

Photolysis of Dialkoxy Disulfides: A Convenient Source of Alkoxy Radicals for Addition to the Sphere of Fullerene C₆₀

R. Borghi,¹ L. Lunazzi,* and G. Placucci*

Dipartimento di Chimica Organica "A. Mangini", Università, Risorgimento, 4, Bologna 40136, Italy

G. Cerioni

Dipartimento di Scienze Chimiche, Università, via Ospedale, 72, Cagliari, Italy

A. Plumitallo

Dipartimento Farmaco Chimico Tecnologico, Università, via Ospedale, 72, Cagliari, Italy

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Photolysis of dialkoxy disulfides ROSSOR (R = Me, Et, *i*-Pr, *t*-Bu, *i*-PrCH₂, *t*-BuCH₂) yields the radicals RO•, ROS•, and ROS(O)• that were identified on the basis of product analysis and spin trapping techniques. It has been shown that only the alkoxy radicals RO•, produced from ROSSOR, add to the sphere of fullerene C₆₀ in steady state conditions to yield the RO-C₆₀• adducts which can be detected by ESR spectroscopy. The different trend of the hydrogen splitting constants in the RO-C₆₀• with respect to the corresponding RS-C₆₀• adducts previously reported has been interpreted as a consequence of the different C–O and C–S bond lengths.

It has been recently reported² that alkoxy radicals (RO•), photolytically generated from their peroxides (ROOR), add to the sphere of fullerene C₆₀ yielding the RO-C₆₀• radical adducts which can be detected by ESR spectroscopy. However, the very simple peroxides (R = Me, Et, *i*-Pr...) are dangerous to make and to handle (e.g., MeOOME is a gas³ requiring special apparatus to be conveniently employed) and are thus not well suited for use as reactants for this purpose. Indeed, only three RO-C₆₀• radical adducts (i.e., those with R = *t*-Bu, PhCMe₂, and CF₃) could so far be detected with such a method, contrary to the case of the analogous RS-C₆₀• adducts which can be conveniently obtained for any type of substituent R by means of the photolysis of the corresponding disulfides RSSR.² Because of these limitations the characteristic properties of the alkoxyfulleryl radical adducts could not be thoroughly investigated nor meaningfully compared to those of the corresponding (alkylthio)fulleryl analogs.

It occurred to us that a more convenient photolytic source of alkoxy radicals for addition to fullerene might possibly be dialkoxy disulfides ROSSOR. These compounds are either liquids or solids and can be easily (and safely) prepared⁴ with any kind of R group by reacting the appropriate alcohols with ClSSCl.

Of course, photolysis of dialkoxy disulfides might not yield, as we had anticipated, the desired alkoxy radicals, or even if produced, they might be accompanied by a number of other unwanted radicals which would make the spectral appearance much more complex, thus making the investigation either extremely difficult or impossible. As a consequence, it was important to identify all the radicals produced by photolysis of the ROSSOR derivatives.

In addition to product analysis (see the following text) a convenient approach for this purpose is the spin trapping technique⁵ which allows the identification of the radicals produced in a reaction by means of the ESR spectra of the corresponding stable nitroxides.

Accordingly, photolysis of various ROSSOR derivatives (R = Me, Et, *i*-Pr, *t*-Bu, *i*-PrCH₂, *t*-BuCH₂) was performed in the presence of 2-methyl-2-nitrosopropane (*t*-Bu-NO) so that the ESR spectra of the corresponding nitroxides *t*-BuN(O)X could be observed, X being the group derived from the fragmentation of the photolyzed compounds.

By far the most intense ESR signals observed, in all cases, between –20 and +80 °C, were those of a nitroxide (see Figure 1 for the case of MeOSSOMe) having a 1:1:1 nitrogen splitting of 12.4 G without any further fine structure and a *g*-factor equal to 2.0061₅ ± 1.5 × 10^{–4} (Table 1). Clearly, these data indicate that X• radicals different from the desired alkoxy radicals have been trapped. For, alkoxy nitroxide of the type *t*-BuN(O)OR (i.e., those expected from the trapping of RO•) are known⁶ to have much larger *a*_N splittings (their range being 27–30 G) and to display, quite often, an additional fine structure due to the hydrogens of the R group. We identified these intense signals as those of nitroxides *t*-BuN(O)S(O)R, due to the trapping of ROS(O)•. The latter radical can be thought as derived by the cleavage of the ROSSOR bond, yielding the ROS• radical which subsequently undergoes an oxidation.⁷ An analogous oxidation process had been observed, albeit in a different environment, when disulfides RSSR are photolyzed to

(5) (a) Janzen, E. G. *Acc. Chem. Res.* **1971**, 4, 31. (b) Perkins, M. J. In *Advances in Physical Organic Chemistry*; Gold, V., Bethelle, D., Eds.; Academic Press: London, 1980; Vol. 17, p 1. (c) Cowley, D. J.; Nonehebel, D. C. In *Organic Reaction Mechanism 1979*; Knipe, A. C., Watts, W. E., Eds.; John Wiley and Sons: London, 1981; Chapter 3, p 75.

(6) Forrester, A. R. In *Landolt Börnstein Magnetic Properties of Free Radicals*; Fischer, H., Hellewege, K.-H., Eds.; Springer Verlag: Berlin, 1979; Vol. 9, Part C1, Chapter 6.31, p 914.

(7) Of course, the result would be the same if oxidation had occurred first, yielding ROS(O)SOR, which might have subsequently produced ROS(O)• by cleavage of the S–S(O) bond. However the absence of EtOS(O)SOEt amongst the reaction products of photolysis of EtOSSOEt makes this hypothesis less plausible.

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(1) In partial fulfillment of the requirements for the Ph.D. Thesis in Chemical Sciences, University of Bologna.

(2) Cremonini, M. A.; Lunazzi, L.; Placucci, G.; Krusic, P. J. *J. Org. Chem.* **1993**, 58, 4735.

(3) Rieche, A. *Ber.* **1928**, 61, 951.

(4) (a) Lengfeld, F. *Ber.* **1895**, 28, 449. (b) Thompson, Q. E.; Crutchfield, M. M.; Pieron, E. *J. Org. Chem.* **1965**, 30, 2692.

Table 1. Hyperfine Splittings (Gauss) of the Various Nitroxides Obtained by Trapping the Radicals Generated from the Photolysis of ROSSOR with *t*-BuNO

R	ROS(O)N(O [•])Bu- <i>t</i> ^a	RON(O [•])Bu- <i>t</i> ^b		ROS(O)N(O [•])Bu- <i>t</i> ^c
	<i>a</i> _N	<i>a</i> _N	<i>a</i> _H	<i>a</i> _N
Me	12.4	29.6	1.5 (3H)	15.5
Et	12.1	29.0	1.0 (2H)	18.4
<i>i</i> -Pr	12.4	28.6		
<i>t</i> -Bu	12.4	27.0		
<i>i</i> -PrCH ₂	12.5	29.2	1.25 (2H)	
<i>t</i> -BuCH ₂	12.5	26.8	1.6 (2H)	18.6

^a *g*-factors = $2.00615 \pm 1.5 \times 10^{-4}$. ^b *g*-factors = $2.0055 \pm 1 \times 10^{-4}$. ^c *g*-factors = $2.0070 \pm 1.5 \times 10^{-4}$.

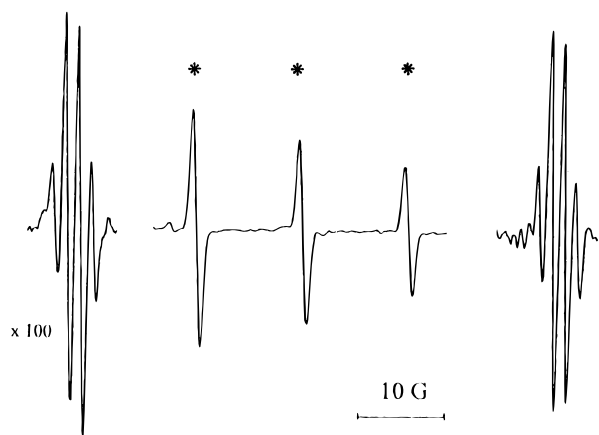


Figure 1. ESR spectrum (central star-shaped triplet) of the nitroxide MeOS(O)N(O[•])Bu-*t* obtained by photolysis of MeOSSOMe in the presence of *t*-BuNO at -20°C . At the edges appear the wings (N-spin quantum number +1 and -1) of the spectrum (vertically amplified 100 times) of the nitroxide MeON(O[•])Bu-*t*, due to the trapping of the MeO[•] radical as revealed by the additional 1:3:3:1 hydrogen fine structure.

yield the RS(O)[•] radicals.⁸ The reason we feel that the trapping of the initially formed ROS[•] radical does not occur in these conditions, but it is the oxidated species ROS(O)[•] which is trapped to yield the most intense ESR signal, is based on the following experiment. Photolysis (and thermolysis as well) of diethyl sulfite EtOS(O)OEt, in the presence of *t*-BuNO, does yield a nitroxide spectrum equal to the more intense triplet (*a*_N = 12.1 G) obtained from photolysis of EtOSSOEt. Since it is expected that cleavage of either of the two EtO-S bonds of EtOS(O)OEt would generate the EtOS(O)[•] radical, the identity of the most intense signals derived from EtOS(O)OEt and EtOSSOEt strongly supports the proposed assignment.⁹

As shown in Figure 1, in addition to the intense (starred) spectrum [here assigned to *t*-BuN(O[•])S(O)OMe], a second spectrum is also observed, in a smaller proportion (about 1:20). This second spectrum comprises a 1:1:1 triplet (*a*_N = 29.6 G) further split into a 1:3:3:1 quartet (*a*_{3H} = 1.5 G). Owing to the similarity of the *g*-factors of the two spectra, the central signal of the weaker spectrum is obscured under the central line of the more intense one. The *a*_N and *a*_H splittings, as well as the

g-factor (Table 1) of this second spectrum, are typical of an alkoxyalkyl nitroxide [in this example *t*-BuN(O[•])OMe], produced by the trapping of the RO[•] radicals. This interpretation is fully confirmed by the additional fine structure observed for the analogous nitroxides obtained by photolysis of ROSSOR having R = Et, *i*-PrCH₂, and *t*-BuCH₂, i.e., a 1:2:1 triplet due to the coupling with the hydrogens of the CH₂ moieties (Table 1). These features agree with those reported for the same nitroxides produced in a matrix by γ -radiolysis of the corresponding alcohols.⁶ Also, the absence of a doublet, due to the CH hydrogen, might have been expected for the case of *i*-PrON(O[•])Bu-*t* (derived from photolysis of *i*-PrOSSOPr-*t*), is confirmed by the literature report⁶ (this splitting is in fact too small to be resolved, owing to an unfavorable conformational disposition). Finally, the nitroxide obtained by trapping the *t*-BuO[•] radical derived from *t*-BuOSSOEt does not exhibit, as expected,⁶ any further fine structure (Table 1) in that the H-atoms are too far away from the radical center.

Quite similar results, both with regard to the relative proportion of the two nitroxide signals and to the values of the spectral parameters, were obtained when an analogous spin trap, such as 2,3,5,6-tetramethylnitrosobenzene, was used under the same conditions (the only drawback being a lower resolution due to broader line widths).

Analysis (GC-MS) of the products derived from the photolysis of EtOSSOEt (in benzene as solvent) showed, in addition to a certain amount of elemental sulfur (S₈), the presence of only two products, namely the diethyl sulfite EtOS(O)OEt and diethyl sulfoxylate EtOSOEt, approximately in a 2:1 relative proportion. These products were identified by comparing their mass spectra with those of two authentic samples. Whereas in this comparison isolated EtOS(O)OEt was employed, the diethyl sulfoxylate EtOSOEt was obtained *in situ* by reacting EtOSSOEt with EtONa, according to the literature.¹⁰ The GC-MS of the products of the latter reaction showed how the fragmentation pattern of EtOSOEt (*M*⁺ = 122) was identical (as was the corresponding retention time) to that of the compound (also having *M*⁺ = 122) we had observed in the photolysis of EtOSSOEt.

The two mentioned products resulting from the photolysis of EtOSSOEt are conceivably accounted for by the coupling of the radical EtO[•] (unambiguously identified by the spin trapping experiment) with the radicals EtOS(O)[•] and EtOS[•], respectively. Such a product analysis, therefore, makes even more plausible the structural assignment of the nitroxides responsible for the most intense ESR spectra, i.e., ROS(O)N(O[•])Bu-*t*.

It is also worth mentioning that when the spin trapping is carried out at very low temperature (i.e., below -100°C in cyclopropane as solvent) the spectra of the two nitroxides we had observed at higher temperature become much less intense, and very weak signals, due to a third, quite labile nitroxide, are visible. The latter spectra comprise 1:1:1 triplets (*a*_N = 15.5–18.6 G, depending on the substituent R) with *g*-factors = $2.0070 \pm 1.5 \times 10^{-4}$ (Table 1). It is not unreasonable to suggest that at such a low temperature the ROS[•] radical, initially formed by cleavage of the S-S bond, is more persistent, owing to a slower oxidation rate. Consequently, it might survive long enough to be trapped by *t*-BuNO, yielding

(8) (a) Kawamura, T.; Krusic, P. J.; Kochi, J. K. *Tetrahedron Lett.* **1972**, 4075. (b) Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C.; Laue, H. A. H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 497.

(9) Further proof of this interpretation is offered by the observation that photolysis of diethyl sulfite EtOS(O)OEt yields, simultaneously, a second spectrum due to the trapping of the EtO[•] radical, which is the other fragment produced by the cleavage of the EtO-S bond. The ESR parameters of this second spectrum correspond, ⁶ in fact, to those of the *t*-BuN(O[•])OEt radical reported in Table 1.

(10) (a) Meuwesen, A.; Gebhardt, H. *Ber.* **1936**, 69, 937. (b) Thompson, Q. E. *J. Org. Chem.* **1965**, 30, 2703.

the spectrum of $\text{ROSN}(\text{O}^{\bullet})\text{Bu-}t$ which is sufficiently long living, at such low temperatures, to be detected. Although independent spectra of such nitroxides are not available for comparison, the absence of additional proton fine structure and the values of the a_{N} splittings and g -factors (Table 1) appear to be reasonable for the proposed structure. For instance, nitroxides such as $\text{RSN}(\text{O}^{\bullet})\text{Bu-}t$ have¹¹ $a_{\text{N}} = 18.9$ G with $g = 2.0064$ when $\text{R} = \text{Me}$, $a_{\text{N}} = 17.4$ G with $g = 2.0063$ when $\text{R} = \text{Et}$, and $a_{\text{N}} = 17.0$ G with $g = 2.0069$ when $\text{R} = i\text{-Pr}$. In addition, this interpretation is in keeping with the presence of EtOSOEt as one of the two reaction products derived from photolysis of EtOSSOEt .

The larger intensity of the spectra of the $\text{ROS}(\text{O})\text{N}(\text{O}^{\bullet})\text{Bu-}t$ nitroxides with respect to those of nitroxides due to the trapping of the EtO^{\bullet} and EtOS^{\bullet} radicals is somehow at variance with the much smaller ratio observed for the reaction products $\text{EtOS}(\text{O})\text{OEt}$ and EtOSOEt (2:1, as mentioned above). Such a large excess of the $\text{ROS}(\text{O})^{\bullet}$ radicals in the spin trapping experiment seems to be the consequence of a favorable oxidizing environment, which might be provided by the $t\text{-BuNO}$ itself.

Thus, it seems likely to expect that in the absence of such a spin trap the amount of the $\text{ROS}(\text{O})^{\bullet}$ radicals might be much lower. Furthermore, with many substrates other than $t\text{-BuNO}$, the reaction rate for addition of RO^{\bullet} might be faster than that of the bulkier $\text{ROS}(\text{O})^{\bullet}$ radicals. If these conditions were actually verified, photolysis of ROSSOR would then become a convenient source of RO^{\bullet} radicals.

This prediction was, apparently, confirmed by experiments we carried out with a quite different spin trap, i.e., 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO).¹² Thermolysis (50–70 °C) of ROSSOR ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, i\text{-PrCH}_2$) in the presence of DMPO yielded ESR spectra whose most intense signals correspond to nitroxide spectra (all having $g = 2.0061$) with hyperfine splittings (the values cover the ranges $a_{\text{N}} = 12.8\text{--}13.0$ G, $a_{\text{1H}} = 6.5\text{--}7.0$ G, and $a_{\text{1H}} = 2.0$ G) very close to those reported¹² for nitroxides produced by DMPO trapping RO^{\bullet} radicals generated by reaction of lead tetraacetate with various alcohols. Also, room temperature photolysis of $t\text{-BuOSSOBu-}t$ in the presence of DMPO yields the spectrum of a nitroxide ($g = 2.0061$) with splittings ($a_{\text{N}} = 13.1$ G, $a_{\text{1H}} = 8.0$ G, and $a_{\text{1H}} = 2.0$ G) which are indistinguishable from those we obtained, in the same experimental conditions, when using $t\text{-BuOOBu-}t$ as a source of $t\text{-BuO}^{\bullet}$ radicals.

We therefore took advantage of this behavior by photolyzing $t\text{-BuOSSOBu-}t$ in the presence of fullerene C_{60} to obtain the ESR spectrum of a *single* radical adduct which was *identical* to the one observed¹³ when reacting $t\text{-BuOOBu-}t$ under the same conditions with C_{60} . There is, therefore, no doubt that photolysis of dialkoxy disulfides can be employed to add RO^{\bullet} radicals to one of the 30 double bonds of fullerene C_{60} , without their ESR spectra being interfered by the presence of other visible radical adducts.

In Figure 2 the ESR spectra of a few $\text{RO-C}_{60}^{\bullet}$ radical adducts ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, \text{and } t\text{-Bu}$), produced by using the appropriate ROSSOR dialkoxy disulfides, are dis-

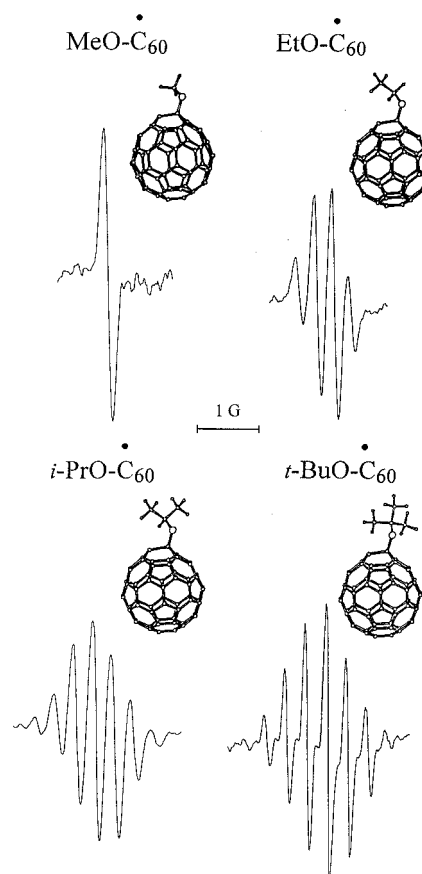


Figure 2. ESR spectra of the radical adducts $\text{RO-C}_{60}^{\bullet}$ ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, \text{and } t\text{-Bu}$) obtained by photolysis of the corresponding ROSSOR derivatives in the presence of fullerene C_{60} (in the case of $\text{R} = t\text{-Bu}$ the first and the 10th line have a signal to noise ratio too low to be detected).

played, the corresponding spectral parameters being collected in Table 2.

At first glance the spectral multiplicity of these spectra appears quite surprising in that there is no splitting due to the hydrogens bonded to the carbons in the α -position to the oxygen atom. On the contrary, noticeable splittings are observed for the more distant hydrogens bonded to carbons in the β -position. Indeed, the spectrum of $\text{MeO-C}_{60}^{\bullet}$ displays a single line (owing to the absence of splittings due to the three methyl hydrogens) whereas the hydrogens of the methyl groups in the β -position to oxygen yield a four-line, a seven-line, and a 10-line multiplet in the case, respectively, of $\text{EtO-C}_{60}^{\bullet}$, $i\text{-PrO-C}_{60}^{\bullet}$, and $t\text{-BuO-C}_{60}^{\bullet}$ (the appropriate binomial intensity distribution is slightly distorted by a small CIDEP effect¹⁴ which makes the upfield lines appear somewhat taller than the corresponding downfield lines). Accordingly, the spectrum of $\text{Me}_2\text{CHCH}_2\text{OC}_{60}^{\bullet}$ displays a doublet due to the methine hydrogen (Table 2), without any fine structure from the methylene hydrogens (a small additional splitting was also observed for the six hydrogens of the two methyl groups). For the same reason photolysis of $\text{PhCH}_2\text{OSSOCH}_2\text{Ph}$ yields a single line spectrum due to the $\text{PhCH}_2\text{O-C}_{60}^{\bullet}$ adduct which, not having any hydrogen bonded to the carbon in the β -position to the oxygen atom, does not display any fine structure (photolysis at higher temperature also yields, superimposed to the single line

(11) See ref 6, Chapter 6.35, p 986.

(12) Janzen, E. G.; Liu, J. E. P. *J. Magn. Reson.* **1973**, *9*, 510.

(13) In both cases photolysis was carried out at low temperature (+10 °C) to make negligible the amount of the $\text{MeC}_{60}^{\bullet}$ adduct due to the addition of the methyl radical² deriving from the β -scission of $t\text{-BuO}^{\bullet}$.

(14) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Knight, L. B., Jr. *Chem. Phys. Lett.* **1993**, *204*, 481.

Table 2. Hyperfine Splittings (Gauss) of the Radical Adducts $RX-C_{60}^{\bullet}$ (X = O, S)^a

R	X = O ^b			X = S ^c		
	a(CH ₃)	a(CH ₂)	a(CH)	a(CH ₃)	a(CH ₂)	a(CH)
Me	3H _δ ≈ 0			3H _δ = 0.38		
Et	3H _ε = 0.37	2H _δ ≈ 0		3H _ε = 0.29	2H _δ = 0.31	
<i>i</i> -Pr	6H _ε = 0.27 ₅		1H _δ ≈ 0	6H _ε = 0.21		1H _δ = 0.22
<i>t</i> -Bu	9H _ε = 0.35			9H _ε = 0.25		
<i>i</i> -PrCH ₂	6H _ε = 0.15	2H _δ ≈ 0	1H _ε = 0.47 ₅	6H _ε = 0	2H _δ = 0.40	1H _ε = 0.21

^a The values for X = S are from ref 2. ^b The *g*-factors are in the range 2.002 30–2.002 35. ^c The *g*-factors are in the range 2.002 34–2.002 40.

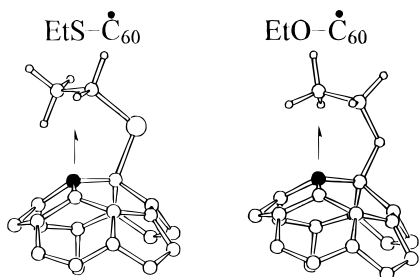


Figure 3. Representation of the top portion of the computed structure of the radical adducts EtS- C_{60}^{\bullet} (left) and EtO- C_{60}^{\bullet} (right), showing how both the CH₃ and CH₂ groups are in a position allowing the interaction with the spin of the unpaired electron in the former case, whereas only the CH₃ group can experience such an interaction in the latter case (the MM calculations¹⁸ were carried out for the whole sphere, although only the part of interest is reported for convenience).

spectrum, a second spectrum with the same splittings reported¹⁵ for the PhCH₂- C_{60}^{\bullet} adduct: the benzyl radical is obviously a byproduct of the high-temperature photolysis of PhCH₂OSSOCH₂Ph.¹⁶

To comply with the usual labeling of radicals, where the atomic positions are counted with respect to the radical center indicated as α, the hydrogens bonded to the carbon directly attached to the oxygen atom will be called δ in Table 2, those one carbon further away ε, and so on.²

Whereas we have seen how the H_δ splittings of the RO- C_{60}^{\bullet} radical adducts are too small to be resolved, those of the corresponding RS- C_{60}^{\bullet} were found to be equal to or larger than their H_ε splittings.² Also, the H_ε splittings of all the RO- C_{60}^{\bullet} radical adducts we made available with these experiments (Table 2) are definitely larger than those of the corresponding RS- C_{60}^{\bullet} analogs.²

A possible explanation for this behavior can be found in the different geometry engendered by the longer C–S with respect to the C–O bonds. As shown in the molecular mechanics calculated¹⁸ structures displayed, as an example, in Figure 3 for the EtX- C_{60}^{\bullet} radical adducts (X = O, S), the CH₃ and CH₂ moieties occupy a position, when X = S, where both groups can similarly overlap with the p_z orbital bearing the unpaired electron

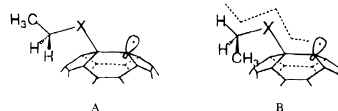
(Figure 3, left).¹⁹ Since in these systems the spin density experienced by the H-atoms should mainly originate from a direct overlap of the 1s H-orbital with the mentioned carbon p_z-orbital, the geometry accounts for the appreciable values of both the H_δ and H_ε splittings observed in EtS- C_{60}^{\bullet} and in the analogous alkylthio adducts. On the contrary, when X = O, the shorter lengths of the pair of the C–O bonds pull the δ-hydrogens of the CH₂ group away from the p_z-orbital (Figure 3, right), thus reducing the extent of the overlap and, hence, the a_H values of the δ-hydrogens which eventually become too small to be detected. At the same time, the ε-hydrogens of the CH₃ group are placed in a position allowing an even better overlap with the p_z-orbital, thus explaining the larger a_H splittings observed for H_ε in the RO- C_{60}^{\bullet} with respect to the RS- C_{60}^{\bullet} radical adducts. Analogous geometrical considerations, based on this model, also account for the negligible splitting (0.15 G) of the methyl hydrogens in the ζ-position in *i*-PrCH₂O- C_{60}^{\bullet} to be compared with the corresponding null value² in *i*-PrCH₂S- C_{60}^{\bullet} (Table 2).²⁰

Experimental Section

Material. (EtO)₂SO, *t*-BuOOBu-*t*, *t*-BuNO, ArNO (Ar = 2,3,5,6-tetramethylphenyl), and DMPO are commercially available. The dialkoxo disulfides ROSSOR were prepared according to the general method described in ref 4b. Derivatives with

(19) Although the unpaired electron density is, in part, also delocalized upon other carbons of the sphere, all the calculations (carried out for the H- C_{60}^{\bullet} radical) agree in indicating that the density upon the carbon marked as black in Figure 3 is the largest one. See, for instance: Matsuzawa, N.; Dixon, D. A.; Krusic, P. J. *J. Phys. Chem.* **1992**, *96*, 8317. Percival, P. W.; Wlodeck, S. *Chem. Phys. Lett.* **1993**, *207*, 31. Morton, J. R.; Negri, F.; Preston, K. F. *Can. J. Chem.* **1994**, *72*, 776. Reid, I. D.; Roduner, E. *Hyperfine Interact.* **1994**, *86*, 809. Borghi, R.; Lunazzi, L.; Placucci, G.; Krusic, P. J.; Dixon, D. A.; Matsuzawa, N.; Ala, M. Submitted for publication.

(20) An alternative explanation, for which we are indebted to an anonymous reviewer, might be based on the assumption that conformations having the RX group (X = O, S) pointing away from the direction of the p_z orbital (as shown below for EtXC₆₀[•]) are also significantly populated:



Within this framework one might further assume that conformation A should be preferred when X = O, whereas conformation B should be preferred when X = S in that the longer C–S bond lengths would allow the methyl group not to “bump” against the C₆₀ surface. The possibility of a through-bond transmission of the hyperfine interactions when “zig-zag” (or W) pathways²¹ are available would thus make the CH₂ splitting larger for X = S (structure B) than for X = O (structure A). The same assumptions would predict an opposite trend for the splitting of the CH₃ group, which lies along a “zig-zag” path when X = O (structure A), but not when X = S (structure B). This explanation, however, does not exclude the one we proposed, and both might occur simultaneously.

(21) (a) Krusic, P. J.; Rettig, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 722. (b) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Angria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. (c) Chatgililoglu, C.; Lunazzi, L.; Macciantelli, D.; Placucci, G. *J. Am. Chem. Soc.* **1984**, *106*, 5252.

(15) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Wasserman, E. J. *Chem. Soc., Perkin Trans. 2* **1992**, 1425.

(16) In ref 15 the splitting due to the pair of aromatic protons of the PhCH₂- C_{60}^{\bullet} adduct was not assigned. By repeating the experiment using 3,5-dimethylbenzyl bromide as a source of ArCH₂[•] radicals (Ar = 3,5-dimethylphenyl), we did not observe any change with respect to the spectral patterns of the PhCH₂- C_{60}^{\bullet} adduct. As a consequence, the mentioned splitting must originate from the pair of ortho protons, contrary to what was observed¹⁷ in the Ph- C_{60}^{\bullet} adduct, where the aromatic splitting originates from the meta protons.

(17) Borghi, B.; Lunazzi, L.; Placucci, G.; Krusic, P. J.; Dixon, D. A.; Knight, L. B., Jr. *J. Phys. Chem.* **1994**, *98*, 5395.

(18) MMX forcefield as in PCMODEL, Serena Software, Bloomington, IN.

R = Me, Et, and *i*-Pr had been previously reported.⁴ The dialkoxy disulfides employed in the present investigation were identified as follow.

Dimethoxy Disulfide, MeOSSOMe. ¹H NMR (CDCl₃) δ: 3.66 (s). ¹³C NMR (CDCl₃) δ: 61.54 (CH₃). IR: ν 975, 675, 650.

Diethoxy Disulfide, EtOSSOEt. ¹H NMR (CDCl₃) δ: 1.21 (m, 6H), 3.78 (m, 2H), 3.90 (m, 2H). ¹³C NMR (CDCl₃) δ: 15.48 (CH₃), 70.89 (CH₂). IR: ν 1000, 870, 695, 650.

Diisopropoxy Disulfide, *i*-PrOSSOPr-*i*. ¹H NMR (CDCl₃) δ: 1.30 (d, 6H), 1.45 (d, 6H), 4.12 (m, 2H). ¹³C NMR (CDCl₃) δ: 22.19 (CH₃), 22.84 (CH₃), 78.25 (CH). IR: ν 1100, 905, 825, 700.

Di-*tert*-butoxy Disulfide, *t*-BuOSSOBu-*t*. Bp (1 mm): 49 °C. ¹H NMR (CDCl₃) δ: 1.20 (s). ¹³C NMR (CDCl₃) δ: 28.40 (CH₃), 81.17 (C(CH₃)₃). IR: ν 1160, 835, 765, 670. Anal. Calcd for C₈H₁₈O₂S₂: C, 45.68; H, 8.62; S, 30.48. Found: C, 45.88; H, 8.79; S, 30.55.

Diisobutoxy Disulfide, *i*-PrCH₂OSSOCH₂Pr-*i*. Bp (1 mm): 58 °C. ¹H NMR (CDCl₃) δ: 0.90 (d, 12H), 1.90 (m, 2H), 3.50 (dd, 2H), 3.62 (dd, 2H). ¹³C NMR (CDCl₃) δ: 18.98 (CH₃), 19.03 (CH₃), 28.75 (CH), 82.15 (CH₂). IR: ν 980, 720, 675. Anal. Calcd for C₈H₁₈O₂S₂: C, 45.69; H, 8.62; S, 30.48. Found: C, 45.75; H, 8.73; S, 30.67.

Dineopentoxy Disulfide, *t*-BuCH₂OSSOCH₂Bu-*t*. Bp (0.8 mm): 72 °C. ¹H NMR (CDCl₃) δ: 0.89 (s, 18 H), 3.41 (d, 2H), 3.57 (d, 2H). ¹³C NMR (CDCl₃) δ: 26.43 (CH₃), 32.53 (C(CH₃)₃), 86.00 (CH₂). IR: ν 970, 770, 715. Anal. Calcd for C₁₀H₂₂O₂S₂: C, 50.38; H, 9.30; S, 26.90. Found: C, 50.29; H, 9.44; S, 27.14.

Bis(benzyloxy)disulfide, PhCH₂OSSOCH₂Ph. Mp: 58–59 °C. ¹H NMR (CDCl₃) δ: 4.93 (d, 2H), 4.82 (d, 2H), 7.37 (s, 10 H). ¹³C NMR (CDCl₃) δ: 76.58 (CH₂), 128.16 (CH), 128.4 (CH), 128.59 (CH), 136.18 (C-quat). IR: ν 945, 910, 655. Anal. Calcd for C₁₄H₁₄O₂S₂: C, 60.40; H, 5.07; S, 23.04. Found: C, 60.33; H, 5.02; S, 23.13.

ESR Spectroscopy. The spin trapping experiments were carried out by mixing the various precursors with the nitroso compound in benzene as solvent. The samples were degassed by connecting to a vacuum line the Suprasil quartz tubes, containing the solutions, which were subsequently sealed *in vacuo*. Photolysis was carried out in the cavity of an ESR spectrometer (Varian E 104) using a 500 W high-pressure Hg lamp. For the low-temperature experiments cyclopropane, condensed in the tubes by means of liquid nitrogen, was added to the solutions.

The ESR spectra of the radical adducts of fullerene C₆₀ were obtained by mixing benzene solutions of C₆₀ with dialkoxy disulfides ROSSOR (the equivalent ratios covering the range 1:1–1:5). The samples were degassed and photolyzed as previously described^{2,17} at about 60 °C and 80 °C (only *t*-BuOSSOBu-*t* having been photolyzed at 10 °C). The *g*-factors of the nitroxide radicals were determined with respect to that of DPPH (contained in an internal capillary sample) and those of the RO–C₆₀[•] radical adducts with respect to that of the line due to the C₆₀ excited triplet (*g* = 2.001 35).²²

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