EPR-Active Adducts of $^3C_{60}$ to Anthracenes: Biradicals or Triplet Zwitterions?

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The photophysical properties of fullerenes have been the subject of numerous investigations, but their photochemistry has received little attention, and most attempts to functionalize C_{60} have been based on thermal chemistry, such as thermal Diels–Alder reactions, resulting in the formation of mono- or multiple adducts.[1] After initial difficulties with the unequivocal identification of these cycloadducts, the reaction products of C_{60} with anthracene were synthesized, isolated, and characterized by mass spectrometry and by ^1H and ^{13}C NMR spectroscopy.[2] Photochemically, [2 + 2]-cycloadditions of cyclohexenones[3] and of *N,N*-diethylpropynylamine[4] to C_{60} as well as addition of alcohols and hydrocarbons to a crown ether–methanofullerene[5] are known.

In order to obtain the triplet energy of C_{60} and the extinction coefficient for triplet–triplet absorption, quenching experiments with anthracene were carried out.[6,7] It was found that C_{60} (E_T = 36.3 kcal/mol)[8] quenches the triplet state of anthracene (E_T = 42 kcal/mol)[9] with a rate constant of $(6.1 \pm 1.0) \times 10^9$ M^{-1} s^{-1},[6] but nothing is mentioned about the mechanism of this quenching process. In such systems we now observe transient intermediates by EPR,[10] and we note that a chemical reaction between anthracene and $^3C_{60}$ (formed either by energy transfer from triplet anthracene or by direct excitation of C_{60}) takes place. As a result of this reaction the irradiated solutions have a brownish color, and at temperatures above 270 K a brown precipitate is formed. To our knowledge, the possibility of a photochemical reaction of $^3C_{60}$ with anthracene has not yet been discussed. However, Anderson et al.[11] observed significant changes in the absorption spectrum of a dihydrofullerene during anthracene quenching.

EPR spectra obtained during photolysis[12] of a solution of C_{60}[13] and different anthracenes are shown in Figure 1, and the hyperfine coupling constants and the line widths of the products are summarized in Table 1. The single line at higher field with a *g*-factor of 2.001 33 is present in all spectra and is due to the triplet state of C_{60}.[14] In Figure 1a, the spectrum of an irradiated solution of C_{60} and anthracene shows, in addition to the signal of $^3C_{60}$, a doublet of a new species. The splitting corresponds to one proton with a hyperfine coupling constant of 72 μT (720 mG). The same spectrum is also obtained with 1-methylanthracene or 2-methylanthracene instead of anthracene.[15] This suggests that the proton in the 9- or 10-position of anthracene is responsible for the hyperfine coupling. The behavior of the polarization of this adduct is remarkable. At 300 K the signal appears in absorption, at 270 K in emission (shown), whereas the signal of $^3C_{60}$ is absorptive at both temperatures. Electron spin polarization is observed in the spectra of all systems with a phase that depends not only on temperature but also on the actual anthracene derivative and on its concentration. Due to this polarization it is not possible to estimate the efficiency of adduct formation. Similar effects have been observed and discussed in systems in which the hydrogen adduct of C_{60} is formed.[16]

The result of a second experiment, carried out with perdeuterioanthracene, is illustrated in Figure 1b. It shows a spectrum consisting of a 1:1:1 triplet corresponding to one deuterium atom with the expected hyperfine coupling constant of 11.2 μT. The line width is much smaller than that observed in the first system,

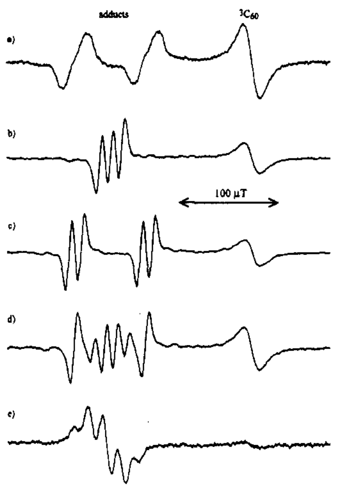

Figure 1. EPR spectra obtained with a solution of 1.5×10^{-4} M C_{60} in *tert*-butylbenzene at 270 K in the presence of 2.5×10^{-4} M anthracene (a), anthracene-d_{10} (b), anthracene-*1,2,3,4,5,6,7,8*-d_8 (c), anthracene-*1,2,3,4,5,6,7,8,9*-d_9 (d), and 9-methylanthracene (e).

Table 1. Hyperfine Coupling Constants (μT) and Line Widths[a] (μT) of the Adducts[b] at 270 K

system	hyperfine coupling constants	line width
anthracene	72 (1H)	25
anthracene-d_{10}	11.2 (1D)	6
anthracene-*1,2,3,4,5,6,7,8*-d_8	72 (1H) 12.5 (1H)	5.5
anthracene-*1,2,3,4,5,6,7,8,9*-d_9	72 (1H)	7
	12 (1H) 12 (1D)	5
9-methylanthracene	17.5 (1H) 12.5 (3H)	11

[a] ΔH_{pp}. [b] All *g*-factors lie in the range 2.002 18 to 2.002 20.

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(10) Steady state EPR experiments were performed using an X-band Bruker ESP-300 spectrometer equipped with a field frequency lock and with a flow system containing degassed solutions of C_{60} in *tert*-butylbenzene.

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(12) The solutions were irradiated in a quartz cell of 1 mm optical path length with light from a 1000 W Hg–Xe lamp filtered with aqueous $CuSO_4$ which has an optical window between 300 and 600 nm.

(13) C_{60} was prepared in a Krätschmer–Huffman type apparatus (7 mm graphite rods, 100 A dc discharge, 200 mbar of He) followed by toluene extraction of the soot and chromatographic purification, yielding C_{60} of about 99% purity.

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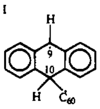
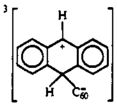
which indicates the presence of unresolved hyperfine coupling constants in the species leading to Figure 1a. This is confirmed by the use of anthracene deuterated in all positions except 9 and 10, as shown in Figure 1c. The resulting reduced line width, when compared with the line width in Figure 1a, allows the observation of a second hyperfine coupling, which is considerably smaller than the first one. Obviously, there are splittings due to two inequivalent hydrogen or deuterium atoms bound at the 9- and 10-positions of anthracene. To prove this we used anthracene completely deuterated except for the 9-position. The resulting spectrum, shown in Figure 1d, clearly indicates the presence of two different species. The first one, in which the larger splitting is due to the proton, leads to the outer doublet. The hyperfine coupling constant of the deuterium is here expected to be (12.5/6.5) μT and thus too small to be resolved. However, this unresolved coupling of the deuterium does affect the line width of the doublet, making it noticeably larger than observed in Figure 1c. For the second species the spectrum is described by a doublet of a triplet due to the presence of one atom with $I = {}^1/_2$ and another atom with $I = 1$. The hyperfine coupling constants of the two atoms are equal, and thus a quartet with an intensity ratio of 1:2:2:1 is observed.

The inequivalence of the anthracene 9- and 10-protons rules out an assignment to the triplet state of a Diels–Alder adduct. A second possibility is a triplet biradical formed by addition of $^3C_{60}$ to the 9- or 10-position of anthracene with one electron located on C_{60} and the other one on the anthracene residue (**I**). The latter subunit would resemble the dibenzocyclohexadienyl radical and should lead to splittings of 1344 and 1600 μT for the 9- and 10-protons[17] if the electron exchange is weak, or half of these values if it is strong.[18] The present observation of much smaller couplings rules out this structure, however. Furthermore, it is also not possible to explain the spectra by a structure obtained by addition of a second C_{60} molecule to the anthracene subunit of this biradical, because then the two atoms in the 9- and 10-positions should be equivalent. An alternative explanation involves a triplet zwitterion (**II**). In this species the two electrons could occupy two of the closely spaced orbitals at C_{60}, and a positive charge arises at the anthracene subunit. In analogy to $^3C_{60}$, in which the distance between the two electrons is only slightly smaller than the diameter of the molecule,[19] it is reasonable to assume that one electron is located close to the point of addition and the other one on the opposite side of C_{60}. Therefore, the H atom in the 10-position has a larger hyperfine coupling constant than the one in the 9-position.

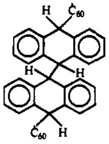
I



II



III



The inequivalence of the substituents in the 9- and 10-positions is explained also by structure **III**. This biradical could arise by dimerization of biradical **I** at the anthracene moieties. For this structure the electron exchange is expected to be weak; therefore the EPR spectrum is that of the monoradical. It is also understandable that the splitting of the proton at the point of dimerization is much smaller, since it is far away from the electron on C_{60}. The latter assignment is supported by the g-factors of the adducts (2.00218-2.00220), which are nearly equal to the g-factors of various radical adducts to C_{60} (2.0022-2.0023).[20] A comparison of the larger coupling constant with those of γ-protons of alkyl adducts of C_{60},[20] however, shows that even for the isopropyl adduct with the largest coupling of 49 μT they are clearly smaller than the 72 μT observed in the anthracene adduct. In the isopropyl adduct, free rotation about the bond between C_{60} and the substituent is precluded, and in the equilibrium configuration the axis of the π atomic orbital at C_α and the directions of the bonds $C_\alpha-C_\beta-C_\gamma-H$ form a planar zigzag arrangement (W plan).[21] This gives the maximum of 49 μT for the hydrogen coupling constant. The same configuration is proposed for the zwitterion **II** and the biradical **III**, and consequently an additional contribution is needed to explain the even higher coupling constant. Such contributions are possibly through-space interactions between the γ-proton and the electron at C_{60}, and additional spin polarization or greater localization due to the other unpaired electron. The second splitting of 12.5 μT is also unusually high, considering that this proton is even further away from the electron at C_{60}. On the basis of the present results we cannot exclude one of the structures, **II** or **III**.

A further point of interest is the steric requirement for the formation of **II** or **III**. In order to investigate this, the reactions of various substituted anthracenes with C_{60} were studied. Figure 1e displays a spectrum obtained from photolysis of C_{60} and 9-methylanthracene which consists of lines from only one species. For structure **II** the observed hyperfine couplings are compatible with C_{60} addition at both the methylated and the unsubstituted carbon, while for structure **III** C_{60} needs to be bound at the methyl-substituted carbon. During photolysis of either 9-phenylanthracene or 9,10-diphenylanthracene with C_{60} we did not observe any adduct, and the only signal in the EPR spectrum was due to the triplet state of C_{60}. Therefore, we conclude that species **II** or **III** are formed only when the substituents in the 9- and 10-positions of anthracene are small or absent.

In the case of 9,10-dimethylanthracene a reaction with C_{60} to a Diels–Alder adduct[22] occurs at room temperature even without irradiation. No signal at all was observed by EPR when this Diels–Alder adduct was irradiated in *tert*-butylbenzene. However, in polar solvents such as benzonitrile, a single line with a g-factor of 2.000 73 was observed. Signals with the same g-factor were also observed during photolysis of anthracene and C_{60} in polar solvents and are assigned to the anion of the Diels–Alder adduct. The low g-factor supports this assignment, because the anion of C_{60} has a g-factor close to 2.000.[23] A full account of EPR-active species during the photochemical reactions of C_{60} and C_{70} with different polycyclic aromatics in nonpolar and polar solvents is in progress.

Conclusion. C_{60} reacts with anthracenes not only thermally but also photochemically, and this should kept in mind during quenching experiments of C_{60} with aromatics.[24] We propose that the EPR-active intermediates are triplet zwitterions or biradicals. Due to steric hindrance such adducts are formed only with anthracenes with small substituents in the 9- and 10-positions.

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(15) A doublet with a slightly higher coupling constant is obtained on photolysis of anthracene and C_{70}. Photochemical reaction with anthracenes is thus not restricted to C_{60}.

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