Electron Paramagnetic Resonance Spectra of R–C_{60} Radicals Part 2: Hindered Rotation in Alkyl- and Silyl-C_{60} Radicals*

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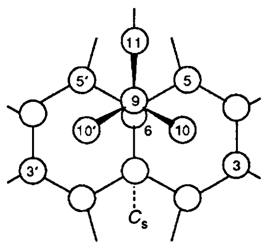
Photolytically generated alkyl (R) and silyl (SiR'_3) radicals react with C_{60} forming adducts readily identifiable by EPR spectroscopy. The temperature dependence of the spectra of R–C_{60} radicals indicates a barrier to rotation about the R–C_{60} bond (ΔH) which varies from *ca.* 3 kcal mol^{-1} for CH_3–C_{60} to *ca.* 7 kcal mol^{-1} for *tert*-butyl-C_{60}. Silyl–C_{60} radicals, on the other hand, are freely rotating about the Si–C_{60} bond although the Si–R′ bonds are non-rotating on the EPR timescale.

Photolytically generated alkyl and silyl radicals R add to C_{60} forming adducts R–C_{60} detectable by EPR spectroscopy.[1–3] These adducts are readily identifiable by the proton hyperfine structure originating with the incoming radical R. In certain instances, notably R = *tert*-butyl and CCl_3,[4] the EPR spectrum was so powerful that ^{13}C hyperfine structure associated with several carbon nuclei of the C_{60} framework was detected and analysed. This analysis led to the conclusion that the radical R–C_{60} was a σ radical having a $^2A'$ ground state in the C_s point group, and that the unpaired spin was confined to carbon atoms close to the point of attack, namely C1, C3, C3′, C5 and C5′.[5]

As noted in Part 1,[4] the proton hyperfine structure of *tert*-butyl-C_{60}, $(CH_3)_3C$–C_{60}, was that of nine equivalent protons (0.17 G†) at 370 K. At 225 K, however, the hyperfine structure had changed to that of three protons at 0.34 G and six at 0.088 G, indicating hindered rotation on the EPR timescale about either C6–C9 or C9–CH_3. ^{13}C enrichment of the methyl groups and analysis of the low-temperature spectrum of $^{13}CH_3(CH_3)_2$ C–C_{60} has been used to distinguish between the two possibilities.[6] In the present article we discuss this analysis, and report the discovery of significant barriers to free rotation about C6–C9 in several other R–C_{60} radicals, including R = methyl, ethyl and isopropyl. In another series of experiments photolytically generated silyl radicals were added to C_{60}. It appears that at room temperature, rotation about C6–Si is unhindered, but rotation about the Si–R'_3 bonds is frozen on the EPR timescale for R′ = ethyl and isopropyl.



Experimental

A mixture of C_{60} (*ca.* 90%) and C_{70} (*ca.* 10%) was purchased from Texas Fullerenes, Houston, Texas. Its components were separated chromatographically using activated, neutral alumina (Aldrich) and hexane as the eluent.[7] Alkanes and alkyl halides enriched in ^{13}C were purchased from MSD Isotopes, Pointe Claire, Que. Dialkyl mercury compounds were purchased from Organometallics Inc., East Hampstead NH. Silanes and other compounds were purchased from the Aldrich Chemical Corporation.

Our three sources of alkyl and silyl radicals R were as follows: (*a*) the alkane or silane RH, (*b*) the bromide RBr, and (*c*) the dialkylmercury R_2Hg. In method (*a*), the hydrogen atom was abstracted by photolyticially generated *tert*-butoxyl radicals, a typical sample consisting of 350 mm^3 C_{60}-saturated benzene, 5 mm^3 RH, and 5 mm^3 di-*tert*-butyl peroxide. A disadvantage of this method was the high freezing point of benzene, a solvent which, however, appears to be relatively inert to attack by *tert*-butoxyl radicals. In the second and third methods, about 5 mm^3 RBr or R_2Hg were added to 350 mm^3 C_{60}-saturated toluene or *tert*-butylbenzene. In general, method (*c*) gave the strongest spectra, but methods (*a*) or (*b*) were employed when ^{13}C-enriched materials were used, these being available as the hydrocarbon or the bromide.

The solutions were mixed in a glove-box continually flushed with dry argon, and placed in a 5 mm thin-walled Suprasil™ tube. They were subsequently photolysed in the cavity of the EPR spectrometer, using a 1000 W Schoeffel Hg/Xe lamp the output of which was focused onto the sample with a quartz lens and filtered through distilled water to remove infrared radiation. The Varian E-12 (NRCC) or Bruker ESP-300 (du Pont) spectrometers were equipped with the usual devices for readout of the temperature, microwave frequency and magnetic field. A magnetic field modulation frequency of 25 kHz was chosen, in order to avoid modulation sidebands associated with extremely narrow lines. The spectrometers were operated in the critically coupled mode, usually with a microwave power of *ca.* 0.2 mW, above which the spectra tended to saturate.

Results and Discussion

EPR Spectra of Alkyl-C_{60} Radicals.—The individual lines in the spectra of alkyl–C_{60} radicals are extremely narrow, ΔB_{ms} (ms = maximum slope) being typically *ca.* 0.02 G. Identification of the radicals as mono-adducts was therefore possible by analysis of the proton hyperfine structure, which was usually well resolved (Table 1). For example, the spectrum of methyl–C_{60} at 295 K has the hyperfine structure of three equivalent protons at 0.032 G, whereas that of ethyl–C_{60} is three equivalent protons (the methyl group, 0.12 G) plus two more protons at 0.28 G [Fig. 1(*a*)]. Similarly, the hyperfine structure of the spectrum of isopropyl–C_{60} [Fig. 1(*b*)] is that of six equivalent

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* NRCC No. 35249, Du Pont No. 6546.

† 1 G = 0.1 mT.

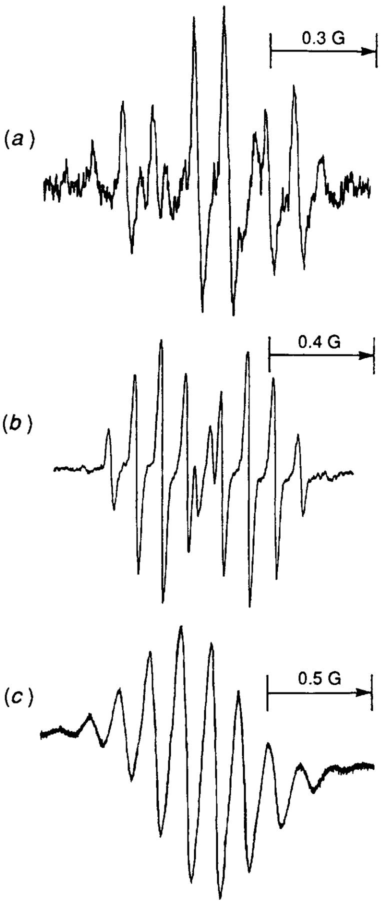


Fig. 1 First derivative EPR spectra of (*a*) $CH_3CH_2–C_{60}$ at 425 K; (*b*) $(CH_3)_2CH–C_{60}$ at 440 K; (*c*) $(CH_3)_3C–C_{60}$ at 325 K

Table 1 Proton and ^{13}C hyperfine interactions (gauss) of R in $R–C_{60}$ radicals[a]

R	^1H	$^{13}C_\delta$	*T*/K
CH_3	$3\,H_\gamma = 0.035$[b,c]		300
CH_2CH_3	$2\,H_\gamma = 0.28$[c] $3\,H_\delta = 0.12$	0.17[b]	425
$CH(CH_3)_2$	$1\,H_\gamma = 0.47$[c] $6\,H_\delta = 0.14$	0.28[b]	440
$C(CH_3)_3$	$9\,H_\delta = 0.17$[b,d]	0.40[b]	325
$C(CH_3)_3$	$6\,H_\delta = 0.088$[b] $3\,H_\delta = 0.34$	0.34[b] (C10) 0.53 (C11)	225
$Si(CH_3)_3$	$9\,H_\delta = 0.11$[d]		320
$Si(CH_2CH_3)_3$	$3\,H_\delta = 0.30$[d] $3\,H_\delta = 0.025$ $9\,H_\varepsilon = 0.15$		320
$Si[(CH_3)_2CH]_3$	$3\,H_\delta = 0.28$[d] $9\,H_\varepsilon = 0.14$		295
$Si[C(CH_3)_3]_3$	$27\,H_\varepsilon = 0.075$[d]		310

[a] All *g*-factors lay in the range 2.0022–2.0023. [b] Photolysis of RBr as source of R. [c] Photolysis of R_2Hg as source of R. [d] Photolysis of di-*tert*-butyl peroxide + RH as source of R.

protons (the two freely rotating methyl groups) at 0.14 G, plus a lone proton (0.47 G). At 325 K the spectrum of *tert*-butyl–C_{60} is a hyperfine manifold of 10 lines 0.17 G apart [Fig. 1(*c*)], having intensities proportional to the coefficients in the expansion of $(1 + x)^9$, (1:9:36:84:126:126:84:36:9:1), indicating equivalence of all nine protons, and free rotation about both C6–C9 and the C9–CH_3 bonds.

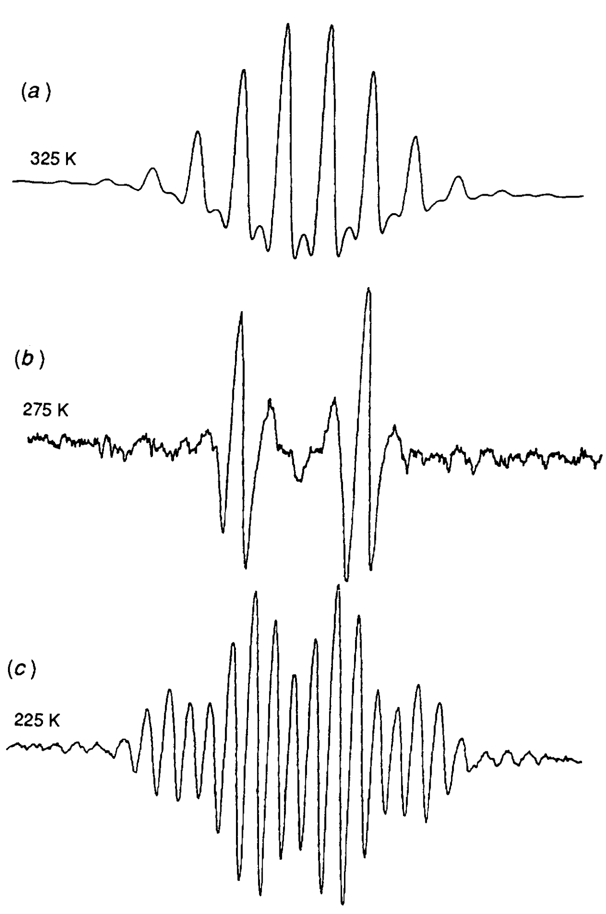


Fig. 2 Second-derivative EPR spectra of $(CH_3)_3C–C_{60}$ at (*a*) 325 K; (*b*) 275 K; (*c*) 225 K

As a sample containing *tert*-butyl–C_{60} is slowly cooled (under continuous irradiation) from 325 K to 225 K, its spectrum changes gradually from that of nine equivalent protons (0.17 G) at 325 K [Fig. 2(*a*)] to that of six protons of one kind (0.088 G) and three of another (0.34 G) at 225 K [Fig. 2(*c*)]. Throughout this process, two lines remain sharp, and at 275 K these are the only lines detectable [Fig. 2(*b*)]. They are the $M_I = \pm 1.5$ transitions of the 325 K spectrum, and they remain sharp because the $M_I = \pm 1$, $M_{I'} = \pm 0.5$ transitions of the 225 K spectrum are found at the same position. These changes in the spectrum of *tert*-butyl–C_{60} could be due to either (a) hindered rotation about C6–C9 resulting in inequivalence of the methyl groups, or (*b*) hindered rotation about C9–CH_3, resulting in inequivalence of the protons of the methyl groups. ^{13}C-enrichment of one methyl carbon atom of *tert*-butyl–C_{60} shows that at 225 K the hyperfine structure is that of two kinds of methyl carbon, just as there are two kinds of proton (Table 1 and Fig. 3). The six protons at 0.088 G are associated with a 0.34 G ^{13}C hyperfine interaction, while the three protons at 0.34 G are associated with a 0.53 G ^{13}C hyperfine interaction, proving that at 225 K rotation about C6–C9 is hindered, but that the C9–CH_3 bonds are freely rotating on the EPR timescale. The observed and simulated spectra of $^{13}CH_3(CH_3)_2C–C_{60}$ are shown in Fig. 3(*a*) and 3(*b*), respectively.

The effects of cooling to 225 K on the spectrum of *tert*-butyl–C_{60} has been simulated using the Bloch equations modified for chemical exchange,[5,8] reproducing remarkably well the changes in the spectrum, as well as yielding estimates of the barrier

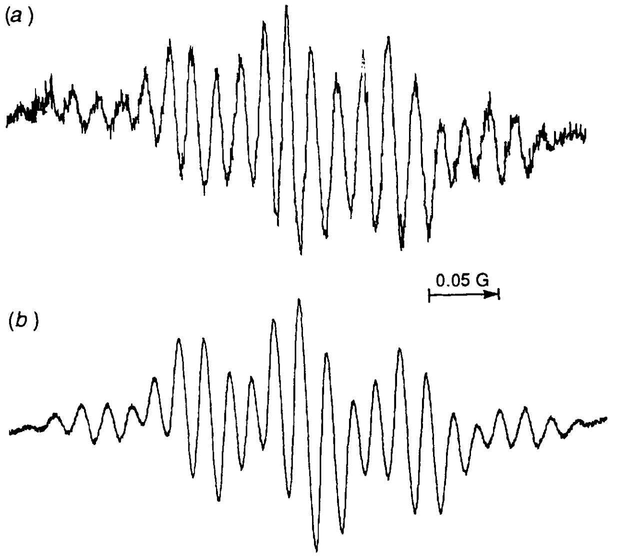


Fig. 3 The observed (*a*) and simulated (*b*) first-derivative EPR spectra of $^{13}CH_3(CH_3)_2C–C_{60}$ at 225 K. Simulation parameters are: ΔB_{ms} = 0.02 G; 3 H = 0.34, 6 H = 0.088, C11 = 0.53, C10 or C10′ = 0.34 G.

parameters $\Delta H^{\ddagger} = 7.3$ kcal*mol^{-1}, $\Delta S^{\ddagger} = -2.9$ cal mol^{-1} K^{-1}. Such a barrier seems to be entirely reasonable in view of the estimate of 9.6–10.0 kcal mol^{-1} for the rotation of two *tert*-butyl groups against each other in hexamethylethane,[9] and the recently reported barrier of 9.3 kcal mol^{-1} for C6–C9 rotation in the *tert*-butyl–C_{60} anion.[10]

Isopropyl– and ethyl–C_{60} have lost the sixfold barrier of methyl– and *tert*-butyl–C_{60}, and the barrier to rotation about C6–C9 in these adducts might therefore be expected to differ significantly from that of either methyl– or *tert*-butyl–C_{60}. The possibility of a large barrier to rotation about C6–C9 in isopropyl–C_{60} was suggested by the fact that its spectrum is invariant over the temperature range 200–400 K, and by the spectrum of $^{13}CH_3(CH_3)CH–C_{60}$, for which a ^{13}C hyperfine interaction of 0.28 G was observed. This value is close to that of methyls in positions C10 and C10′ in *tert*-butyl–C_{60} at 225 K (0.34 G). Indeed, it could be argued that any significant contribution from a configuration of isopropyl–C_{60} having a methyl group at C11 would have resulted in a ^{13}C hyperfine interaction larger than 0.34 G, not smaller, as observed. We therefore conclude that as seen by the EPR spectrometer, isopropyl–C_{60} is locked into the symmetric configuration in which C11 = H.

By the same token, the observation of a small ^{13}C hyperfine interaction (0.17 G) for $^{13}CH_3CH_2–C_{60}$ also suggests a configuration in which the methyl group occupies position C10 or C10′. This notion of an asymmetric configuration for ethyl–C_{60} was confirmed by the observation that its spectrum changes dramatically on cooling. The outer 1:3:3:1 quartets in Fig. 1(*a*) remain sharp, but the central quartet broadens beyond detection near 240 K. The broadening of the inner quartet implies an *asymmetric equilibrium configuration* for ethyl–C_{60} with exchange of the methyl group between positions C10 and C10′.

This process results in the methylene (γ) protons exchanging positions, and the observation of an average γ-proton hyperfine interaction at high temperatures. From the temperature of coalescence (240 K) of the central quartet we estimate a barrier height of *ca.* 5 kcal mol^{-1} for the exchange between the two equivalent sites (C10 and C10′) for the methyl group.[11]

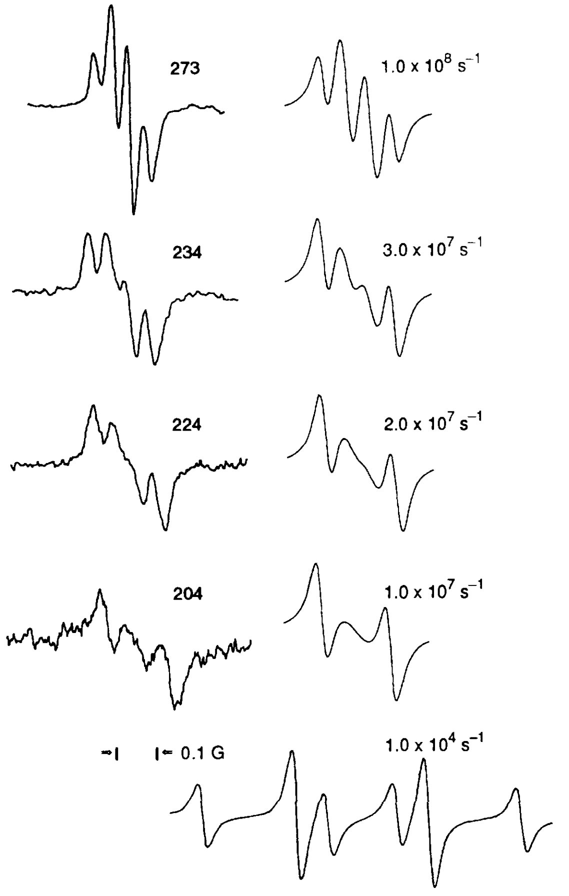
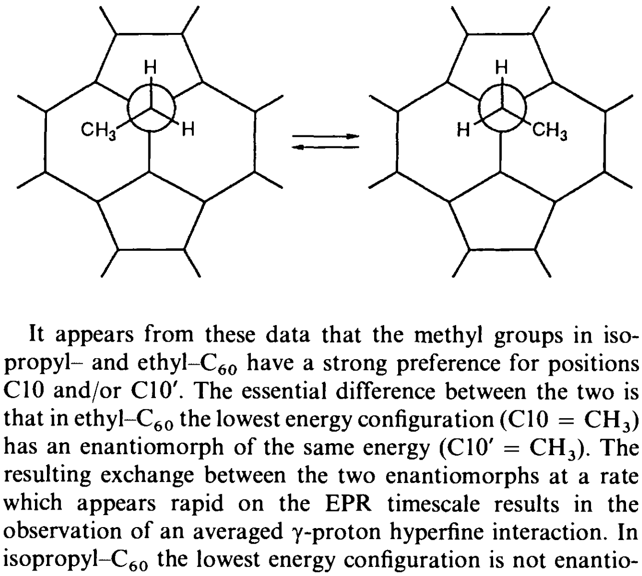


Fig. 4 EPR spectrum of $CH_3–C_{60}$ between 204 and 273 K and simulations thereof using a_H = 0.45 G at position 11, and −0.34 G at positions 10 and 10′; ΔB_{pp} = 0.04 G



It appears from these data that the methyl groups in isopropyl– and ethyl–C_{60} have a strong preference for positions C10 and/or C10′. The essential difference between the two is that in ethyl–C_{60} the lowest energy configuration (C10 = CH_3) has an enantiomorph of the same energy (C10′ = CH_3). The resulting exchange between the two enantiomorphs at a rate which appears rapid on the EPR timescale results in the observation of an averaged γ-proton hyperfine interaction. In isopropyl–C_{60} the lowest energy configuration is not enantiomorphic; the asymmetric conformers (H at 10 or 10′) are at much higher energy and are not significantly populated at the temperatures of our experiments.[12]

The most remarkable feature of the spectrum of $CH_3–C_{60}$ is the small proton hyperfine interaction of 0.032 G, an order of magnitude less than that observed for γ protons in ethyl– and isopropyl–C_{60}. We conclude that in a non-librating $CH_3–C_{60}$ protons at positions 10 and 10′ would have hyperfine interactions of opposite sign to that of a proton at position 11. Some evidence that this is so can be obtained from a comparison of the spectrum of $CH_3–C_{60}$ over the temperature range 200–275 K

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* 1 cal = 4.184 J.

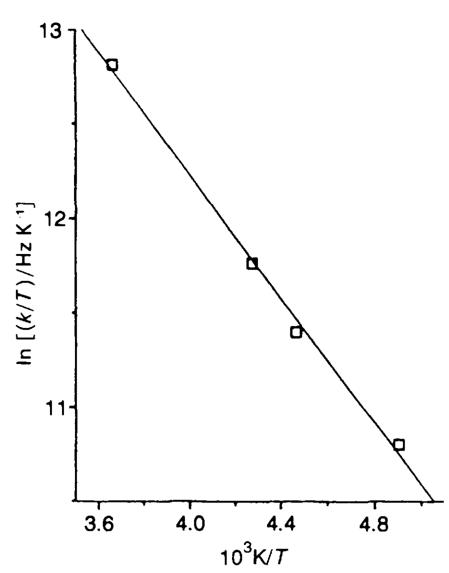

Fig. 5 Graph of $\ln(kT)$ *versus* 10^3 K/T for rotation about C6–C9 in $CH_3–C_{60}$ using the data of Fig. 4 (k is the reorientation rate in Hz)

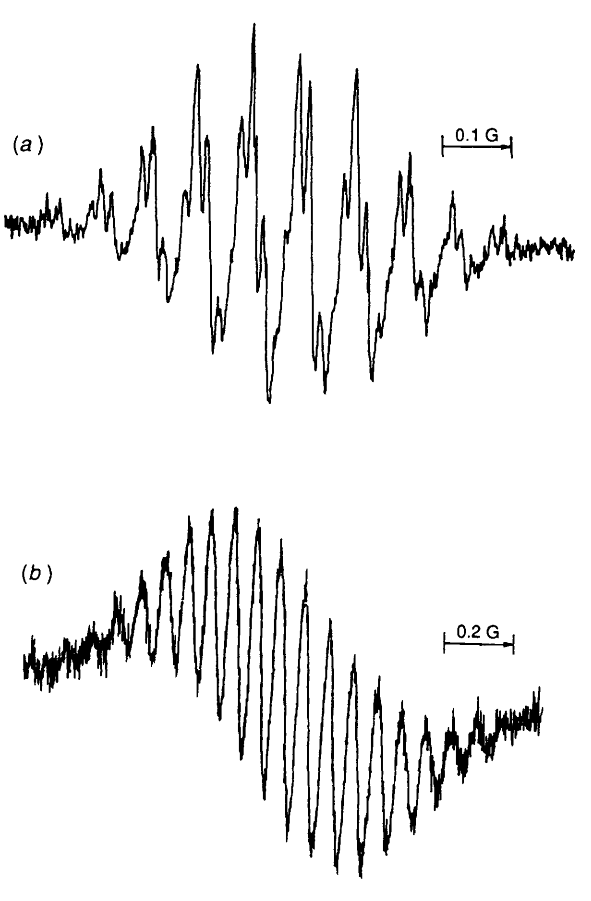

Fig. 6 First-derivative EPR spectra of (*a*) triethylsilyl–C_{60}, and (*b*) tri-*tert*-butylsilyl–C_{60}

with simulations based on the opposite sign assumption (Fig. 4). Although we were unable to observe the spectrum of non-librating $CH_3–C_{60}$, the similarity between the observed and simulated spectra clearly confirms (*a*) the opposite signs assumption, and (*b*) a rate constant for rotation about C6–C9 in the 10–100 MHz range. By plotting $\ln(k/T)$ against $1000/T$ for the values of k and T shown in Fig. 4, a straight line of slope -1.6 ± 0.1 was obtained (Fig. 5), leading to the barrier parameter $\Delta H^\ddagger = 3.3 \pm 0.2$ kcal mol⁻¹. This barrier is similar to the barrier to free rotation between a methyl and a *tert*-butyl group (4.7 kcal mol⁻¹),[13] a not unexpected result in view of the probable sp^3 configuration at C6. Slightly smaller values have been tabulated[12,13] for $CH_3–CF_3$ (3.5 kcal mol⁻¹), $CH_3–CH_3$ (2.9) and $CH_3–CCl_3$ (2.72).

EPR Spectra of Silyl–C_{60} Radicals.—In the alkyl–C_{60} radicals discussed so far, the dominant barrier to free rotation is that about C6–C9: rotation about C9–C10, C9–C10′ and C9–C11 appears to be unhindered, at least when R is not more bulky than *tert*-butyl. Of course, it is possible to stop C9–C10 rotation by incorporating C10, C10′ and C11 into a cage structure, as in 1-adamantyl–C_{60}.[4] Another way is to use a more complex R group than *tert*-butyl, a route we have explored with several substituted-silyl–C_{60} radicals. Starting with trimethylsilyl–C_{60}, we have successively replaced the hydrogen atoms with methyl groups, forming the series trimethylsilyl–C_{60}, triethylsilyl–C_{60}, triisopropylsilyl–C_{60} and tri-*tert*-butylsilyl–C_{60}.

The spectrum of trimethylsilyl–C_{60}, although very much weaker than that of its carbon analogue *tert*-butyl–C_{60}, also has hyperfine structure due to nine equivalent protons at 300 K. The Si–C_{60} bond is doubtless slightly longer than the C–C_{60} bond in *tert*-butyl–C_{60}, resulting in a lower barrier to rotation about C6–Si. Probably it is for this reason that we have been unable to observe any indication of hindered rotation in trimethylsilyl–C_{60}. At the other end of the series, the hyperfine structure of the spectrum of tri-*tert*-butylsilyl–C_{60} is clearly that of 27 equivalent protons [Fig. 6(*b*)]. In other words, in spite of the bulkiness of this ligand, there is free rotation on the EPR time-scale about C6–Si, Si–C10 and C10–CH_3 bonds.

The middle members of the series, triethylsilyl– and triisopropylsilyl–C_{60}, gave spectra which were very similar to each other. In both cases the hyperfine manifold was an even number of lines (at least 12) with intensity ratios approximately as follows 1:3:6:12:16:20:20:16:12:6:3:1. The line-to-line separation $\Delta\alpha$ was also very similar: 0.15 G for triethylsilyl–C_{60} [Fig. (6(*a*)] and 0.14 G for triisopropylsilyl–C_{60}. With the aid of computer simulation, we concluded that this structure was due to hyperfine interactions with nine equivalent protons at $\Delta\alpha$ G, plus another three protons at $2\Delta\alpha$ G. The only difference between the two spectra (apart from the slight difference in $\Delta\alpha$) was that for triethylsilyl–C_{60} an extra hyperfine interaction could be resolved at very low modulation amplitudes, namely that of three equivalent protons at 0.025 G [Fig. 6(*a*)].

Our explanation of these results is as follows. Each R′ group (ethyl or isopropyl) contributes to the hyperfine structure *one* δ-proton whose interaction is $2\Delta\alpha$ G, and *one* methyl group whose three protons have hyperfine interactions of $\Delta\alpha$ G. With free rotation about C6–Si, the overall effect is that of three δ-protons at $2\Delta\alpha$, and nine methyl protons at $\Delta\alpha$ G, as required by the analysis of the spectra. It will be apparent that this analysis requires non-rotation about the Si–R′ bonds, in order to accommodate non-equivalence of the two methyls of the isopropyl groups and the two methylene protons of the ethyl groups. In the latter case, the second proton reveals itself by its hyperfine interaction of 0.025 G. When R′ = isopropyl, the hyperfine interaction of the second methyl group is not resolved. An obvious further corollary of this analysis is free rotation about *all* C–CH_3 bonds for both R′ = ethyl and isopropyl. It is also obvious that both R′ groups (ethyl and isopropyl) must have asymmetric configurations with respect to the plane defined by the bonds C6–Si and Si–R′. A hint as to the geometry of this configuration comes from the hyperfine interactions of the six δ protons in 1-adamantyl–C_{60}. In this molecule, the δ protons are obliged by the adamantane structure to point towards the C_{60} surface, a configuration which evidently leads to a very small δ-proton hyperfine interaction (0.044 G). We suspect that in triethylsilyl–C_{60} one of the two C–H_δ bonds of

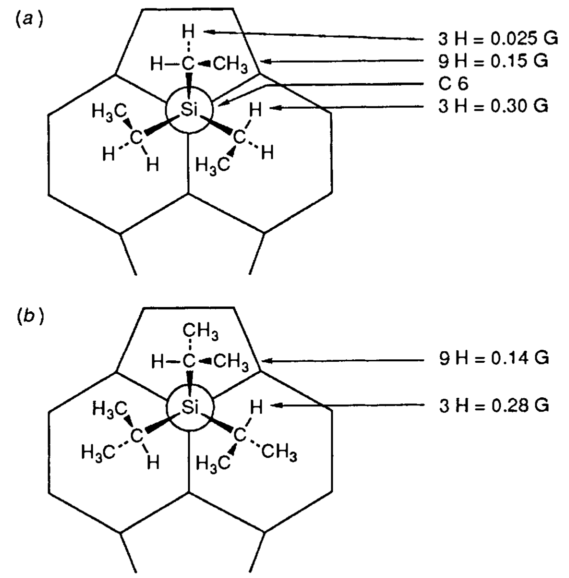

Fig. 7 Newman projection down the Si–C6 bond showing the configuration of (*a*) the ethyl groups in triethylsilyl–C_{60}, and (*b*) the isopropyl groups in triisopropyl–C_{60}

each ethyl group is in such a configuration, and that these protons have 0.025 G hyperfine interactions [Fig. 7(*a*)]. The other three δ-protons lie more or less in the plane perpendicular to C6–Si and have much larger hyperfine interactions (0.30 G). In triisopropylsilyl–C_{60} [Fig. 7(*b*)], the configuration of the latter proton is retained, but the other has been replaced by a second methyl group, whose hyperfine interaction is too small to be resolved. As confirmation of these deductions, we note that the average δ-proton hyperfine interaction in triethylsilyl–C_{60} (3 H = 0.025, 3 H = 0.30 G) is 0.16 G, very close to the 0.11 G observed for the nine equivalent δ protons in trimethylsilyl–C_{60} at 325 K. Also, the average ε-proton hyperfine interaction in triisopropylsilyl–C_{60} (9 H = 0.14, 9 H = 0.00 G) is 0.070 G, virtually identical with that obtained for the 27 ε protons in tri-*tert*-butylsilyl–C_{60} (0.075 G).

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