A being almost coincident in the unique case (i.e. CF_3-$C_{70}^•$) where isomer E could be detected.[5] The *g* factor of the corresponding R-$C_{60}^•$ radical adducts (R being always a carbon-centered substituent) lies in between those of the isomers of type B and D, although closer to that of B. The reason for such a near coincidence is that the spin density distribution of the latter is much closer to that of R-$C_{60}^•$ than the spin density distribution of any other R-$C_{70}^•$ isomer.[5]

Unfortunately such a criterion does not apply to the present case since the *g* factor of MeO-$C_{60}^•$ (2.00233), although almost equal to those of the various R-$C_{60}^•$ adducts having R as a carbon-centered group,[4] is *higher* than the *g* factors of all the MeO-$C_{70}^•$ regioisomers, except one. Similarly the MeS-$C_{60}^•$ radical has a *g* factor higher than those of the three observed MeS-$C_{70}^•$ adducts (Table 1). On the contrary the *g* values of the various R-$C_{60}^•$ adducts (due to carbon-centered R$^•$ radicals adding to C_{60}) were found *lower* than those of the corresponding R-$C_{70}^•$ regioisomers, except one.[4,5] Such a difference in the trend of the *g* factors had been also observed when another non

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[8] Five regioisomers have been observed by transverse field muon spin rotation in the case of the muonium atoms (Mu ≡ μ^+e^-) adding to solid C_{70}. See: Lappas, A.; Vavekis, K.; Prassides, K. *J. Chem. Soc., Chem. Commun.* **1994**, 2743.

carbon-centered radical (i.e. the fluorine atom) was added to C_{70}.[9] The *g* factor of F-$C_{60}^{\bullet}$ is, in fact, higher than those of the four observed regioisomers of F-$C_{70}^{\bullet}$.[9] This indicates that *there is a not* a parallel behavior between the trend of *g* factors for carbon-centered and that for heteroatom-centered substituents R in the R-$C_{70}^{\bullet}$ radicals. Thus we do not have a reliable method to assign the three regioisomers of MeS-$C_{70}^{\bullet}$ nor the five regioisomers of MeO-$C_{70}^{\bullet}$. We can only propose an incomplete and approximate hypothesis for the assignement in the latter case, since in MeO-$C_{70}^{\bullet}$, at least, none of the possible isomers is missing. Most likely the less intense signal (5%, $g = 2.00193$) should correspond to the structure E (Figure 3) since the latter adduct is known to be, by far, the less stable species on theoretical ground.[2,3,9] For this reason it has not been observed before by ESR spectroscopy, with the notable exception of the mentioned addition of $CF_3^{\bullet}$ to C_{70} (which however required a particular experiment to be observed).[5] The most intense signal (50%, $g = 2.00216$) is likely to correspond to the structure D of Figure 3 since in all the reported cases this appeared to be the most prominent isomer, its assignment having been confidently obtained by a combination of symmetry properties and computed spin density distribution.[4] Finally it might be conceivable to suggest that the signal with a *g* factor (2.00231) almost coincident with that of MeO-$C_{60}^{\bullet}$ (2.00233) has some chance to be identified with the isomer B, because of the mentioned similarity between the corresponding spin density distributions. It is worth stressing that in the case of H-$C_{70}^{\bullet}$ the structure assigned [3,4,9] to the isomer B appears to have a *g* factor (2.00213) as close to that of H-$C_{60}^{\bullet}$ (2.00216) as observed here for the corresponding pair of MeO adducts.

Which of the two remaining signals corresponds to the structure A and which to the structure C of Figure 3 cannot be proposed, for the time being, on any reasonable ground.

Experimental Section

The samples were prepared by adding to a saturate solution of C_{70} an excess (molar ratio about 5−10:1) either of MeSSMe or of MeOSSOMe.[10] The solvent was *tert*-butylbenzene in the case of MeSSMe and benzene in the case of MeOSSOMe. The best spectra of MeS-$C_{70}^{\bullet}$ were obtained at low temperature (about −20 °C) and those of MeO-$C_{70}^{\bullet}$ at high temperature (about +70 °C). The samples, degassed and sealed *in vacuo* in suprasil quartz tubes, were photolyzed in the cavity of an ESR spectrometer by means of a high-pressure Hg lamp. Accurate measurements of the *g* factors for MeX-$C_{60}^{\bullet}$ (X = O, S) were obtained by using, as a reference, the simultaneously observed sharp line of the excited triplet state of C_{60} ($g = 2.00135$).[11] Addition of a controlled amount of C_{60} to the C_{70} solutions allowed us to observe the RX-$C_{60}^{\bullet}$ spectrum together with that of the most intense of the corresponding RX-$C_{70}^{\bullet}$ signals and, accordingly, to determine the *g* factor of the latter, hence also those of the remaining regioisomers. Such a calibration was accurate enough as to unambiguously estimate the difference between the two similar *g* factors of MeO-$C_{60}^{\bullet}$ (2.00233) and of the MeO-$C_{70}^{\bullet}$ isomer having a 18% relative proportion (2.00231).

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