The EPR Spectra of Free Radical Adducts of C_{70}†

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EPR spectroscopy indicates that C_{70} forms three dominant isomeric forms of R–C_{70} (where R = various photolytically generated radicals) resulting from different points of attachment of R to the C_{70} surface.

We have reported[1-3] the addition of free radicals (R) to the symmetric buckminsterfullerene C_{60},[4] forming $R_{2n+1}C_{60}$ radicals identifiable by hyperfine interactions of magnetic nuclei in R or ^{13}C nuclei of the C_{60} molecule. A noteworthy observation was that the monoadduct radicals RC_{60}, tended to dimerize, forming the diamagnetic products $RC_{60}C_{60}R$.[3,5] With the availability of pure C_{70}, we have extended the above studies to include the addition of R radicals to C_{70}, with a view to differentiating, by means of EPR spectroscopy, between the five possible isomers of RC_{70}. The possibility of isomeric forms of RC_{70} exists because unlike C_{60}, in which all carbon atoms are identical, C_{70} has five distinguishable carbon atoms with abundances 10 : 10 : 10 : 20 : 20.[6]

Mixtures of C_{60} and C_{70} (Strem, Aldrich) were separated by column chromatography, using activated, neutral alumina (Aldrich) and eluents of hexane or hexane–toluene.[7] Solutions of C_{70} in benzene are wine-red in colour, in contrast to solutions of C_{60} in benzene which are magenta. The attacking radicals R were generated by one of two methods. The first method involved UV photolysis of halides RX, for example CCl_4. The second method was indirect, using *tert*-butoxy radicals as intermediates [eqns. (1) and (2)].

$$Me_3COOCMe_3 \xrightarrow{UV} 2Me_3CO \quad (1)$$

$$Me_3CO + RH \Longrightarrow Me_3COH + R \quad (2)$$

A typical sample consisted of 350 μl of a saturated solution of C_{70} in benzene (*ca.* 0.003 mol dm^{-3}), with either 10 μl of a halide RX, or 10 μl of the hydride RH plus 1 μl of di-*tert*-butyl peroxide. The solutions, contained in 4 mm i.d. quartz tubes, were photolysed with the focused light of a high pressure Hg/Xe lamp, filtered through an aqueous $NiSO_4/CoSO_4$ filter to remove infra-red radiation. The photolysis was carried out in the cavity of a Varian E-12 spectrometer, which was equipped with the usual devices to monitor the microwave frequency and the magnetic field strength. The temperature of the sample could be varied from 77 to 450 K. Isotopically enriched chemicals were purchased from MSD Isotopes, Pointe Claire, Quebec.

The EPR spectrum obtained by photolysis of di-*tert*-butyl peroxide in the presence of C_{70} and isobutane is shown in Fig. 1. This spectrum indicates addition of *tert*-butyl radicals to the C_{70} molecule, forming Me_3C–C_{70} in three isomeric forms, having *g*-factors of 2.00271 (species **1**), 2.00248 (species **2**) and 2.00210 (species **3**). Hyperfine interactions with the protons of the *tert*-butyl groups are clearly visible in Fig. 1(*a*), and in Fig. 1(*b*) the proton hyperfine interaction is removed by the use of perdeuterio-isobutane. This spectrum more clearly demonstrates the presence of three predominant isomers of *tert*-butyl-C_{70}. Confirmation of the identity of these isomers as mono-adducts of C_{70} was provided by the use of isobutane enriched with ^{13}C on the central carbon atom. In Fig. 1(*c*), it is seen that each radical contains only one *tert*-butyl group, identified by its ^{13}C hyperfine interaction of 14.2, 11.3 or 13.8 G‡ for radicals **1**, **2** and **3** respectively.

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† NRCC No. 34210.

‡ 1 G = 10^{-4} T.

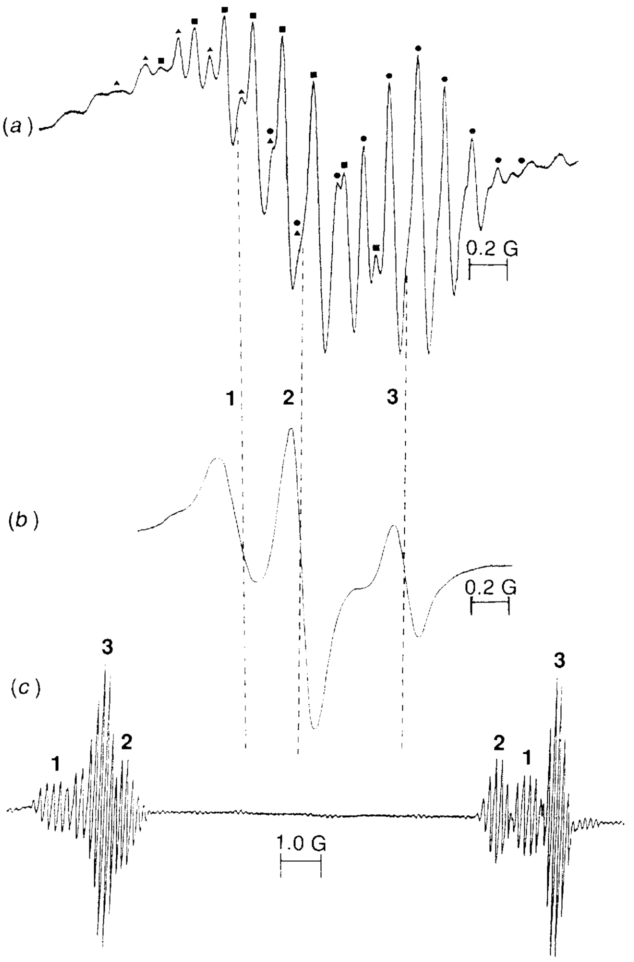


Fig. 1 EPR spectra of *tert*-butyl-C_{70} radicals, showing three isomers of (*a*) $Me_3C–C_{70}$ at 300 K, (*b*) $(CD_3)_3C–C_{70}$ at 300 K and (*c*) $Me_3{}^{13}C–C_{70}$ at 345 K. In (*a*), ▲, ■ and ● indicate the hyperfine manifolds of radicals **1**, **2** and **3**, respectively.

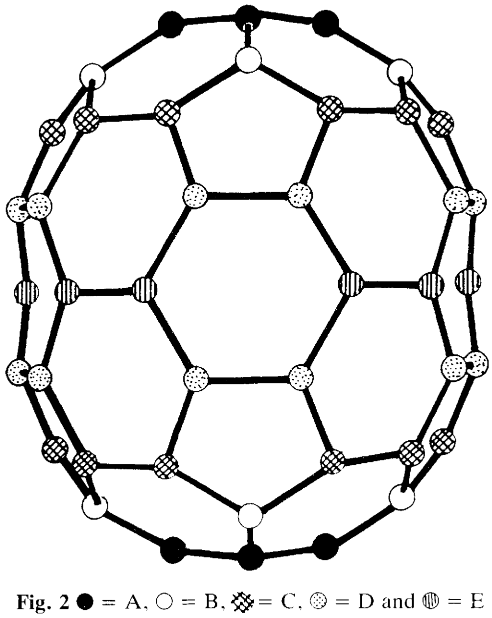
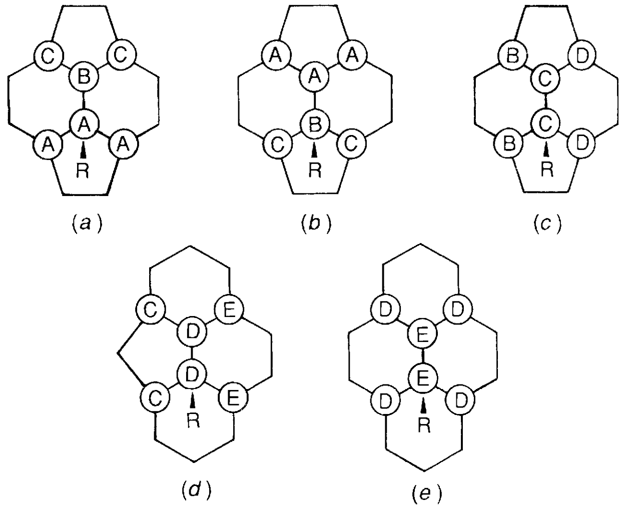


Fig. 2 ● = A, ○ = B, ▩ = C, ◎ = D and ⦶ = E



(*a*) (*b*) (*c*)

(*d*) (*e*)

Fig. 3

A similar result was obtained by photolysis of solutions of C_{70} in ^{13}C-enriched CCl_4; three isomers of CCl_3C_{70} were observed, having ^{13}C hyperfine interactions of 34.6, 30.5 and 26.7 G. Finally, photolysis of a solution of di-*tert*-butyl peroxide in benzene containing C_{70} and dimethyl phosphite gave a spectrum of three isomers of $(MeO)_2POC_{70}$ distinguishable by their ^{31}P hyperfine interactions of 71.2, 66.8 and 55.9 G. These radicals also showed additional hyperfine structure of *ca.* 0.12 G due to the six methoxy protons.

Following the convention of Taylor *et al.*[6] we label the distinct carbon atoms of C_{70} A, B, C, D and E, starting from the poles and working towards the equator. The numbers of these carbons in the C_{70} molecule are 10, 10, 20, 20 and 10, respectively.

The question is: which three of these five types of carbon atoms (Fig. 2) produce stable RC_{70} radicals? Consider the immediate locale of the carbon atom bearing the radical R. For attack at carbons A, B and C the local configuration is that of two fused hexagons with adjoining pentagons [Fig. 3(*a*), (*b*) and (*c*)]. Attack at carbon D is different in that D–D is the fusion of a pentagon and a hexagon, with adjoining hexagons Fig. 3(*d*), and attack at E is different again because E–E is the fusion of two hexagons, with adjoining hexagons Fig. 3(*e*). In all five cases, the line of fusion is a double bond in the dominant Kékulé structure of C_{70}.

In *tert*-butyl-C_{60}, the hyperfine interaction of the incoming ^{13}C nucleus was 13.1 G, and those of the two ^{13}C nuclei *ortho* and the one ^{13}C *para* to the point of attack were 17.8, 9.4 and 8.9 G, respectively. Other ^{13}C nuclei, *meta* to the point of attack, had hyperfine interactions of 5.6 and 4.5 G.[2] Comparing these data with those for the three isomers of *tert*-butyl-C_{70} (Table 1), we note that from this point of view only radical **3** can be regarded as truly C_{60}-like. We therefore associate *tert*-butyl attack at position A with species **3**, since carbons A are the most like C_{60}. Moreover, because a *g*-difference of only 0.00005 would blur the proton hyperfine structure of these radicals, we do not believe that $g = 2.00210$ is a superposition of spectra corresponding to attack at A, B and C. This conclusion is confirmed [Fig. 1(*c*)] by the integrity of the proton hyperfine structure even in ^{13}C-enriched samples. The similarity of the spectrum of radical **3** with *tert*-butyl-C_{60} was confirmed by the temperature-dependence of its intensity, which increased with increasing temperature contrary to expectations based on the Curie law. This behaviour was attributed in the case of *tert*-butyl-C_{60} to the dissociation of a dimer.[3] The temperature dependence of the intensity of the spectrum of **3** is also characteristic of the dissociation of a dimer [$\Delta H = ca.$ 11 kcal mol^{-1} (1 cal = 4.184 J)], a characteristic not shared by the other entries in Table 1.

It is difficult to be as certain about the other two isomeric forms of *tert*-butyl-C_{70}, due to their weaker spectra and consequent lack of ^{13}C hyperfine structure associated with the

Table 1 Isotropic *g* factors, ^1H, ^{13}C and ^{31}P hyperfine interactions (G) of RC_{70} radicals in benzene at 300 K

R	*g*-Factors	Hyperfine interactions/G	
Me_3C	2.00271 (radical **1**)	9H = 0.17	1C = 14.2[a]
	2.00248 (radical **2**)	9H = 0.17	1C = 11.3[a]
			1C = 4.2[b]
			4C = 2.0[b]
	2.00210[c] (radical **3**)	9H = 0.17	1C = 17.3
			1C = 13.8[a]
			2C = 8.3
			2C = 8.5
			2C = 5.8
			2C = 3.6
			4C = 2.0
Cl_3C	2.00425	—	1C = 34.6[a]
	2.00382	—	1C = 30.5[a]
	2.00345	—	1C = 26.7[a]
$(MeO)_2P(O)$	2.00277	6H = 0.12	1P = 71.2[a]
	2.00269	6H = 0.12	1P = 66.8[a]
	2.00248	6H = 0.08	1P = 55.9[a]

[a] Hyperfine interaction of incoming atom. [b] Measured with enriched sample [Fig. 1(*c*)] at 300 K. [c] Strongest at 345 K, owing to dissociation of the dimer.

C_{70} surface. However, the transition at $g = 2.00248$ (radical **2** in Fig. 1) does not have the large ^{13}C hyperfine interactions associated with carbon atoms *ortho* and *para* to the point of attack. Indeed, apart from the 11.3 G hyperfine interaction of the incoming $^{13}CMe_3$ radical, the largest hyperfine interaction was 4.2 G. The unpaired spin in this isomer seems to be more delocalized than is the case for C_{60}-like adducts. Such delocalization of the unpaired spin would probably occur in the case of addition at D and E, since these positions are associated, in the dominant Kékulé form of C_{70}, with an equatorial ring of aromaticity.[8] However, this does not explain the apparent absence of radical addition at positions B and C, although (unlike C_{60}) there is no requirement that the reactivity of each kind of carbon on the C_{70} surface be identical.

In the cases of CCl_3 and $(MeO)_2PO$ attack on the C_{70} molecule, we again see a spectrum dominated by three, rather than five, isomers. In the absence of ^{13}C hyperfine structure associated with carbon atoms of the C_{70} surface, it is impossible to associate the three observed isomers with attack on specific carbons. Unlike *tert*-butyl-C_{70}, however, the isomer with intermediate *g*-factor has parameters closest to those of the corresponding RC_{60} radical.

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