EPR-Active Intermediates During Photochemical Reactions of Fullerenes with Anthracenes

Regina Klemt, Emil Roduner† and Hanns Fischer*

Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Klemt, R., Roduner, E. and Fischer, H., 1996. EPR-Active Intermediates During Photochemical Reactions of Fullerenes with Anthracenes. – Acta Chem. Scand. 50: 1050–1059. © Acta Chemica Scandinavica 1996.

During the photochemical reaction of C_{60} and C_{70} with anthracenes (A) two types of transient EPR-active product are observed. The first is found in non-polar and in polar solvents and probably represents biradicals ($\dot{C}_{60}$-A-A-$\dot{C}_{60}$) or monoradicals $\dot{C}_{60}$-A-R with unknown residue R and resulting from a photochemical reaction of preformed 2+4 Diels–Alder adducts of the anthracenes to C_{60}. The second appears only in polar solvents and are tentatively assigned as anions of these Diels–Alder adducts. All species are preferentially formed from anthracenes with small substituents in the 9- and 10-positions. For C_{70} several adducts of each type are found, which is ascribed to the non-equivalence of the C_{70} addition sites. To support the assignments various alkyl radical adducts to C_{60} have also been studied.

In the last years C_{60} has been functionalized in many ways,[1] whereas for C_{70} fewer reactions are known. Most processes are based on thermal chemistry, but several photochemical reactions are also known, such as the [2+2] cycloadditions of cyclohexenones[2] and of N,N-diethylpropynylamine[3] to C_{60}, additions of alcohols and hydrocarbons to a crown-ether methanofullerene[4] and a cycloaddition of disilirane to C_{70}.[5] A photochemical reaction between $^3C_{60}$ and anthracene has been found by Goldshleger et al.[6] under conditions where anthracene does not absorb. The product is identical with the thermal 2+4 Diels–Alder adduct,[7] and is proposed to be formed via an exciplex intermediate. This reaction was not observed in studies involving C_{60} or C_{70} and anthracenes to obtain the fullerene triplet energies and the extinction coefficients for their triplet–triplet absorption.[8-10] There, the triplet state of anthracene ($E_T = 42$ kcal mol^{-1})[11] was quenched by C_{60} ($E_T = 36.3$ kcal mol^{-1})[12] with a rate constant of $(6.1 \pm 1.0) \times 10^9$ M^{-1} s^{-1},[8] and by C_{70} ($E_T = 35.3$ kcal mol^{-1})[13] with a rate constant of $(6.2 \pm 0.6) \times 10^9$ M^{-1} s^{-1}.[10]

Recently, we reported the detection of transient intermediates by EPR during the photochemical reaction between C_{60} and several anthracenes in a non-polar solvent.[14] They exhibit hyperfine splittings by anthracene substituents in the 9- and 10-position. The non-equivalence of the coupling constants for equivalent 9,10-substituents rules out an assignment to the triplet state of a Diels–Alder adduct. We considered the singly bonded species **Ia** and **Ib**, and excluded the non-polar

biradical structure **Ia** on the basis of the magnitudes of the couplings. The triplet zwitterion **Ib**, in which the two electrons could be located on the C_{60} residue, and the biradical **II** seemed compatible with the observed hyperfine coupling constants. For **II** the large distance between the two unpaired electrons weakens their electron exchange, and, consequently, its EPR spectrum should be close to that of a monoradical. Unfortunately, it was not possible to make a definite assignment.

To obtain more information we have now extended the study by the inclusion of additional anthracene derivatives, varied the solvent and also employed C_{70}. It is shown that in polar solvents a second type of adduct is formed, and that in general C_{60} and C_{70} lead to very similar species. We also present EPR data for several new radical adducts to C_{60} which were studied to support the interpretation of the hyperfine coupling constants.

Ia   **Ib**   **II**
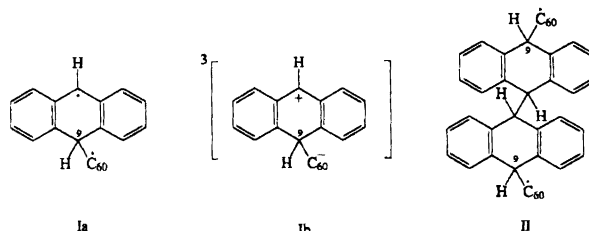
Experimental

C_{60} and C_{70} were prepared in a Krätschmer–Huffman type apparatus (7 mm graphite rods, 100 A dc discharge, 200 mbar of He). C_{60} of about 99% purity and C_{70} of about 97% purity were obtained by toluene extraction of

---

† Permanent address: Institut für Physikalische Chemie, Universität Stuttgart, D-70550 Stuttgart, Germany.

the soot and subsequent chromatographic purification with toluene and 1,2-dichlorobenzene as eluents. tert-Butylbenzene and anhydrous argon-packed benzonitrile were purchased from Aldrich and used as received. The non-deuteriated anthracenes were from Aldrich or Fluka, tetrabutylammonium perchlorate [(TBA)ClO₄] from Fluka, and anthracene-d_{10} from Cambridge Isotopes Laboratories. Anthracene-1,2,3,4,5,6,7,8,9-d_9, anthracene-1,2,3,4,5,6,7,8-d_8, 9-methylanthracene-1,2,3, 4,5,6,7,8,10-d_9, and 9-bromoanthracene-1,2,3,4,5,6,7,8, 10-d_9 were synthesized from anthracene-d_{10}.[15]

Steady state EPR experiments were performed using an X-band Bruker ESP-300 spectrometer equipped with a field frequency lock and a flow system on oxygen-free solutions of C₆₀ or C₇₀ (1.5×10^{-4} M) and the anthracenes (3×10^{-5} to 5×10^{-4} M) in tert-butylbenzene or in benzonitrile–tert-butylbenzene (4:1). Except for 9,10-dimethylanthracene and C₆₀ (vide infra) there was no obvious reaction on mixing of the components. The flowing solutions were continuously irradiated in quartz cells of 1 mm or 0.5 mm optical path length with light from a 1000 W Hg–Xe lamp filtered with aqueous CuSO₄ which has an optical window between 300 and 600 nm. The small linewidths of the paramagnetic species required the use of 25 kHz modulation frequency and the field stabilization with the field frequency lock, and the often low stationary concentrations dictated high filter time constants (typically about 1.25 s) and some overmodulation of the spectra presented in the figures. All signals were transient and decayed after illumination with the experimental time constant.

To investigate the product of the spontaneous reaction of C₆₀ and 9,10-dimethylanthracene these compounds (C₆₀: 18 mg, 0.5 mmol; 9,10-dimethylanthracene: 5 mg, 0.49 mmol) were stirred together in benzene at ambient temperature for 1 h to form a brown solution. The solvent was removed under vacuum, and the dark brown residue was washed with methanol and pentane and dried. The NMR spectrum revealed the 2+4 Diels–Alder adduct as the main component: ¹H NMR (200 MHz, CD₂Cl₂): δ (ppm) 2.83 (s, 6 H, CH₃), 7.75–7.80, 7.47–7.52 (4 H and 4 H, AA′BB′ similar to the data for the anthracene adduct[7]). It could not be separated from unreacted C₆₀ by column chromatography and decomposed slowly at room temperature. Electrochemical experiments were carried out using a commercial cell (Bruker) in the cavity of the EPR spectrometer.[16] A mercury pool served as the working electrode and a platinum wire as the counter electrode. The reference electrode was saturated calomel (SCE), and the solvent a mixture of benzonitrile–tert-butylbenzene (4:1) containing 0.1 M (TBA)ClO₄. The solutions for electrolysis were degassed by several freeze–thaw cycles and purged with argon during the experiments.

Results and discussion

Adducts to C₆₀ in tert-butylbenzene. Table 1 gives the hyperfine coupling constants and peak-to-peak line-

Table 1. Hyperfine coupling constants (mG) and linewidths (mG) of anthracene adducts to C₆₀ in tert-butylbenzene at 270 K.

System	Coupling constants		ΔH_{pp}
Anthracene (Fig. 1a)[a]	720	(1H_γ)	250[b]
1-Methylanthracene	720	(1H_γ)	250[b]
2-Methylanthracene	720	(1H_γ)	250[b]
Anthracene-d_{10}	112	(1D_γ)	60
Anthracene-1,2,3,4,5,6,7,8-d_8	720	(1H_γ)	55
	125	(1H_r)	
Anthracene-1,2,3,4,5,6,7,8,9-d_9 a	720	(1H_γ)	70
b {	120	(1D_γ)	
	120	(1H_r)	50
9-Methylanthracene (Fig. 1b)	175	(1H_r)	110
	125	(3H_s)	
9-Methylanthracene-1,2,3,4,5,6,7,8,10-d_9 (Fig. 1c)	125	(3H_s)	70
9-Hydroxymethylanthracene (Fig. 2a)	390	(1H_s)	
	170	(1H_r)	140
9-Bromoanthracene (Fig. 2b)	150	(1H_r)	130
9-Bromoanthracene-1,2,3,4,5,6,7,8,10-d_9 (Fig. 2c)			110

[a] Also observed in benzene. [b] Including the partially resolved H_r-coupling.

widths for all intermediates during the photoreaction of anthracenes and C₆₀ observed so far, and Figs. 1 and 2 show EPR spectra for several derivatives. Except for the species obtained with 9-bromoanthracenes which have $g = 2.00263$, all other products have $g = 2.00218$–2.00220.
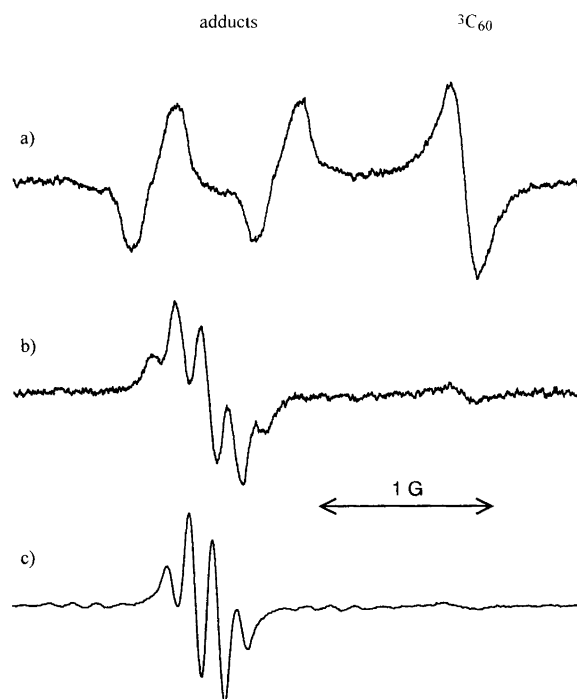

Fig. 1. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C₆₀ in tert-butylbenzene at 270 K in the presence of 2.5×10^{-4} M anthracene (a), 9-methylanthracene (b) and 9-methylanthracene-1,2,3,4,5,6,7,8,9-d_9 (c).
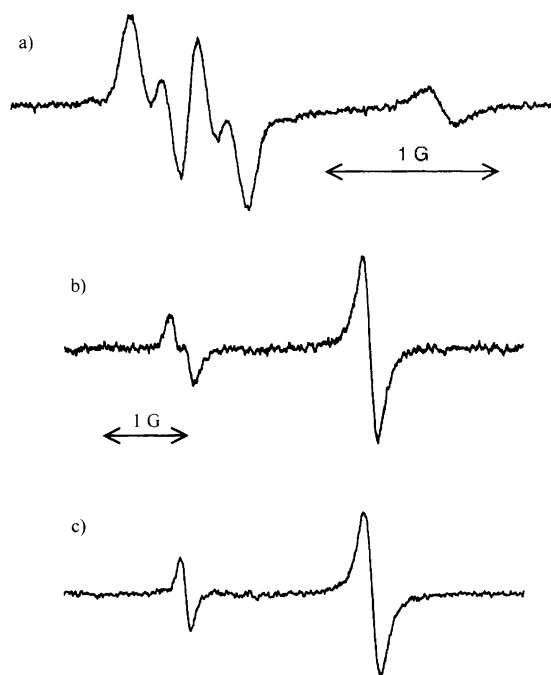
Fig. 2. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C_{60} in *tert*-butylbenzene at 280 K in the presence of 2.5×10^{-4} M 9-hydroxymethylanthracene (a), 3×10^{-4} M 9-bromoanthracene (b) and 3×10^{-4} M 9-bromoanthracene-1,2,3,4,5,6,7,8,10-d_9 (c).

These g-factors are higher than that of the triplet state of C_{60} ($g = 2.00133$),[17] which is present in Figs. 1 and 2 as a singlet at higher field than the adduct lines.

The g-factors, hyperfine coupling constants and line widths of the intermediates are very similar to those of alkyl radical adducts to C_{60}.[18] Hence, they are very probably similar adducts, with the unpaired electron spin density mainly on C_{60} with little delocalization onto the anthracene part. From the variation of the hyperfine coupling constants with anthracene deuteriation we further concluded[14] that all adducts have similar structures, and that the coupling constants are due to the substituents in positions 9 and 10 of one anthracene unit.

In particular, for anthracene and 1- and 2-methylanthracene the same spectrum with one resolved proton coupling and a clear indication of a second smaller doublet splitting is observed (Fig. 1a) which makes it unlikely that C_{60} is linked to an outer anthracene ring. For anthracene-d_{10} the larger proton coupling is replaced by a deuteron coupling of expected magnitude. Anthracene-1,2,3,4,5,6,7,8-d_8 shows two resolved proton couplings and sharper lines. The larger coupling is the same as for anthracene, and the smaller one is also indicated for the undeuteriated anthracenes but partially obscured by the line width. Anthracene-1,2,3,4,5,6,7,8,9-d_9 gives two species in a ratio of about one. The first has a deuterium coupling close to that of anthracene-d_{10} and a proton coupling which is very similar to the smaller proton coupling of anthracene-d_8, and the second has the same proton coupling as anthra-

cene and no resolvable deuterium coupling. For all perdeuteriated species the apparent linewidth is smaller than for the protonated analogs which suggests additional unresolved couplings for the latter. Obviously, the protons or deuterons in the 9- and 10-positions of anthracene are inequivalent, and this suggests a single bond between C_{60} and one of the central carbon atoms of anthracene. In analogy to alkyl radical adducts we assign the larger coupling constant (H: 720 mG, D: 112–120 mG) to the atom at the site of addition and the smaller one (H: 120 mG, D: unresolvably small) to the remote atomic substituent of the central anthracene ring.

9-Methylanthracene yields only one adduct with hyperfine couplings to three methyl protons and to a single proton (Fig. 1b). To confirm the analysis of the spectrum we used in addition 9-methylanthracene completely deuteriated except for the methyl group. The resulting spectrum (Fig. 1c) has somewhat sharper lines and clearly shows the interaction with the methyl group with the same coupling constant as for the undeuteriated compound. The coupling constant of the deuterium atom is now too small to be resolved, and the coupling constant of the single proton of the 9-methylanthracene adduct is similar to that of the remote proton for anthracene-d_8 and -d_9. Hence, we must conclude that for 9-methylanthracene C_{60} is linked to C9, i.e., the more substituted carbon atom. The same situation holds for 9-hydroxymethylanthracene and the 9-bromoanthracenes. The adduct of the former (Fig. 2a) exhibits two hyperfine splittings due to two inequivalent protons, the smaller coupling being similar to that of the remote proton of the aforementioned adducts. Hence, the larger splitting of 390 mG is due to one proton of the CH_2OH group. The EPR spectra obtained during photolysis of C_{60} with 9-bromoanthracene and 9-bromoanthracene-1,2,3,4,5,6,7,8,10-d_9 are shown in the lower part of Fig. 2. 9-Bromoanthracene shows the small remote proton splitting, whereas 9-bromoanthracene-1,2,3,4,5,6,7,8,10-d_9 exhibits a single line, in agreement with an unresolved small coupling of a remote deuterium atom.

Several additional anthracenes were employed to search for similar adducts. For 9-phenylanthracene, 9,10-diphenylanthracene, 9-anthraldehyde, 9-cyanoanthracene, 9,10-dibromoanthracene and 9,10-dichloroanthracene we did not observe a photochemical reaction, and the only observation was the triplet state of C_{60}. For 9-nitroanthracene and 9-chloromethylanthracene a photochemical reaction took place, but no adducts were detected. For 9,10-dimethylanthracene, reaction with C_{60} to give a Diels–Alder adduct occurs at room temperature even without irradiation. No EPR signal at all was observed when this Diels–Alder adduct was irradiated in *tert*-butylbenzene, and only $^3C_{60}$ was found during photolysis of 9,10-dimethylanthracene and C_{60} solutions which were precooled to prevent the thermal reaction. However, EPR-active adducts were observed during photolysis of C_{60} with tetracene and rubrene. The spectrum obtained for tetracene is similar to that for

anthracene, whereas for rubrene a complicated pattern arises which was not analyzed. No reaction was observed for naphthalene, phenanthrene and benzo[a]pyrene.

With respect to the structure of the EPR-active species it appears to us now that both forms Ia and Ib with a single bond between the anthracenes and C_{60} and no further substituents are unlikely. Ia should give much larger coupling constants especially for the proton in position 10 which is at the center position of a cyclohexadienyl fragment.[19] RHF-PM3 calculations on the triplet state showed that the open form Ia is an energy minimum with a bond length of 156 pm between C_{60} and C9. The spin density distribution is as expected for Ia and there is no extensive charge separation as suggested by Ib. Furthermore, triplet states of Diels–Alder adducts to C_{60}, i.e., species that also carry two unpaired electrons on the fullerene part as in Ib, have recently been found[20] to exhibit rather broad EPR lines and g-factors outside the range found here.

On the other hand, a general structure III, which includes biradical II, appears reasonable and is supported by the analogy of the observed coupling constants with those of known alkyl radical adducts. (a) At first sight, the coupling constant of 720 mG for a proton of a CH group linked to C_{60} appears high in comparison with reported H_γ-coupling constants of alkyl adducts,[18] such as 470 mG for $(CH_3)_2CH$. However, recently larger values have been reported for fluorinated alkyl adducts,[21] and Table 2 shows that cyclohexyl, α-hydroxybenzyl (assignments by analogy with $C_6H_5CH_2$[22]) and formyl adducts (photolysis of CH_3CH_2CHO[23]) exhibit H_γ-couplings which are also fairly large. Hence, the assignment of the large coupling is reasonably justified, and indicates that H_γ is placed over the cyclopentyl ring. (b) The coupling constant of the methyl protons in the 9-methylanthracene adduct (125 mG) agrees very well with other data on δ-CH_3-couplings.[18] For 9-hydroxymethylanthracene only one γ-proton of the

CH_2 group has an appreciable coupling, but a similar situation is known for the adduct of $Si(CH_2CH_3)_3$.[24] (c) The coupling to the remote proton (125 mG for anthracene-d_8) is without precedence for alkyl adducts for which appreciable couplings are only known for γ-, δ- and ε-protons.[18] However, the MM$^+$structure of III calculated with R = H given below indicates that the remote proton should be very close (275 pm) to the C_{60} atom with the largest spin density,[25] and this may well explain the long-range coupling. Further support is the similarity of the g-factors with those of alkyl adducts, including the slightly higher value for the brominated species.

III
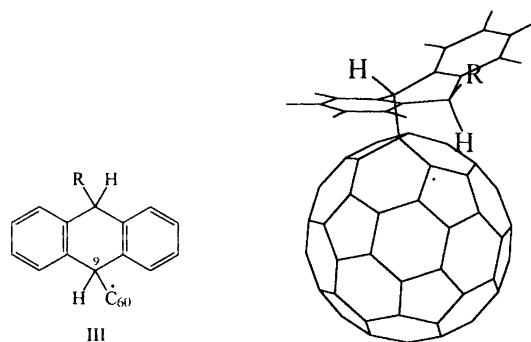
On the basis of the magnetic properties it is not possible to ascertain the nature of our adducts beyond structure III with an unspecified group R, but, as shown later on, the biradical structure II seems chemically reasonable. For anthracene-d_8 we found no temperature dependence of the line positions from −38 to +70 °C, which suggests a fairly rigid adduct structure. The formation of the species must be rather complex, however, as evidenced from the polarization of the signals and its time dependence: As Fig. 1a shows, the adduct of anthracene appears in emission at 270 K, and the same was found for all deuteriated anthracenes earlier.[14] The other adducts show absorption at 270 K but the general polarization pattern depends strongly on the experimental conditions. Low temperatures, low flow rates and low anthracene concentrations favor emission whereas high temperatures, flow rates and anthracene concentrations lead to enhanced absorption. $^3C_{60}$ appears always in absorption. After initiation of the photolysis the anthracene adduct first shows absorption and then emission after several seconds, and $^3C_{60}$ appears only slowly whereas it forms instantaneously in samples without anthracenes. Obviously, the development of the emissive polarizations requires the presence of $^3C_{60}$.

Adducts to C_{70} in tert-butylbenzene. While all carbon atoms of C_{60} are equivalent, C_{70} has five non-equivalent carbon atoms to which additions may occur to produce five isomeric adducts. The five sites are numbered A, B, C, D and E in Fig. 3 and are occupied by 10, 10, 20, 20, and 10 carbon atoms,[26] respectively. During the reaction with monoradicals several of the expected isomers have been observed, namely three for methyl[27] and tert-

Table 2. Hyperfine coupling constants (mG) of radical adducts[a,b] to C_{60}.

Radical	Coupling constants		T/K
$(CH_3)_2\dot{C}CH_2CH_2CH_3$[c]	190	$(6H_\delta)$	360
	100	$(2H_\delta)$	
c-$\dot{C}_6H_{11}$[c,d]	560	$(1H_\gamma)$	320
	360	$(2H_\delta)$	
	120	$(2H_\epsilon)$ or $(2H_\delta)$	
$(CH_3)_2\dot{C}OH$[e]	150	$(6H_\delta)$	320
	90	$(1H_\delta)$	
$\dot{C}H_2OH$[c]	170	$(2H_\gamma)$	320
	75	$(1H_\delta)$	
$C_6H_5\dot{C}HOH$[c]	720	$(1H_\gamma)$	310
	200	$(2H_o)$	
$\dot{C}HO$	2080	$(1H_\gamma)$	320

[a] All g-factors are in the range 2.0022–2.0023. [b] Except where noted in tert-butylbenzene. [c] Photolysis of $(CH_3)_3COOC(CH_3)_3$ + RH. [d] Solvent benzene. [e] Photolysis of $HO(CH_3)_2COC-(CH_3)_2OH$.
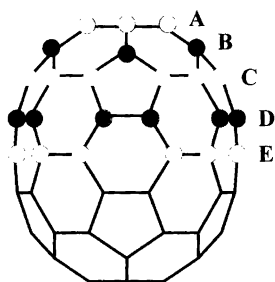
Fig. 3. Schematic structure of C_{70} with the five non-equivalent types of carbon atom.

butyl,[28] four for perfluoromethyl,[27] phenyl,[27] the hydrogen,[29] and the fluorine[30] atoms and five for muonium.[31] Generally, their hyperfine coupling constants do not deviate strongly from those of the corresponding C_{60} adducts but the g-factors of the different isomers show a remarkably large spread.

EPR spectra obtained during photolysis of a solution of C_{70} and anthracenes in *tert*-butylbenzene are shown in Fig. 4. In all cases we find a fourfold repetition of the spectral features of the adducts to C_{60}, i.e., four isomers. They are numbered 1, 2, 3 and 4 according to increasing g-factors, and the positions of the numbers in Fig. 4 indicate the centers of the individual spectra. The triplet state of C_{70} ($g = 2.00185$) is not observed because of its
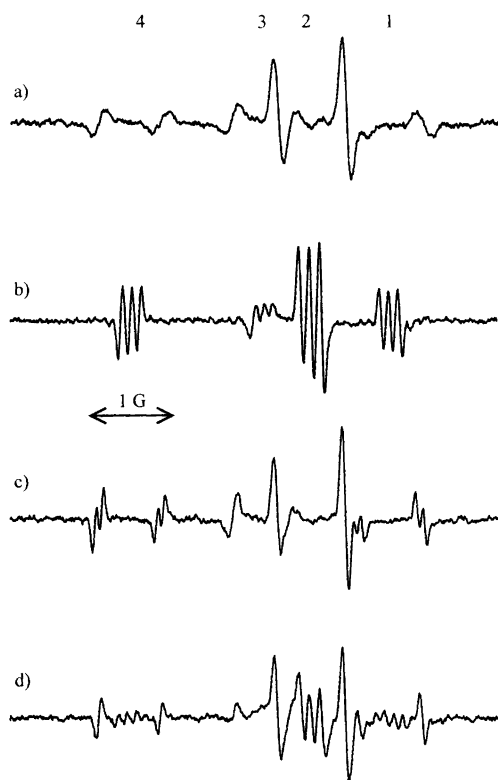

Fig. 4. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C_{70} in *tert*-butylbenzene at 300 K in the presence of 1.2×10^{-4} M anthracene (a), anthracene-d_{10} (b), anthracene-1,2,3,4,5,6,7,8-d_8 (c) and anthracene-1,2,3,4,5,6,7,8,9-d_9 (d).

large linewidth.[17] Table 3 gives the hyperfine coupling constants, peak-to-peak linewidths and g-factors of those isomers for which the line positions could be reliably obtained from the spectra. For the others there are ambiguities due to overlap and strong polarization effects which are similar to those observed with C_{60}.

The four isomers are clearly seen for anthracene, and 1- and 2-methylanthracene (Fig. 4a) as four doublets with proton coupling constants of 710 to 780 mG, anthracene-d_{10} (Fig. 4b), as four deuterium triplets with coupling constants of 100 to 120 mG and anthracene-d_8 (Fig. 4c), as four proton doublets with the same large coupling constant as found for anthracene. Only for the isomers 1 and 4 of anthracene-d_8 is the small remote proton coupling resolved.

Fig. 5 reveals that four isomeric adducts with very low signal intensities and similar g-factors are also obtained for 9-methylanthracene, 9-methylanthracene-1,2,3,4,5, 6,7,8,10-d_9 and 9-hydroxymethylanthracene in *tert*-butylbenzene, and their properties are also given in Table 3 as far as they could reasonably be determined from the spectra. In comparison with the C_{60} adducts (Figs. 1, 2, Table 1), the coupling constants are lower, and for 9-hydroxymethylanthracene only isomers 1 and 4 show resolved hyperfine structure. No adduct was observed during photolysis of C_{70} and 9,10-dimethylanthracene in the same solvent.

The similarity of the hyperfine patterns of the adducts of anthracenes to C_{70} and to C_{60} indicates structures analogous to III or II. For monoradicals the assignment of the different isomers to the different addition sites A to E of C_{70} has proved difficult, and conflicting views have been expressed.[27,29] For carbon-centered radicals one generally finds one adduct with a g-factor smaller than that of the C_{60} adduct and two to three species with larger values. The g-factors range from about $g = 2.0020$ to $g = 2.0028$. The anthracene adducts behave similarly but cover a considerably larger range from $g = 2.0016$ (isomer 1) to $g = 2.0034$ (isomer 4), and the upper value is clearly outside the normal range for radicals consisting only of carbon and hydrogen atoms. Based on the local environment the C_{70} adducts should deviate increasingly from the C_{60} species in the order A to E,[27] and based on this, relative signal intensities, g-factors and coupling constants, the monoradical adducts with the intermediate g-factors (our isomers 2 and 3) have been assigned to the sites of addition D and C.[27,29] Whilst there is agreement on this point, Morton *et al.*[29] attribute the low g isomer (1) to site B and the high g isomer (4) to A, whereas Krusic *et al.*[27] assign the former to B or A or a superposition of both and the latter to E. Krusic *et al.*[27] base their assignment of isomer 4 to E mainly on its g-factor of 2.0026–2.0027 which is compatible with a cyclohexadienyl-type structure though the E isomer should be thermodynamically disfavored.[32] Here, we observe the remote proton coupling for anthracenes and a coupling to one δ-proton for 9-hydroxymethylanthracene only for the isomers 1 and 4, i.e., their struc-

Table 3. Hyperfine coupling constants (mG), linewidths (mG) and g-factors of anthracene adducts to C_{70} in *tert*-butylbenzene at 270 K. Isomers with strongly overlapping lines are not included.

System	Isomer	Coupling constants		ΔH_{pp}	g-factor
Anthracene (Fig. 4a)	2	780	(1H$_\gamma$)	110[a]	2.00214
	4	710	(1H$_\gamma$)	150[a]	2.00342
1-Methylanthracene	2	790	(1H$_\gamma$)	130[a]	2.00216
	4	710	(1H$_\gamma$)	170[a]	2.00342
2-Methylanthracene	2	780	(1H$_\gamma$)	110[a]	2.00215
	4	710	(1H$_\gamma$)	150[a]	2.00341
Anthracene-d_{10} (Fig. 4b)	1	110	(1D$_\gamma$)	60	2.00161
	2	120	(1D$_\gamma$)	60	2.00216
	3	100	(1D$_\gamma$)	60	2.00249
	4	110	(1D$_\gamma$)	60	2.00341
Anthracene-1,2,3,4,5,6,7,8-d_8 (Fig. 4c)	1	{ 720 / 80	(1H$_\gamma$) / (1H$_r$)	} 50	2.00161
	2	780	(1H$_\gamma$)	80	2.00214
	4	{ 710 / 80	(1H$_\gamma$) / (1H$_r$)	} 50	2.00341
Anthracene-1,2,3,4,5,6,7,8,9-d_9 (Fig. 4d)	1a	720	(1H$_\gamma$)	60	2.00161
	1b	{ 110 / 80	(1D$_\gamma$) / (1H$_\gamma$)	} 60	2.00161
	2a	780	(1H$_\gamma$)	70	2.00215
	2b	120	(1D$_\gamma$)	60	2.00215
	4a	710	(1H$_\gamma$)	60	2.00341
	4b	{ 110 / 80	(1D$_\gamma$) / (1H$_r$)	} 60	2.00341
9-Methylanthracene[a] (Fig. 5a)	1			200[a]	2.00158
	2			140[a]	2.00201
	3			200[a]	2.00239
	4			200[a]	2.00345
9-Methylanthracene-1,2,3,4,5,6,7,8,10-d_9[a] (Fig. 5b)	1	85	(3H$_\delta$)	50	2.00159
	2	Multiplet[b]			≈2.0022
	3	Multiplet[b]			≈2.0024
	4	75	(3H$_\delta$)	50	2.00341
9-Hydroxymethylanthracene[c] (Fig. 5c)	1	≈270	(1H$_\delta$)	≈140[a]	≈2.0016
	2			150[a]	2.00202
	3			190[a]	2.00239
	4	≈270	(1H$_\delta$)	≈130[a]	≈2.0034

[a] Partially caused by unresolved hyperfine structure. [b] Distorted quartet. [c] T=230 K.

tures should be closer to that of the C_{60} adduct than 2 and 3. Hence, we prefer the assignment of Morton *et al.*[29] and attribute the isomers 1, 2, 3 and 4 to the sites of addition B, D, C and A, noting that the very high g-value of our isomer 4 in is any case far from what is expected for a cyclohexadienyl-type structure. So far, the large differences in the g-factors cannot be used for an assignment since the excited states of the radical adduct isomers are not known.

Adducts to C_{60} in benzonitrile–tert-butylbenzene. If the photolysis of C_{60} and anthracenes is carried out in a 4:1 by volume mixture of benzonitrile and *tert*-butylbenzene, i.e., in a more polar solvent, one observes additional intermediates besides the adducts of anthracenes and C_{60} described above (Figs. 1, 2, Table 1) and named adducts A, hereafter. Fig. 6 displays spectra obtained with pro-tonated and deuteriated anthracenes. The new adducts

B appear at higher fields than $^3C_{60}$ and thus have rather low g-factors. Anthracene, 1-methylanthracene, 2-methylanthracene (Fig. 6a) and anthracene-1,2,3,4,5,6,7,8-d_8 (Fig. 6c) yield a triplet with a 300 mG coupling to two equivalent protons, anthracene-d_9 gives a 300 mG doublet (Fig. 6d) and anthracene-d_{10} a single peak (Fig. 6b) with a linewidth that suggests unresolved deuterium couplings. These patterns suggest that the 300 mG couplings are due to the 9- and 10-protons of anthracene, and that the expected 50 mG couplings for deuterium atoms in these positions are too small to be resolved. Intermediates of type B are also observed for various more substituted anthracenes (Figs. 7, 8 and 9). 9-Methylanthracene gives the 300 mG coupling to one proton and no hyperfine interaction with the protons of the methyl group, and 9-methylanthracene-1,2,3,4,5,6,7,8,10-d_9 leads essentially to a single peak. 9,10-Dimethylanthracene, which does not produce
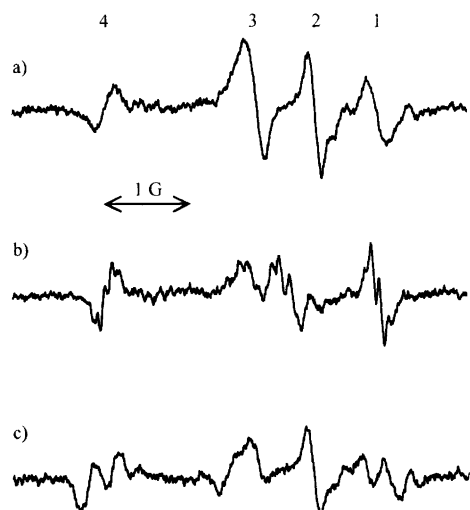
Fig. 5. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C_{70} in *tert*-butylbenzene at 230 K in the presence of 2.5×10^{-4} M 9-methylanthracene (a), 9-methylanthracene-1,2,3,4,5,6,7,8,10-d_9 (b) and 9-hydroxymethylanthracene (c).
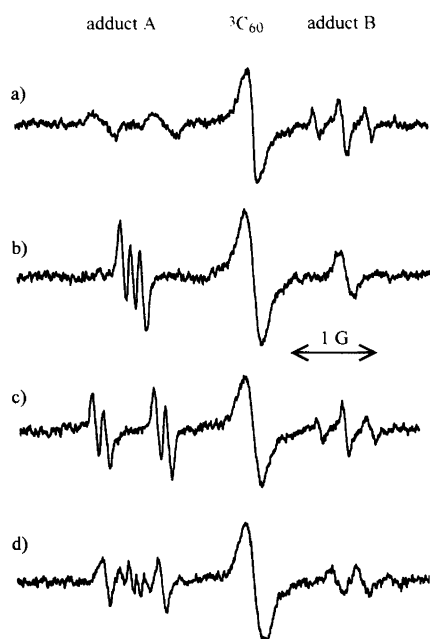

Fig. 6. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C_{60} in benzonitrile-*tert*-butylbenzene (4:1) at 300 K in the presence of 1.2×10^{-4} M anthracene (a), anthracene-d_{10} (b), anthracene-1,2,3,4,5,6,7,8-d_8 (c), and anthracene-1,2,3,4,5,6,7,8,9-d_9 (d).

Fig. 7. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C_{60} in benzonitrile–*tert*-butylbenzene (4:1) at 300 K in the presence of 3×10^{-5} M 9-methylanthracene (a), 9-methylanthracene-1,2,3,4,5,6,7,8,10-d_9 (b) and 9,10-dimethylanthracene (c).

Fig. 8. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C_{60} in benzonitrile–*tert*-butylbenzene (4:1) at 300 K in the presence of 1.1×10^{-4} M 9-hydroxymethylanthracene (a), and 2.4×10^{-4} M 9-phenylanthracene (b).

adducts A, gives a strong singlet exhibiting even some ^{13}C satellites which were however too weak to be analyzed. The same singlet is obtained if the thermally synthesized Diels–Alder adduct of C_{60} and 9,10-dimethylanthracene is irradiated in the more polar solvent mixture. 9-Hydroxymethylanthracene (Fig. 8a) gives a doublet of doublets. The larger coupling constant is nearly equal to that observed for anthracene and 9-methylanthracene, i.e., it is due to a ring proton, and
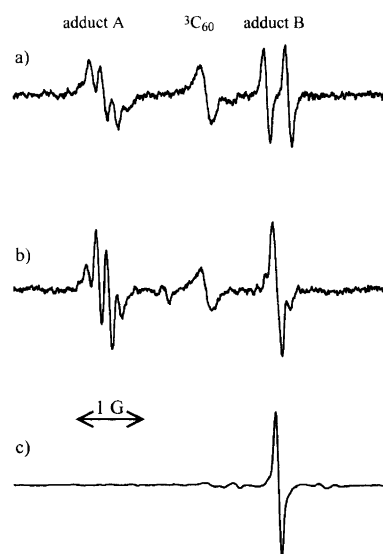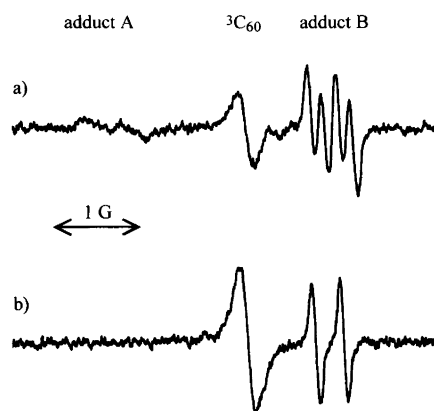
the smaller one must then belong to one of the two alkyl protons. 9-Phenylanthracene leads to the same doublet as methylanthracene (Fig. 8b). Finally, intermediates B are also detected during photolysis of C_{60} with 9-bromoanthracene and 9-bromoanthracene-1,2,3,4,5, 6,7,8,10-d_9 in benzonitrile–*tert*-butylbenzene (Fig. 9), 9-bromoanthracene yielding the now familiar doublet. Owing to the presence of a heavy atom the g-factors of the bromo-containing species are shifted to larger values and the spectra appear on the low field side of C_{60}. All coupling constants, linewidths and g-factors are summarized in Table 4.

For the assignment of the intermediates B we first note that their g-factors are remarkably low and close to data
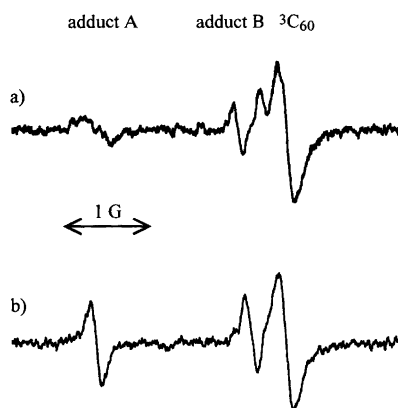
adduct A   adduct B $^3C_{60}$

Fig. 9. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C_{60} in benzonitrile–*tert*-butylbenzene (4:1) at 300 K in the presence of 1.6×10^{-4} M 9-bromoanthracene (a), and 9-bromoanthracene-1,2,3,4,5,6,7,8,10-d_9 (b).

Table 4. Hyperfine coupling constants (mG), linewidths (mG) and g-factors of C_{60} adducts in benzonitrile–*tert*-butylbenzene (4:1) at 300 K.

System	Coupling constants		ΔH_{pp}	g-factor
Anthracene (Fig. 6a)	300	$(2H_\gamma)$	$\leqslant 100$	2.00069
1-Methylanthracene	300	$(2H_\gamma)$	$\leqslant 100$	2.00069
2-Methylanthracene	300	$(2H_\gamma)$	$\leqslant 100$	2.00069
Anthracene-d_{10} (Fig. 6b)			180	2.00068
Anthracene-1,2,3,4,5,6,7,8-d_8 (Fig. 6c)	300	$(2H_\gamma)$	$\leqslant 100$	2.00069
Anthracene-1,2,3,4,5,6,7,8,9-d_9 (Fig. 6d)	300	$(1H_\gamma)$	150	2.00068
9-Methylanthracene (Fig. 7a)	300	$(1H_\gamma)$	70	2.00073
9-Methylanthracene-1,2,3,4,5,6,7,8,10-d_9 (Fig. 7b)			140	2.00071
9,10-Dimethylanthracene (Fig. 7c)			55	2.00073
9-Hydroxymethyl-anthracene (Fig. 8a)	320 150	$(1H_\gamma)$ $(1H_\delta)$	$\leqslant 100$	2.00073
9-Phenylanthracene (Fig. 8b)	320	$(1H_\gamma)$	$\leqslant 100$	2.00078
9-Bromoanthracene (Fig. 9a)	350	$(1H_\gamma)$	120	2.00156
9-Bromoanthracene-1,2,3,4,5,6,7,8,10-d_9 (Fig. 9b)			150	2.00156

reported for the monoanion of C_{60} and for anions of C_{60}-molecule adducts.[33,34] Further, the 9- and 10-protons of the anthracene residue are equivalent. Hence, we suggest that species B are the anions of the Diels–Alder adducts between C_{60} and the anthracenes, and that their formation is facilitated by the polar solvent. In fact, it is known that such adducts are as easily reduced as the parent C_{60}.[7c] It appears very unlikely that we observe the triplet states of the Diels–Alder adducts since for

such species much larger linewidths have been reported.[20] However, the nature of the counter radical cation is unclear.

The rather small hyperfine coupling constants of the adducts B are compatible with previous findings: at 160 K the anion of 1,2-$C_{60}H_2$ shows $g = 2.000$ and a linewidth of 3 G[34] which may bury only a small unresolved hyperfine coupling. For the anionic part of a donor$^+$–bridge-$\dot{C}_{60}^-$ supramolecule $g = 1.990$ and a linewidth of 1.4 G have been reported at 80 K,[35] and the hyperfine interaction to adjacent protons was not resolved. Obviously, in the anions of 1,2-adducts to C_{60} the spin density distribution is spread out more over the fullerene part than in monoadducts of radicals. This was confirmed by spin density calculations using RHF/MNDO in the PM3 parametrization. For the anion of $C_{60}H_2$ the total spin populations are 2.2×10^{-4} at the hydrogen atoms and 1.8×10^{-3} at the carbon atoms neighboring the addition sites whereas the H-atom of the $C_{60}H$ radical carries a PM3 spin density of about 0.03.[25c] For the anion of the anthracene adduct we obtained a similar spread of spin distribution over the C_{60} part and very small spin populations at the anthracene atoms such as about 6×10^{-6} for the coupling protons. These results support the assignment of the adducts B to anions of Diels–Alder adducts, but are not strong evidence since very small hyperfine coupling constants are generally difficult to interpret.

We have also tried to generate the anionic species electrochemically. In our hands, reduction of the parent C_{60} in benzonitrile at -0.4 V (vs. SCE) gave initially the two narrow lines which have been extensively discussed recently.[36] Later on, an additional broad linewidth $g = 2.0000$ appeared superimposed, as also observed in earlier work.[37] *In-situ* electrochemical reduction of the thermally synthesized Diels–Alder adduct of C_{60} and 9,10-dimethylanthracene at a potential of about -0.5 V vs. SCE in benzonitrile–*tert*-butylbenzene leads to the observation of three single-line species. In the beginning the EPR-spectrum was a superposition of a relatively broad line with $g = 2.0005$ and 1.6 G linewidth and a narrow line with $g = 2.0007$ and 0.4 G linewidth, and later on an additional line with $g = 2.0008$ and 0.7 G linewidth grew in. Of the three species the intermediate with $g = 2.0007$ is closest to the adduct B found photochemically (Table 4, $g = 2.00073$), and the enlarged linewidth in the electrochemical experiments may be due to degenerate electron exchange of the anions with unreduced precursor molecules, but this remains ambiguous.

Adducts to C_{70} in benzonitrile-tert-*butylbenzene.* Photolysis of C_{70} with anthracenes in the more polar solvent mixture also lead to new but very weak and only partially reproducible EPR signals, and clear signatures were obtained only for methylated anthracenes (Fig. 10). For 9-methylanthracene-1,2,3,4,5,6,7,8,10-d_9 (Fig. 10b) and 9,10-dimethylanthracene (Fig. 10c) three single-line isomers 1, 2 and 3 with some indications of further
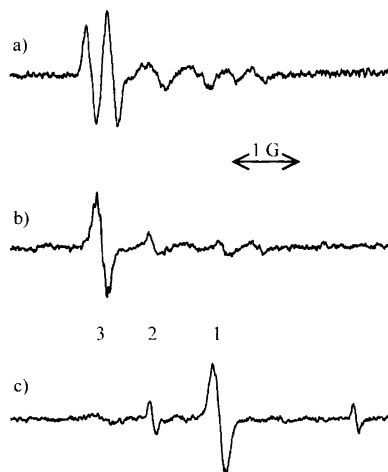
Fig. 10. EPR spectra observed during photolysis of a solution of 1.5×10^{-4} M C_{70} in benzonitrile–tert-butylbenzene (4:1) at 300 K in the presence of 10^{-4} M 9-methylanthracene (a), 9-methylanthracene-1,2,3,4,5,6,7,8,10-d_9 (b), and 9,10-dimethylanthracene (c).

hyperfine splitting appear in addition to adducts of type A and lower g adducts to the C_{60} impurity. For 9-methylanthracene (Fig. 10a) the isomer 3 with a doublet splitting is certainly not due to type A adducts but the other signals may well be. The data of the new species are given in Table 5. It is noteworthy that the coupling constants of the adducts obtained for 9-methylanthracene and C_{70} or C_{60} in the polar solvent are identical. Hence, the species of Fig. 10 may well also be radical anions of Diels–Alder adducts. Furthermore, as for adducts of type A, the g-factors of the C_{70} adducts are generally larger than those of the C_{60}-derived species. Because there are only a few examples the assignment of the isomers 1, 2 and 3 to the different sites of addition to C_{70} is not yet possible.

Formation mechanisms. We have pointed out above that the intermediates observed in this work are probably not primary photochemical reaction products between the fullerenes and the anthracenes but may have a more

Table 5. Hyperfine coupling constants (mG), linewidths (mG) and g-factors of C_{70} adducts in benzonitrile–tert-butylbenzene (4:1) at 300 K.

System	Isomer	Coupling constants		ΔH_{pp}	g-factor
9-Methylanthracene (Fig. 10a)	3	300	$(1H_\gamma)$	110	2.00291
9-Methylanthracene-1,2,3,4,5,6,7,8,10-d_9 (Fig. 10b)	1[a]				1.00191
	2[a]				2.00248
	3[a]				2.00291
9,10-Dimethylan-thracene (Fig. 10c)	1[a]				2.00191
	2			60	2.00248
	3			250	2.00290

[a] Partially resolved hyperfine structure.

complicated formation mechanism. This point is strengthened by the finding that for other concentrations and temperatures than those employed here, additional EPR signals appear in many cases which may be multiple adducts, as is common in alkyl radical additions.[25a,38]

The intermediates of type A in non-polar solvents have been reasonably explained in terms of the general structure III. The residue R can be any diamagnetic group and even a hydrogen atom or the replica of the basic structure. In the latter case the intermediates are the biradicals II. Since the spectra did not change with the solvents used which would deliver different groups R we favor the explanation of biradical II. One attractive pathway for its formation starts from excitation of preformed 2+4 Diels–Alder adducts which are known to absorb in the applied wavelength region[6] and are expected to be photochemically reactive. Reaction with the ground state Diels–Alder adduct may lead directly to biradicals II by coupling at the anthracene residues in position 10. In analogy to the parent anthracenes the dimerization at the site of the substitution is expected to be strongly sterically hindered,[39] and this may explain why our intermediates A for the 9-substituted anthracenes carry the substituent at the carbon atom linked to the fullerene and why no adducts A are formed for 9,10-disubstituted anthracenes.

In the more polar solvent, the preformed Diels–Alder adduct may undergo a photochemical electron transfer reaction with a suitable electron donor. From the Rehm–Weller equation and the photophysical properties and reduction potentials of Diels–Alder adducts,[7c] which are similar to those of the fullerenes,[33,40] an electron transfer to the triplet state of the adducts is not feasible from the solvents benzonitrile and tert-butylbenzene and from the fullerenes, but is possible for anthracene and its derivatives. The observation of anthracene cations could be obscured by exchange broadening of their EPR lines.

References

1. For review, see (a) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* 32 (1993) 1138; (b) Taylor, R. and Walton, D. R. M. *Nature 363* (1993) 685.
2. Wilson, S. R., Kaprinidis, N., Wu Y. and Schuster, D. I. *J. Am. Chem. Soc. 115* (1993) 8495.
3. Zhang, X., Romero, A. and Foote, C. S. *J. Am. Chem. Soc. 115* (1993) 11024.
4. Lem, G., Schuster, D. I., Courtney, S. H., Lu, Q. and Wilson, S. R. *J. Am. Chem. Soc. 117* (1995) 554.
5. Akasaka, T., Mitsuhida, E., Ando, W., Kobayashi, K. and Nagase, S. *J. Am. Chem. Soc. 116* (1994) 2627.
6. Goldshleger, N. F., Denisov, N. N., Lobach, A. S., Nadtochenko, V. A., Shulga, Y. M. and Vasilets, V. N. *Dokl. Chem. 340* (1995) 41.

7. (a) Tsuda, M., Ishida, T., Nogami, T., Kurono, S. and Ohashi, M. *J. Chem. Soc., Chem. Commun.* (1993) 1296; (b) Schlueter, J. A., Seaman, J. M., Taha, S., Cohen, H., Lykke, K. R., Wang, H. H. and Williams, J. M. *J. Chem. Soc., Chem. Commun.* (1993) 972; (c) Komatsu, K., Murata, Y., Sugita, N., Takeuchi, K. and Wan, T. S. M. *Tetrahedron Lett. 34* (1993) 8473.

8. Arbogast, J. W., Darmanyan, A. P., Foote, C. S., Rubin, Y., Diederich, F. N., Alvarez, M. M., Anz, S. J. and Whetten, R. L. *J. Phys. Chem. 95* (1991) 11.

9. Palit, D. K., Sapre, A. V., Mittal, J. P. and Rao, C. N. R. *Chem. Phys. Lett. 195* (1992) 1.

10. Arbogast, J. W. and Foote, C. S. *J. Am. Chem. Soc. 113* (1991) 8886.

11. Birks, J. B. *Photophysics of Aromatic Molecules,* Wiley-Interscience: New York, 1970.

12. Zeng, Y., Biczok, L. and Linschitz, H. *J. Phys. Chem. 96* (1992) 5237.

13. Wasielewski, M. R., O'Neil, M. P., Lykke, K. R., Pellin, M. J. and Gruen, D. M. *J. Am. Chem. Soc. 113* (1991) 2774.

14. Klemt, R., Roduner, E. and Fischer, H. *J. Am. Chem. Soc. 117* (1995) 8019.

15. Charlton, J. L. and Agagnier, R. *Can. J. Chem. 51* (1973) 1852.

16. (a) Geske, D. H. and Maki, A. H. *J. Am. Chem. Soc. 82* (1960) 2671; (b) Poole, C. P. *Electron Spin Resonance,* Wiley-Interscience, New York 1970.

17. Closs, G. L., Gautam, P., Zhang, D., Krusic, P. J., Hill, S. A. and Wasserman, E. *J. Phys. Chem. 96* (1992) 5228.

18. Krusic, P. J., Roe, D. C., Johnston, E., Morton, J. R. and Preston, K. F. *J. Phys. Chem. 97* (1993) 1736.

19. Berndt, A. in *Landolt-Börnstein Vol. II/9b,* Fischer, H., Hellwege, K.-H., Eds., Springer-Verlag: Berlin, Heidelberg, New York 1977, p. 689.

20. Dinse, K.-P. *Personal communication.*

21. Morton, J. R., Negri, F., Preston, K. F. and Ruel, G. *J. Phys. Chem. 99* (1995) 10114.

22. Morton, J. R., Preston, K. F., Krusic, P. J., Hill, S. A. and Wasserman, E. *J. Phys. Chem. 96* (1992) 3576.

23. Krusic, P. J. *Personal communication.*

24. Keizer, P. N., Morton, J. R., Preston, K. F. and Krusic, P. J. *J. Chem. Soc., Perkin Trans. 2* (1993) 1041.

25. (a) Morton, J. R., Negri, F. and Preston, K. F. *Can. J. Chem. 72* (1994) 776; (b) Percival, P. W. and Wlodek, S. *Chem. Phys. Lett. 196* (1992) 317; (c) Matsuzawa, N., Dixon, D. A. and Krusic, P. J. *J. Phys. Chem. 96* (1992) 8317; (d) Claxton, T. A. and Cox, S. F. J. *Chem. Phys. Lett. 207* (1993) 31; (e) Claxton, T. A. and Graham, J. *J. Phys. Chem. 97* (1993) 4621.

26. Taylor, R., Hare, J. P., Abdul-Sada, K. and Kroto, H. W. *J. Chem. Soc., Chem. Commun.* (1990) 1423.

27. Borghi, R., Lunazzi, L., Placucci, G., Krusic, P. J., Dixon, D. A. and Knight, L. B. *J. Phys. Chem. 98* (1994) 5395.

28. Keizer, P. N., Morton, J. R. and Preston, K. F. *J. Chem. Soc., Chem. Commun.* (1992) 1259.

29. Morton, J. R., Negri, F. and Preston, K. F. *Chem. Phys. Lett. 218* (1994) 467.

30. Morton, J. R., Preston, K. F. and Negri, F. *Chem. Phys. Lett. 221* (1994) 59.

31. Lappas, A., Vavekis, K. and Prassides, K. *J. Chem. Soc., Chem. Commun.* (1994) 2743.

32. Reid, I. D. and Roduner, E. *Hyperfine Interact. 86* (1994) 809.

33. Dubois, D., Jones, M. T. and Kadish, K. M. *J. Am. Chem. Soc. 114* (1992) 6446.

34. Boulas, P., D'Souza, F., Henderson, C. C., Cahill, P. A., Jones, M. T. and Kadish, K. M. *J. Phys. Chem. 97* (1993) 13435.

35. Sariciftci, N. S., Wudl, F., Heeger, A. J., Maggini, M., Scorrano, G., Prato, M., Bourassa, J. and Ford, P. C. *Chem. Phys. Lett. 247* (1995) 510.

36. (a) Stasko, A., Brezova, V., Biskupic, S., Dinse, K.-P., Schweitzer, P. and Baumgarten, M. *J. Phys. Chem. 99* (1995) 8782; (b) Brezova, V., Stasko, A., Rapta, P., Domschke, G., Bartl, A. and Dunsch, L. *J. Phys. Chem. 99* (1995) 16234.

37. (a) Greany, M. A. and Gorun, S. M. *J. Phys. Chem. 95* (1991) 7142; (b) Allemand, P.-M., Srdanov, G., Koch, A., Khemani, K., Wudl, F., Rubin, Y., Diederich, F., Alvarez, M. M., Anz, S. J. and Whetten, R. L. *J. Am. Chem. Soc. 113* (1991) 2780; (c) Schell-Sorokin, A. J., Mehran, F., Eaton, G. R., Eaton, S. S., Viehbeck, A., O'Toole, T. R. and Brown, C. A. *Chem. Phys. Lett. 195* (1992) 225.

38. Krusic, P. J., Wasserman, E., Keizer, P. N., Morton, J. R. and Preston, K. F. *Science 254* (1991) 1184.

39. Bouas-Laurent, H., Castellan, A. and Desvergne, J.-P. *Pure Appl. Chem. 52* (1980) 2633.

40. Dubois, D., Moninot, G., Kutner, W., Jones, M. T. and Kadish, K. M. *J. Phys. Chem. 96* (1992) 7137.