Electron Paramagnetic Resonance Spectra of R-C_{60} Radicals. Evidence for $RC_{60}C_{60}R$ Dimers†

J. R. Morton,[a] K. F. Preston,[a] P. J. Krusic[b] and E. Wasserman[b]
[a] *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9*
[b] *Central Research and Development Department, E.I. du Pont de Nemours & Company, Wilmington, DE, USA 19880-0328*

Alkyl radicals generated in solution by UV photolysis add to C_{60} to form adducts of the type RC_{60}, whose EPR spectra are discussed. When R = CCl_3, CBr_3, *tert*-butyl or 1-adamantyl, the spectrum is sufficiently powerful to permit the detection of several ^{13}C satellites associated with the C_{60} component of the free radical. It is concluded from the intensities and hyperfine interactions of these satellites that *ca*. 2/3 of the unpaired spin population is located on the three carbon atoms *ortho* to that bearing the incoming radical R.

There is evidence from the temperature dependence of the EPR spectra of certain RC_{60} radicals that they exist in equilibrium with their dimer, $RC_{60}C_{60}R$. For R = isopropyl, *tert*-butyl, 1-adamantyl and CCl_3, the enthalpy of dissociation is 35.5, 22.0, 21.6 and 17.1 kcal mol^{-1} respectively.

The discovery and identification of a new class of quasi-aromatic molecules, the fullerenes,[1] has generated enormous interest in many branches of chemistry and physics. The most fascinating of these molecules is undoubtedly the highly symmetric C_{60}, a hitherto unknown allotrope of carbon.[2] In the present article we begin to explore the chemical reactivity of C_{60} by studying, with the aid of EPR spectroscopy, its reactions with free radicals.

$$nR + C_{60} \longrightarrow R_nC_{60}$$

EPR spectroscopy is the ideal technique for the study of such reactions, since adducts R_nC_{60} are paramagnetic provided n is an odd number. Indeed, we have already discussed elsewhere[3] the EPR spectra of $(C_6H_5CH_2)_3C_{60}$ and $(C_6H_5CH_2)_5C_{60}$. We report here the detection and identification by EPR spectroscopy of several free radicals of the form RC_{60}, where R is, in general, an alkyl radical.

Experimental

A mixture of C_{60} (*ca*. 90%) and C_{70} (*ca*. 10%) was purchased from Texas Fullerenes, Houston, TX. Its components were separated chromatographically using activated, neutral alumina (Aldrich) and hexane as the eluent.[4] Reagents enriched in the isotopes ^{13}C or ^2H (D) were purchased from MSD Isotopes, Pointe Claire, Que.

Solutions of C_{60} in various dried, degassed solvents (benzene, toluene, *tert*-butylbenzene or CCl_4) were prepared in a glove-box continuously flushed with dry argon or nitrogen. Two methods were used to generate the intermediate R radicals in these solutions. In the first method, the R radicals were generated by photolysis of a compound RX. For example, UV photolysis of a saturated solution of C_{60} in CCl_4 yielded the spectrum of $C_{60}CCl_3$. A more general method, however, was the following: *ca*. 10 mg of an alkyl bromide RBr were added to 180 mm^3 of a saturated solution of C_{60} in *tert*-butylbenzene contained in a 4 mm ID, thin-walled, Suprasil™ EPR tube. If the bromide was volatile, the solution containing C_{60} was transferred to a vacuum line and the solute added by distillation. The tube was then sealed and transferred to the cavity of the EPR spectrometer where it was photolysed *in situ* at various temperatures. A second method involved *tert*-butoxy radical intermediates. About 20 mm^3 di-*tert*-butyl peroxide and an equal volume of a hydrocarbon RH were added to 160 mm^3 of C_{60} dissolved in benzene contained in a SuprasilTH EPR tube. This solution was also photolysed inside the EPR cavity.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{UV} 2(CH_3)_3CO$$

$$(CH_3)_3CO + RH \longrightarrow R + (CH_3)_3COH$$

In both methods the light-source was a high pressure Hg–Xe lamp, its light being focussed onto the sample after passing through an aqueous $NiSO_4/CoSO_4$ filter.

Two EPR spectrometers were used: a Varian E-12 spectrometer (NRCC) equipped with the usual accessories for readout of the magnetic field, microwave frequency and temperature. The other spectrometer (du Pont) was a Bruker ESP 300 with multichannel analyser for signal enhancement. The spectrometers were operated at a modulation frequency of 25 kHz because of the very sharp lines and small hyperfine interactions sometimes encountered.

Results and Discussion

The EPR Spectra of RC_{60} *Radicals.*—The simplest experiment in the present series is the UV photolysis of a solution of C_{60} in CCl_4. After only a few seconds irradiation, a powerful signal at $g = 2.0033$ was observed, flanked by satellites corresponding to ^{13}C hyperfine interactions of 29.6, 18.1 and 8.8 G* [Fig. 1(*a*)]. The intensities of the two outer pairs of satellites were correct for hyperfine interactions with single carbon nuclei, whereas the innermost pair of satellites were four times as strong, indicating equal hyperfine interactions with four ^{13}C nuclei. In Fig. 1(*b*) the result of carrying out the same experiment with ^{13}C-enriched CCl_4 is shown: clearly the 29.6 G hyperfine interaction originates with the CCl_4 molecule. In spite of the lack of ^{35}Cl and ^{37}Cl hyperfine structure, there can be little doubt that the spectrum is that of $C_{60}CCl_3$.

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* 1 G = 0.1 mT.

Table 1 Hyperfine interactions (G) and enthalpies of dimerization (kcal mol^{-1}) for RC_{60} radicals

R	hfi (H/D)	hfi (C/P)	ΔH	T/K
CH_3CH_2	2 H = 0.28 3 H = 0.13			473[a,b]
$CH_3{}^{13}CH_2$		1 C = 15.5		473[c]
$(CH_3)_2CH$	1 H = 0.48 6 H = 0.15		35.5	420–450[b]
$C_6H_5CH_2$	2 H = 0.42 2 H = 0.19			350[d,e]
$C_6H_5{}^{13}CH_2$	2 H = 0.42 2 H = 0.19	1 C = 14.9		350[c]
$C_6D_5CH_2$	2 H = 0.42			350[c,d,e]
CCl_3		1 C = 29.6 1 C = 18.1 4 C = 8.8	17.1	250–310[f]
$^{13}CCl_3$		1 C = 29.6		310[c,f]
CBr_3		1 C = 35.3 1 C = 18.0	17.0	300–380[g]
$(CH_3)_3C$	9 H = 0.17	1 C = 17.8 1 C = 13.1 2 C = 9.39 2 C = 8.86 3 C = 5.59 2 C = 4.48 2 C = 4.02	22.0	300–400[b,d]
$(CD_3)_3C$	9 D = 0.028	2 C = 3.59 4 C = 2.41 8 C = 0.84		370[c,d]
$(CH_3)_3C$	3 H = 0.34 6 H = 0.085			225
$(CH_3)_3{}^{13}C$	9 H = 0.17	1 C = 13.1		370[c,d]
$^{13}CH_3(CH_3)_2C$	9 H = 0.17	1 C = 0.40		370[b,c]
$(CH_3)_3Si$	9 H = 0.11			320[d]
$(CH_3CH_2)_3C$	3 H = 0.34 3 H = 0.17			350[d]
$(CH_3CH_2)_3Si$	3 H = 0.34 3 H = 0.17			350[d]
1-$C_{10}H_{15}$[h]	3 H = 0.25 6 H = 0.044	1 C = 17.75 1 C = 12.34 2 C = 9.30 2 C = 8.79 3 C = 5.59 2 C = 4.48 2 C = 4.03	21.6	300–400[d]
$(C_6H_5)_3Ge$	? H = 0.04			320[d]
$PO(OCH_3)_2$	6 H = 0.12	1 P = 64.2		300[d]
$PO(OCH_2CH_3)_2$		1 P = 63.7		300[d]

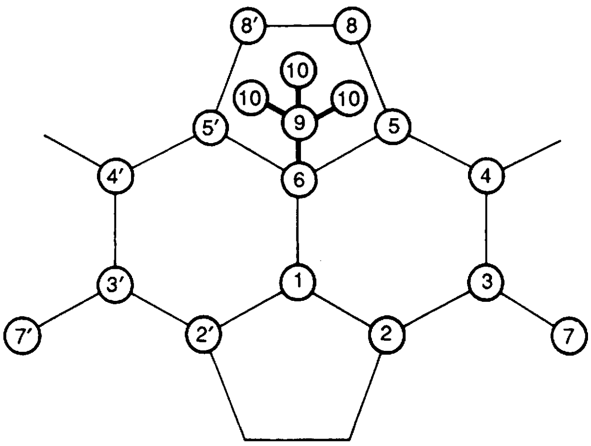
[a] Except where noted [f,g], all *g*-factors lay in the range 2.0023–2.0025. [b] UV photolysis of RBr. [c] Isotopically enriched reagent used. [d] Photolysis of $(CH_3)_3COOC(CH_3)_3$ + RH. [e] Using toluene as solvent. [f] Photolysis of CCl_4 containing dissolved C_{60} ($g = 2.0034$). [g] Photolysis of CBr_4 dissolved in toluene/C_{60} ($g = 2.0091$). [h] 1-Adamantyl.

$$CCl_4 \xrightarrow{UV} CCl_3 + Cl$$

$$C_{60} + CCl_3 \longrightarrow C_{60}CCl_3$$

Multiple addition of CCl_3 radicals would have resulted in more complex spectra from samples prepared with ^{13}C-enriched CCl_4. Indeed, on prolonged photolysis the sharp spectrum of $C_{60}CCl_3$ was replaced by broad, poorly resolved signals which may be evidence of multiple CCl_3 addition.

The radical $C_{60}CCl_3$ has a single plane of symmetry passing through the carbon of the CCl_3 ligand (C-9) and two carbons on the C_{60} surface shared by a pair of hexagons (C-6 and C-1). Prior to attack by the CCl_3 radical, there was a double bond between C-1 and C-6, and so an important canonical form of the free radical $C_{60}CCl_3$ will have the unpaired spin in a 2p orbital on Cp1. We therefore assign the 18.1 G hyperfine interaction to C-1. Two other important canonical forms of $C_{60}CCl_3$ will have unpaired spin in 2p orbitals on C-3, C-3′ and C-5, C-5′, and we therefore assign to each of them the 8.8 G hyperfine interaction. Such an assignment is consistent with the observation that the latter satellites are four times stronger than those due to C-1 and C-9. The spectrum of $C_{60}CBr_3$ was exactly analogous



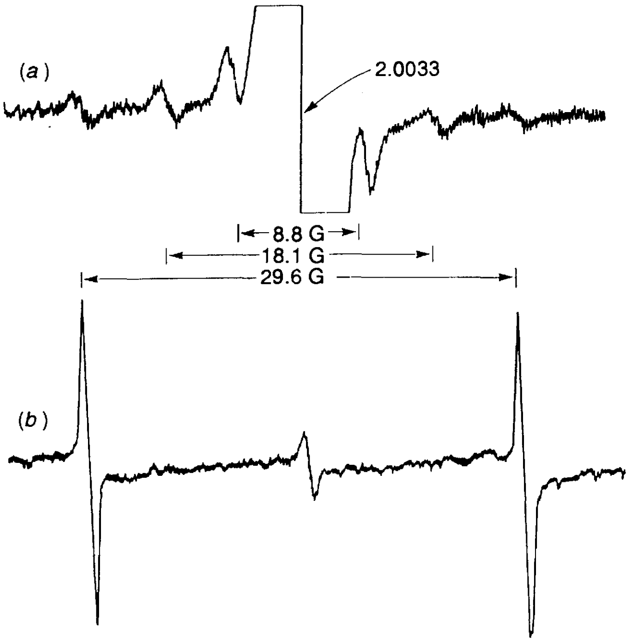


Fig. 1 The EPR spectrum of a solution of C_{60} in CCl_4 photolysed for *ca.* 20 s at 320 K: (*a*) using normal CCl_4, (*b*) using CCl_4 enriched in the isotope ^{13}C

to that of $C_{60}CCl_3$ (Table 1), except that the hyperfine interaction of C-9 has increased to 35.3 G, and the smaller interactions of C-3, C-3′, C-5 and C-5′ were not resolved from the central line.

The isotropic ^{13}C hyperfine interactions associated with the C_{60} portion of RC_{60} radicals provide a qualitative measure of the unpaired spin population distribution over the C_{60} surface. These hyperfine interactions arise from spin population in carbon 1s and 2s orbitals even though the overall s-character is evidently rather small. The dominant contributors to the singly occupied molecular orbital (SOMO) are undoubtedly the various C(2p) orbitals. If it is assumed that the isotropic ^{13}C hyperfine interactions of carbons 1, 3, 3′, 5 and 5′ are in direct proportion to their respective 2p character, and that the unpaired spin population is confined to these five atoms, then the unpaired spin population at C-1 is *ca.* 0.33, and at C-3, C-3′, C-5 and C-5′ *ca.* 0.17 each.

Some confirmation of these estimates can be found in the data for the substituted ethyl radical $CCl_3CH_2CBu^t{}_2$.[5] In this radical the α-^{13}C nucleus (which carries the unpaired spin) has a hyperfine interaction of 45.6 G, and the γ-^{13}C nucleus (the carbon of the CCl_3 group) has a hyperfine interaction of 34.0 G. In $C_{60}CCl_3$, if C-1, C-5 and C-5′ are regarded as α (spin-bearing) carbons, their respective spin-populations can be estimated as fractions of 45.6, namely 0.40, 0.19, 0.19 respectively. Moreover, the prorated hyperfine interaction of the γ-^{13}C nucleus (0.78 × 34.0 = 26.5 G) is in excellent agreement with the experimental value (29.8 G).

As a final point of comparison, we mention the spectra of the two dialkoxyphosphonyl adducts to the C_{60} molecule: $OP(OCH_3)_2C_{60}$ and $OP(OCH_2CH_3)_2C_{60}$. When diethoxyphosphonyl radicals are added to ethene, the resulting radical has an isotropic ^{31}P hyperfine interaction of 90.6 G.[5] In the present case (Table 1) the ^{31}P hyperfine interaction is approximately 64 G, and, as before, arises primarily from unpaired spin population on atoms adjacent (*ortho*) to C-6: C-1, C-5 and C-5′. If the spin population at C-1 is twice that at C-5 and C-5′, as concluded above, then the ^{31}P hyperfine interaction in $OP(OCH_2CH_3)_2C_{60}$ is indicative of a spin population at C-1 of *ca.* 0.35, a value intermediate between the two previous estimates.

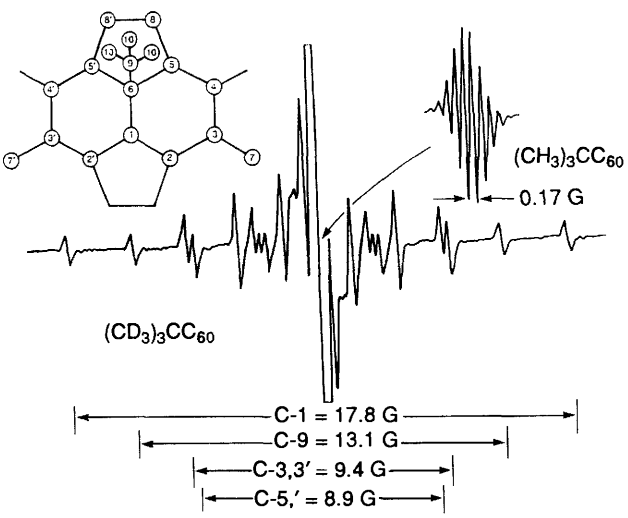


Fig. 2 The EPR spectrum of $(CD_3)_3CC_{60}$ in benzene at 350 K, showing ^{13}C hyperfine satellites. Inset: the spectrum of $(CH_3)_3CC_{60}$.

For R = perdeuterio-*tert*-butyl the spectrum shown in Fig. 2 was obtained, in which many ^{13}C hyperfine satellites of various intensities are seen. The two largest hyperfine interactions were of unit intensity (*ca.* 0.5% of the central line), and enrichment experiments proved that the 13.1 G ^{13}C hyperfine interaction belonged to C-9, a value consistent with other γ-^{13}C hyperfine interactions,[5] but a remarkable decrease from the 29.6 G obtained for R = CCl_3 and 35.3 G for R = CBr_3. The carbon generating the 17.8 G hyperfine interaction was assigned to C-1, a value almost identical to those of $C_{60}CCl_3$ (18.1 G) and $C_{60}CBr_3$ (18.0 G). The next-largest hyperfine interactions (9.4 and 8.9 G) are twice as intense as the outside satellites, and were assigned to C-3, C-3′ and C-5, C-5′ (or *vice versa*), values also close to those obtained for $C_{60}CCl_3$ (8.8 G). Thus, insofar as the hyperfine interaction is a measure of spin-population distribution, it would appear that the spin population at C-1, C-3, C-3′, C-5 and C-5′ is essentially independent of the nature of R. The 5.6 G ^{13}C hyperfine lines are three times as intense as the outside satellites, but cannot be assigned to the methyl carbon nuclei since these have a 0.4 G hyperfine interaction (determined by isotopic enrichment) unresolved in Fig. 2. We therefore conclude that the 5.6 G splitting is due to an accidental equality of two hyperfine interactions: those of C-6 (unit intensity) and perhaps C-7 and C-7′.

We assume that the ^{13}C hyperfine interactions of C-1, C-3, C-3′, C-5 and C-5′ are positive in sign, *i.e.* their carbon atoms bear positive spin population. The spectrum shown in Fig. 2 indicates, however, that in RC_{60} radicals there are significant, albeit smaller, unpaired spin populations at several other carbon nuclei. These may be either positive or negative in sign, the latter arising *via* bond polarisation.[6] It will only be possible to assign these hyperfine interactions to specific carbon atoms on the C_{60} surface with the aid of molecular orbital calculations capable of reliably predicting positive and negative spin-population distributions. To our knowledge, such calculations, even for HC_{60}, have not yet appeared in the literature.

Confirmatory evidence for the addition of free radicals to C_{60} can often be found in the proton hyperfine structure. For example, when R = ethyl, the hyperfine structure is that of two protons at 0.29 G, three at 0.13 G; and with R = isopropyl the hyperfine structure is that of one proton at 0.48 G, six at 0.15 G. The *tert*-butyl adduct has a spectrum of 10 lines 0.17 G apart with the binomial relative intensities (1:9:36:84:126:126:84:36:9:1) required for hyperfine interactions with nine equivalent protons. The proton hyperfine structure of the silicon-containing analogue, $C_{60}Si(CH_3)_3$, is identical except

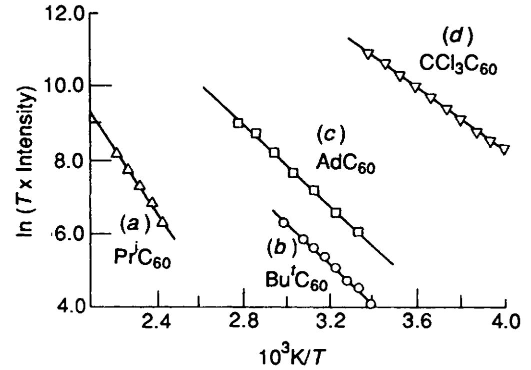


Fig. 3 Graphs of ln(T × Intensity) *vs.* 1000/T for the EPR spectra of (a) $(CH_3)_2CHC_{60}$, (b) $(CD_3)_3CC_{60}$, (c) 1-$C_{10}D_{15}C_{60}$ and (d) CCl_3C_{60}. Plotting ln(T × Intensity) instead of simply ln(Intensity) corrects for loss of signal due to the change in the Boltzmann distribution. Intensity = $\Delta B^2 I$, where ΔB is the maximum-slope line-width and I is the amplitude of the first derivative presentation of the signal.

for a smaller spacing (0.11 G) and is similarly diagnostic of $Si(CH_3)_3$ addition to the C_{60} molecule.

Two other examples of proton hyperfine structure are of particular interest: those of $C_{60}C(CH_2CH_3)_3$ and $C_{60}Si(CH_2CH_3)_3$. Their spectra consist of 10 lines, equally spaced 0.17 G apart. The relative intensities of the 10 lines are approximately 1:3:6:9:12:12:9:6:3:1, a manifold which could not be associated with the three methyl groups (requiring a binomial intensity distribution, see above) but which was analysed with the aid of computer simulation as three protons at 0.17 G, and another three at 0.34 G. Such a combination requires a hyperfine manifold of relative intensities 1:3:6:10:12:12:10:6:3:1, in excellent agreement with experiment. No other simulation was acceptable. This hyperfine pattern was assigned to the six CH_2 protons of the three ethyl ligands: each CH_2 group of each ethyl ligand contributes one proton at 0.17 G, and one at 0.34 G. These results indicate that although there appears to be free rotation about the R–C_{60} bond, there is no free rotation about the C–CH_2 or Si–CH_2 bonds when R is $C(CH_2CH_3)_3$ or $Si(CH_2CH_3)_3$. A similar conclusion may be drawn for $(CH_3)_3C$–C_{60} from the observation of a different hyperfine manifold at 225 K to that at 320 K (Table 1), indicating the onset of hindered rotation. The barrier to the rotation was calculated from line broadening measurements to be 9 ± 1 kcal mol^{-1}.*

In the formulation RC_{60} there are still many double bonds, and it could be argued that some of these may have been attacked by pairs of R radicals which, being remote from C-1, do not reveal their presence by ^{13}C hyperfine interactions. Indeed, in the case of *tert*-butyl-C_{60} and 1-adamantyl-C_{60}, the spectra reported in Table 1 were superimposed on a broad (ΔB = 1.5 G) line without hyperfine structure probably due to multiple addition of *tert*-butyl or 1-adamantyl radicals to C_{60}. With prolonged UV photolysis only the broad line was observed, indicating that the initially-formed mono-adduct had also been attacked by photolytically-generated alkyl radicals.

Experimental determinations[7,8] of the C–C bond lengths and theoretical calculations[9,10] show that the principal Kékulé structure of C_{60} is that in which the hexagon-fusions are double bonds. The chemical reactivity towards organic and transition-metal reagents[7,11–13] conforms with the notion of limited aromaticity, in spite of earlier claims to the contrary.[9,14] In its reaction with free radicals, C_{60} behaves very much like an alkene or a superbenzopyracylene, forming simple RC_{60} adducts. The unpaired spin in these adducts is not extensively delocalized, but is essentially confined to a few atoms near the point of attack.

EPR Evidence for $RC_{60}C_{60}R$ *Dimers*.—The intensity of the spectra of certain RC_{60} radicals exhibited curious behaviour as the temperature was raised. Instead of the expected slight decrease associated with the change in the Boltzmann distribution, the spectra increased markedly in intensity. A plot of ln(T × Intensity) against 1000/T gave a straight line over the temperature range indicated in Table 1 (Fig. 3). We attribute this behaviour to the thermal dissociation of a dimer.

$$RC_{60}\text{–}C_{60}R \rightleftharpoons 2RC_{60}$$

Assuming negligible dissociation of the dimer, the slope of the graph is proportional to the enthalpy change ΔH for the above dissociation. The following values were obtained: $(CH_3)_2CHC_{60}$, 35.5; $(CH_3)_3CC_{60}$, 22.0; $C_{10}H_{15}C_{60}$, 21.6; CCl_3C_{60}, 17.1 kcal mol^{-1}. These values, which are much less than typical C–C bond strengths (*ca.* 80 kcal mol^{-1}), indicate that the strength of the RC_{60}–$C_{60}R$ bond is dependent on the steric hindrance (or lack of it) between the two R groups. This suggests that the C_{60}–C_{60} bond is between carbon atoms close to C-6 on the C_{60} surface. Since C-1 and C-5 are *ortho* to C-6 (*i.e.* probably too close), we suspect that the dimer is bound C-3–C-3.

The existence of a dimerisation process may explain why our attempts to prepare HC_{60}, FC_{60}, CH_3C_{60} and other RC_{60} radicals with small R have failed. In such instances, the C-3–C-3 bond might have normal strength, or a C-1–C-1 dimer might form. Such a dimer might not dissociate in the accessible temperature range. Alternatively, such radicals may be extremely reactive, reacting with C_{60}, with R radicals, or with the solvent. Extremely bulky R groups, on the other hand, would effectively prevent dimerisation, permitting the observation of RC_{60} radicals whose concentration is limited only by the intensity of the light-source and their rate of disappearance.

Conclusions

The Kékulé structure of C_{60} has 30 double bonds. Thus it is not surprising to find that, in its reactions with free radicals, C_{60} behaves very much like an alkene, forming adducts RC_{60}. Estimates from the ^{13}C hyperfine satellites of RC_{60} indicate that its unpaired spin is distributed over a small number of atoms close to the point of attack. When R is a rather bulky group, such as CCl_3, $(CH_3)_3C$ or $(CH_3)_2CH$, there is evidence that RC_{60} exists in equilibrium with its dimer, whose enthalpy of dissociation is between 17 and 35 kcal mol^{-1}.

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