

Electrostatic effects on the C₆₀ surface of alkyl-C₆₀ radicals

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The EPR spectra of alkyl- and fluoroalkyl-C₆₀ radicals are described and discussed. These radicals are of the general type XYZC-C₆₀, where X, Y and Z are CF₃, F, H or CH₃. It is shown that there is a competition among X, Y and Z for the pentagon position adjacent to the C-C₆₀ bond, and that in any given radical this position is gained by the most electronegative of them. Thus, if X, Y, Z is the order of decreasing electronegativity in the above sequence, X will occupy the pentagon position. If Y = X, the equilibrium conformation is asymmetric, with one X over the pentagon and the other over one of the hexagons. This conformation exchanges with its enantiomer above ~200 K. An explanation based on quantum-chemical calculations of charge distribution on the C₆₀ surface indicates that the more electronegative ligands are attracted to regions of more positive charge over the pentagon.

Introduction

Overall, C₆₀ is an electrically neutral molecule and, since all its carbons are identical, the electronic charge on every atom is zero. Free-radical adducts are also electrically neutral. However, lacking the icosahedral symmetry of C₆₀ itself, there is no longer a requirement that the charge on individual atoms of RC₆₀ radicals be zero. EPR spectroscopists are not used to worrying about the electronic charge distribution in free radicals; their main concern is usually with the distribution of the unpaired spin over the various atoms and atomic orbitals of the molecule. In the present article, however, we shall not be concerned so much with the unpaired spin distribution as with the different equilibrium conformation of substituted methyl-C₆₀ radicals. These are imposed by the different electronegativities of the substituents and the charge distribution on the C₆₀ surface.

Experimental

Samples were prepared in a glove box continuously flushed with argon dried over a proprietary adsorbent for water and O₂, levels of which lower than 1 ppm are essential. The usual method was to dissolve the C₆₀ in a suitable sodium-dried solvent (*e.g.* decalin, toluene or *tert*-butylbenzene) and transfer 500 mm³ of the solution to a SuprasilTM electron paramagnetic resonance (EPR) tube fitted with a greaseless stopcock. To this solution ~5 mm³ of the photolytic free-radical source compound was added by microsyringe. If the latter was too volatile for this procedure, it was added to the sample by standard vacuum techniques. In general, the best photolytic source of a given free radical R was the corresponding iodide RI or, if available, the mercury dialkyl R₂Hg. Other sources were occasionally used, such as the bromide (RBr), a ketone (R₂CO), or an aldehyde (RCHO). The use of ketones and aldehydes was sometimes complicated by the formation of more than one species, *e.g.*, RC(=O)C₆₀ as well as RC₆₀. In certain instances, particularly when isotopically enriched (D, ¹³C) R was desired, an indirect method was used. This involved the addition of ~5 mm³ each of the hydrocarbon RH and di-*tert*-butyl peroxide. Photolysis of the latter yielded *tert*-butoxyl radicals which abstracted hydrogen atoms from RH. The photolytic sources of R used to generate the EPR spectra of specific RC₆₀ radicals are listed as footnotes to Table 1. Details regarding the purchase or

Table 1 Hyperfine interactions (hfi/mG) in some alkyl- and fluoroalkyl-C₆₀ radicals^a

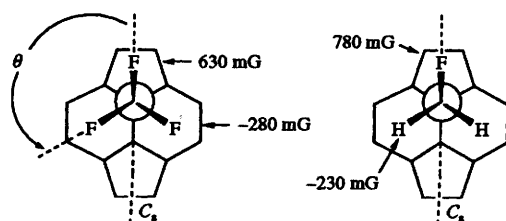
Radical	¹ H hfi	¹⁹ F hfi	T/K	Ref.
CH ₃ C ₆₀	3 H = 35		300	3 ^b
CH ₂ FC ₆₀	2 H = 230	1 F = 780	295–400	1 ^c
CH ₂ (OH)C ₆₀	2 H = 175, 1 H = 85		300–400 300–400	5 ^d
HO ₂ CCH ₂ C ₆₀	2 H = 330		300–400	5 ^e
CHF ₂ C ₆₀	1 H = 150	2 F = 240	300	1 ^c
CF ₃ C ₆₀		1 F = 630, 2 F = 280, 3 F = 74	180 180 285–400	2
CH ₃ CH ₂ C ₆₀	2 H = 280, 3 H = 120		425 425	3 ^b
CH ₃ CF ₂ C ₆₀	3 H = 80	2 F = 150	225–425	8
CF ₃ CH ₂ C ₆₀	2 H = 420	3 F = 2720	225–425	8
CF ₃ CHFC ₆₀	1 H = 530	1 F = 650, 3 F = 2770	250–425 250–425	8
CF ₃ CF ₂ C ₆₀		2 F = 330, 3 F = 2430	225 225	2
(CH ₃) ₂ CHC ₆₀	1 H = 470, 6 H = 140		225–440 225–440	3 ^b
CF ₃ (CH ₃)CHC ₆₀	1 H = 550, 3 H = 140	3 F = 2620	250–425 250–425	8
(CF ₃) ₂ CHC ₆₀	1 H = 520	6 F = 2010	250–425	8
(CF ₃) ₂ CFC ₆₀		1 F = 830, 6 F = 1960	300 300	2

^a All *g*-factors lay in the range 2.0022–2.0023; source of R was RI unless otherwise indicated. ^b Photolysis of CH₃Br or (CH₃)₂Hg. ^c Photolysis of RBr. ^d Photolysis of 1,3-dihydroxyacetone dimer. ^e Photolysis of ICH₂CO₂H.

preparation of these compounds will be found in the references cited therein.

The samples were placed in the cavity of the EPR spectrometer, where they could be photolysed *in situ* with the focused light from a 1000 W high-pressure Hg/Xe arc. To prevent IR heating of the sample, the light was filtered through a 5 cm column of water and an Oriel IR filter No. 59060. The Varian E-102 EPR spectrometer was equipped with the usual devices to monitor the microwave frequency, the magnetic field strength, and the temperature of the sample. The spectrometer was operated in the critically coupled mode, at very low (~5 μW) microwave powers in order to avoid saturation of the signals. Because the individual lines of RC₆₀ radicals tend to be extremely narrow (Δ*H*_{ms} ~ 50 mG†) the spectrometer was

† 1 mG = 0.1 μT.



operated at a modulation frequency of 25 kHz, amplitude 20 mG.

Results and discussion

Methyl- and fluoromethyl- C_{60} radicals

In a discussion of the equilibrium conformation of CH_2FC_{60} and CHF_2C_{60} ,¹ their ^{19}F hyperfine interactions were compared with those of CF_3C_{60} in its 'static' conformation at 180 K (Table 1).² At this temperature, the ^{19}F hyperfine pattern of CF_3C_{60} is that of a unique fluorine (+630 mG) and two equivalent fluorines (-280 mG). Obviously, the unique fluorine is located over the pentagon ($\theta = 0^\circ$), while the equivalent fluorines lie over the two hexagons ($\theta = \pm 120^\circ$). It was, therefore, reasonable to assign the ^{19}F hyperfine interaction (780 mG) of CH_2FC_{60} to a fluorine in the unique, or pentagon, position. It has, unfortunately, proved impossible to observe the analogous 'static' spectrum of CH_3C_{60} , for it would have been instructive to compare the proton hyperfine interactions in CH_3C_{60} with those of CH_2FC_{60} . Even at 200 K the EPR spectrum of CH_3C_{60} is that of a system in the intermediate-temperature regime.³ By contrast, substitution of a single fluorine results in a spectrum of CH_2FC_{60} whose parameters are virtually invariant over the entire temperature range 200–400 K, and which shows no evidence of internal motion. The fluorine atom in CH_2FC_{60} clearly has a very strong preference for the position over the pentagon, rather than over one of the hexagons.

An explanation is provided by the charge distribution on the C_{60} surface computed with the incomplete neglect of differential overlaps (INDO) Hamiltonian⁴ at the unrestricted Hartree-Fock (UHF) level and illustrated in Fig. 1 for the lowest-energy conformations of CH_3C_{60} , CH_2FC_{60} and CHF_2C_{60} . Even in CH_3C_{60} [Fig. 1(a)], it can be seen that the proton in the pentagon position is near positive charges on C-8 and C-8'. All three protons are near negative charges on C-5 and C-5', although the latter are smaller (in absolute value) than the negative charge on C-1. Hence, protons over the hexagons, which are close to C-5, C-5' and C-1, experience interactions with predominantly negative charges (the positive charges on C-2 and C-2' are further away). In replacing an H atom by an F atom in such a situation, one would instinctively place the F over the pentagon. In fact, that is what the INDO calculation predicts [Fig. 1(b)], and the positive charge on C-8 and C-8' doubles to 0.012 in the lower-energy conformer of CH_2FC_{60} . At the same time the negative charge on C-5 is strongly reduced. The rearrangement of charge distribution induced by the F substituent costs a certain amount of energy. However, the rearrangement is relatively modest in the case of the symmetric species, with the result that it is predicted to be the more stable conformer. Thus there is both experimental and theoretical evidence that the more electronegative F atom in CH_2FC_{60} is located over the pentagon. A similar situation arises with the radicals $CH_2(OH)C_{60}$ and $CH_2(CO_2H)C_{60}$:⁵ in both cases the hyperfine pattern over a wide temperature range is that of two equivalent protons (Table 1), indicating that the OH or CO_2H groups had gained the pentagon position.

In the case of CHF_2C_{60} , INDO again indicates that the

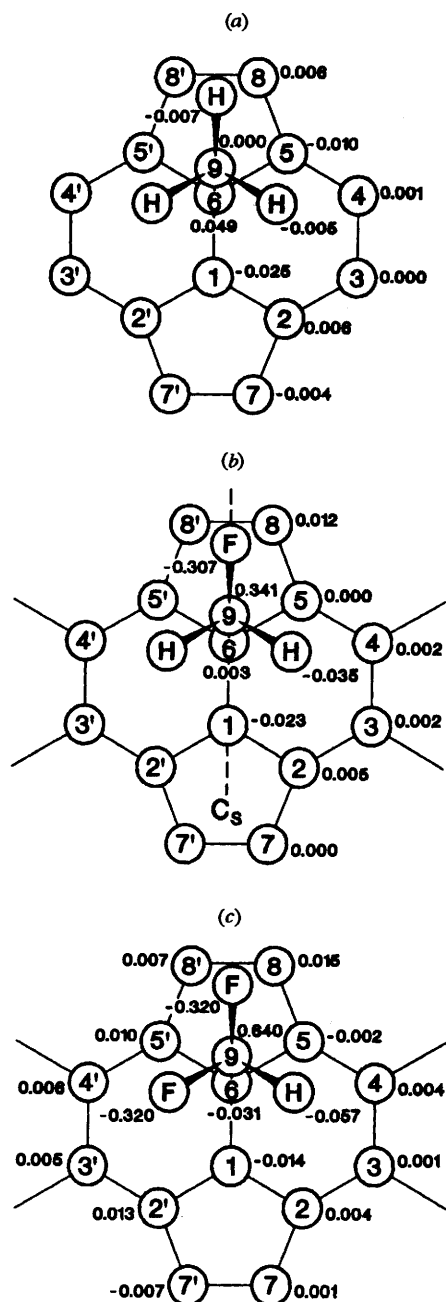
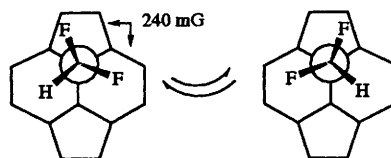


Fig. 1 Electronic charge distribution on the C_{60} surface calculated with the INDO Hamiltonian in (a) CH_3C_{60} , (b) the symmetric configuration of CH_2FC_{60} and (c) the asymmetric configuration of CHF_2C_{60}



minimum-energy conformation is that in which one of the fluorine atoms lies over the pentagon. The hyperfine structure of the EPR spectrum, however, is that of two equivalent ^{19}F nuclei (240 mG), from which we conclude that at accessible temperatures there is exchange between the enantiomers on the EPR time-scale. Since it is known that in (static) CF_3C_{60} the hyperfine interactions of the unique and equivalent ^{19}F nuclei are of opposite sign,² such a process would result in average ^{19}F hyperfine interactions in CHF_2C_{60} of $\sim 0.5 \times (630 - 280) =$

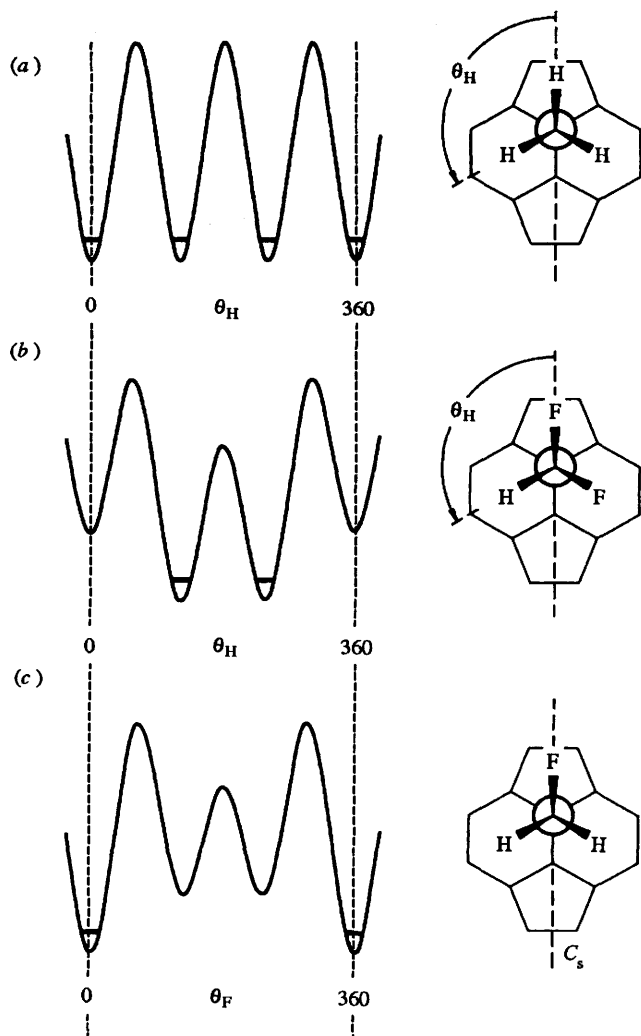


Fig. 2 Form of the potential hindering motion about the C–C₆₀ bond in (a) CH₃C₆₀, (b) CHF₂C₆₀ and (c) CH₂FC₆₀

175 mG. Bearing in mind that in CHF₂C₆₀ there is no requirement that the fluorine atoms lie at $\theta = 0$ and $\pm 120^\circ$ (as they must in CF₃C₆₀), this is not an unreasonable agreement with the observed values of 240 mG.

Fig. 2 illustrates the three situations that can arise in methyl- and fluoromethyl-C₆₀ radicals. In Fig. 2(a) (CH₃C₆₀, CF₃C₆₀) the three identical conformations are separated by barriers 120° apart. Although most of the molecules will be in vibrational states near the bottom of the potential wells, the Boltzmann distribution of energies ensures that some barrier-hopping occurs, the actual rate depending on the barrier-height and, of course, the temperature. A simple calculation based on the Eyring rate equation[‡] shows that for barriers of a few kcal mol⁻¹§ the exchange rate will be fast enough to average out differences in hyperfine interactions of ~1000 mG (3 MHz) between pentagon- and hexagon-located nuclei. This is why, at 300 K, the EPR spectra of both CH₃C₆₀ and CF₃C₆₀ show hyperfine patterns of three equivalent nuclei. At 200 K, however, the exchange rate for CF₃C₆₀ has slowed to the point that distinct hyperfine interactions for ¹⁹F nuclei in the two locations are observed,² whereas CH₃C₆₀ has entered the intermediate-temperature regime (line-broadening).³

It should be pointed out that the postulated¹⁻³ opposite signs

for protons or ¹⁹F nuclei occupying the pentagon and hexagon positions in CH₃C₆₀ and CF₃C₆₀ are not without analogy. The simplest model compound for CH₃C₆₀ is the n-propyl radical, CH₃CH₂CH₂. *Ab initio* calculations carried out on this radical predict opposite signs for the hyperfine interactions of the methyl group in the conformation analogous to that of CH₃C₆₀.⁶ Moreover, methyl protons of certain other alkyl radicals, notably neopentyl (CH₃)₃CCH₂, have been shown experimentally to have hyperfine interactions of opposite sign when in conformations analogous to those of CH₃C₆₀.⁷ However, in these examples the barriers to C–CH₃ rotation were explained in terms of steric effects rather than the electrostatic effects invoked here.

Fig. 2(b) shows the very similar situation which arises for radicals such as CHF₂C₆₀, whose equilibrium conformation is asymmetric. Barrier-hopping results in interchange of the enantiomers and a hyperfine pattern of two apparently equivalent ¹⁹F nuclei. The situation in Fig. 2(c) is different in kind from the foregoing. The equilibrium conformation is symmetric, as in CH₂FC₆₀, for example. There is no question of exchange between isoenergetic conformers, since the asymmetric conformation represents a more energetic structure whose contribution to the hyperfine pattern will be negligible even for quite small energy differences. The EPR spectrum of this type of radical will not show any of the dramatic low-temperature linewidth effects which are characteristic of the other two situations.

Ethyl- and fluoroethyl-C₆₀ radicals

In the case of CH₃CF₂C₆₀ we observed direct evidence for the exchange of the enantiomers.⁸ The central component of the 1:2:1 triplet due to the exchanging ¹⁹F nuclei broadened to undetectability near 225 K, indicating that the system had entered the intermediate-temperature regime. This behaviour establishes beyond doubt that the equilibrium conformation of CH₃CF₂C₆₀ is asymmetric; *i.e.*, the fluorine atoms share possession of the pentagon position and the methyl group oscillates between equivalent positions over the hexagons.

The INDO-calculated charge distribution (Fig. 3) for the asymmetric and symmetric conformers of CH₃CF₂C₆₀ provides support for the higher stability of the former. Compared with Fig. 1(a) (CH₃C₆₀), it is seen that in the asymmetric conformer [Fig. 3(a)] the fluorine over the pentagon induces increased positive charge on C-8 and C-8', while the fluorine over the hexagon induces increased positive charge on C-3' and C-4'. At the same time, the negative charge on C-5, C-5' and C-1 is considerably decreased as compared with the charge distribution predicted for CH₃C₆₀. In summary, the charge on surface atoms close to the fluorines in CH₃CF₂C₆₀ undergoes remarkable rearrangement, but remains similar to that of CH₃C₆₀ for carbon atoms near the methyl group. In addition, the overall charge redistribution is rather similar for the two conformers, and it is reasonable to assume that the energetic costs will therefore be similar. However, we notice that for a fluorine atom over the pentagon the interatomic distances to atoms on the C₆₀ surface are smaller than those for a fluorine atom over one of the hexagons. This will tend to stabilize the asymmetric conformer due to the attraction between the fluorine over the pentagon and atoms C-8, C-8' and particularly C-5' (closest), all of which are positively charged.

The situation for CH₃CF₂C₆₀ is exactly analogous to that of CH₃CH₂C₆₀, reported two years ago.³ These results indicate that both fluorine atoms and hydrogen atoms gain the pentagon position against competition from a methyl group. Since it was established earlier that an F atom, a CO₂H group or an OH group gain the pentagon position against competition from a hydrogen atom, we conclude that the sequence F > CO₂H > OH > H > CH₃ tends to control access to the pentagon

‡ Rate = $(kT/h)\exp(-\Delta G/RT)$.

§ 1 cal = 4.184 J.

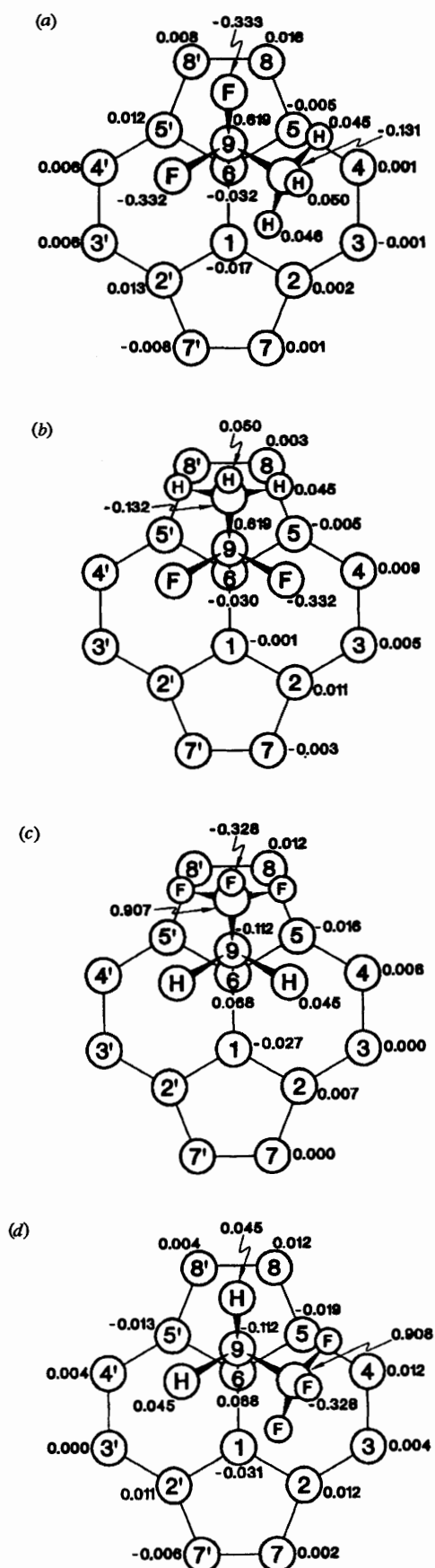


Fig. 3 Electronic charge distribution on the C_{60} surface calculated with the INDO Hamiltonian in (a) the asymmetric conformation of $CH_3CF_2C_{60}$, (b) the symmetric conformation of $CH_3CF_2C_{60}$, (c) the symmetric conformation of $CF_3CH_2C_{60}$ and (d) the asymmetric configuration of $CF_3CH_2C_{60}$

position. This sequence is clearly related to the electronegativity of its members. Indeed, Charton's⁹ inductive effect parameter σ_I parallels the sequence F, CO_2H , OH, H, CH_3 precisely: 0.52, 0.36, 0.25, 0.00 and -0.05 . We can, however, add another member to the series: the CF_3 group ($\sigma_I = 0.42$), the question being whether CF_3 can gain the pentagon position against competition from H and F atoms. The answer is provided by the spectra of $CF_3CH_2C_{60}$ [Fig. 4(a)] and $CF_3CF_2C_{60}$ [Fig. 4(b)], respectively.⁸ The hyperfine pattern in the spectrum of $CF_3CH_2C_{60}$ is that of two equivalent protons and three equivalent ^{19}F nuclei over a wide temperature range, with no suggestion of broadening of the central components which characterizes enantiomeric exchange. The three ^{19}F nuclei have hyperfine interactions of 2720 mG, and there is no doubt that $CF_3CH_2C_{60}$ has the symmetric conformation with the CF_3 group over the pentagon. Indeed, INDO charge distributions for the two conformers of $CF_3CH_2C_{60}$ [Figs. 3(c) and 3(d)] illustrate clearly why this is so. As indicated in Figs. 3(c) and 3(d), the substitution of a CF_3 group for an H atom induces a redistribution of charges which is rather different to the effect of substitution of an F atom (see above). The most striking difference is that the negative charge on C-5, C-5' and C-1 increases in spite of the fact that the CF_3 contains three strongly negative fluorine atoms. The explanation appears to be that the CF_3 group also contains a strongly positive carbon atom which is primarily responsible for the increased charge on C-5, C-5' and C-1. Contrariwise, the effect on atoms further away, such as C-8 and C-8' (for the symmetric conformer) and C-2 and C-4 (for the asymmetric conformer) is induced mainly by the negatively charged fluorines, so that these carbons become more positive. The higher stability of the symmetric conformer of $CF_3CH_2C_{60}$ appears to be due to the fact that negative charges on C-5 and C-5' (symmetric conformer) are less than those on C-5 and C-1 (asymmetric conformer), these being the surface atoms closest to the fluorines of the CF_3 group in the two conformations.

Turning to the question of CF_3 versus F in the battle for the pentagon position, consider the spectrum of $CF_3CF_2C_{60}$ [Fig. 4(b)]. There is very little change in the spectrum over the temperature range 225–425 K,² and at the lowest accessible temperatures there is no suggestion of broadening of the 1:2:1 triplets which would presage the onset of enantiomeric exchange. This suggests that, in spite of its slightly smaller σ_I -value, the CF_3 group has gained the pentagon position. The same conclusion can be drawn from the spectrum of CF_3CHFC_{60} [Fig. 4(c)], which is also remarkably unchanged over the temperature range 250–425 K. Moreover, it would appear that ^{19}F hyperfine interactions in the range 2400–2700 mG are characteristic of CF_3 groups in the pentagon position. Indeed, this conclusion is consistent with data for the radical $(CF_3)_3CC_{60}$ at 225 K.² At this temperature, rotation about the C– C_{60} bond had stopped on the EPR time-scale, and the ^{19}F nuclei of the CF_3 group in the pentagon position had average hyperfine interactions of 2260 mG, whereas those of the CF_3 groups over the hexagons had average hyperfine interactions of 1630 mG. Although 2260 mG is just beyond the range mentioned above, this result confirms that ^{19}F nuclei of CF_3 groups have significantly larger hyperfine interactions when in the pentagon position than when over one of the hexagons. This result is not surprising since CH_3 groups show exactly the same behaviour: in $(CH_3)_3CC_{60}$ their protons have 340 mG hyperfine interactions when over the pentagon, but only 88 mG over one of the hexagons.³

Isopropyl- C_{60} radicals

Isopropyl- C_{60} , $(CH_3)_2CHC_{60}$, has the symmetric conformation,³ in accordance with the above sequence. For the slightly more complex spectrum of the radical $CF_3(CH_3)CHC_{60}$ [Fig.

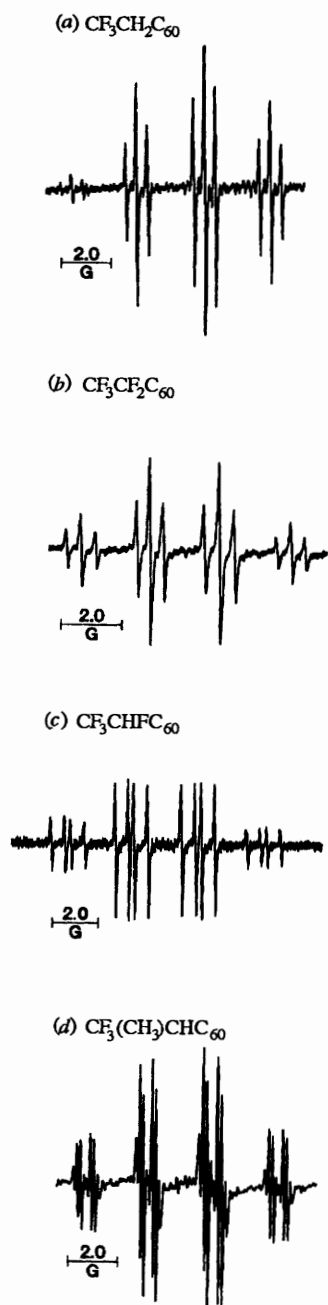


Fig. 4 EPR spectra of (a) $\text{CF}_3\text{CH}_2\text{C}_{60}$, (b) $\text{CF}_3\text{CF}_2\text{C}_{60}$, (c) $\text{CF}_3\text{CHFC}_{60}$ and (d) $\text{CF}_3(\text{CH}_3)\text{CHC}_{60}$

4(d)] the three ^{19}F nuclei had hyperfine interactions of 2620 mG and, bearing in mind the above discussion, we assign the

CF_3 group of $\text{CF}_3(\text{CH}_3)\text{CHC}_{60}$ to the pentagon position. In other words, the CF_3 group has gained the pentagon position against competition from a hydrogen atom and a methyl group. Bearing in mind the σ_1 -value of CF_3 (0.42) compared with those of H (0.00) and CH_3 (-0.05), this was only to be expected.

A final point: if a CF_3 group can gain the pentagon position against either hydrogen ($\text{CF}_3\text{CH}_2\text{C}_{60}$) or fluorine ($\text{CF}_3\text{CF}_2\text{C}_{60}$) atoms, then the radicals $(\text{CF}_3)_2\text{CHC}_{60}$ and $(\text{CF}_3)_2\text{CFC}_{60}$ should have the asymmetric conformation in which exchange between the enantiomers enables the two CF_3 groups to share access to the pentagon position. Indeed, there is evidence in both cases that this is so. The six ^{19}F nuclei of $(\text{CF}_3)_2\text{CHC}_{60}$ have equal hyperfine interactions of 2010 mG,⁸ a figure close to the average ^{19}F hyperfine interaction of CF_3 groups in the pentagon and hexagon positions in $(\text{CF}_3)_3\text{CC}_{60}$,² i.e. $0.5 \times (2260 + 1630) = 1945$ mG (see above). For $(\text{CF}_3)_2\text{CFC}_{60}$ the six equivalent ^{19}F nuclei have hyperfine interactions of 1960 mG at 300 K (almost exactly equal to the above average). There was also clear evidence from line-broadening effects that at ~ 225 K the enantiomeric exchange process had entered the intermediate-temperature regime.² This confirmed that, in spite of a slightly smaller σ_1 coefficient, the CF_3 groups shared the pentagon position, and must be placed to the left of fluorine in the sequence controlling access to the pentagon position.

Acknowledgements

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