Equilibrium configurations of fluoromethyl-C_{60} radicals. An EPR and theoretical study of interactions with the C_{60} surface

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Abstract

The EPR spectra of CH_2FC_{60} and CHF_2C_{60} are presented, and the dominant conformer for each species identified. It is suggested that the equilibrium configurations of fluoromethyl-C_{60} radicals are determined not by steric effects, but by Coulombic interactions between highly polarizable fluorine atoms and the C_{60} surface. The dominant effect appears to be a preference for the conformation in which a fluorine atom lies over the pentagon adjacent to the point of attachment of the CH_nF_{3-n} ($3 \geqslant n \geqslant 0$) ligand. These effects are discussed on the basis of semi-empirical calculations of the equilibrium structures and charge distributions on the C_{60} surface.

1. Introduction

In recent years we have been exploring, by means of EPR spectroscopy, the addition of free radicals to C_{60} and C_{70} [1–5]. Of particular interest has been the barrier hindering rotation about the R–C_{60} bond and the equilibrium configuration of RC_{60} radicals [3]. Somewhat to our surprise, the configuration adopted when rotation about R–C_{60} had stopped on the EPR time-scale was not the same for an alkyl radical as for its perfluoro-analog [6]. For example, isopropyl-C_{60}, $(CH_3)_2CHC_{60}$, is locked into the symmetric configuration even at 425 K, whereas perfluoroisopropyl-C_{60}, $(CF_3)_2CFC_{60}$, adopts an asymmetric configuration in which there is exchange between its enantiomers even at 180 K. The converse is true for ethyl- and perfluoroethyl-C_{60} [6]:
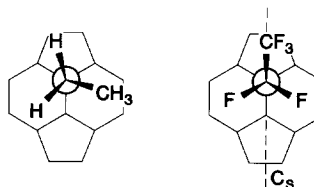
These configurations are not determined by steric effects, but by some other interaction between the CF_3 and/or CH_3 groups and the C_{60} surface. Simply put, it would appear that a CF_3 group is more comfortable over the pentagon, whereas a CH_3 group is more comfortable over one of the hexagons. In order to explore these interactions more closely we decided to simplify the system as much as possible and to examine the series of radicals $CH_nF_{3-n}C_{60}$ ($3 \geqslant n \geqslant 0$).

2. Experimental procedure

C_{60} (99.9%) was obtained from SES Research Inc., Houston TX; CH_2FBr from Central Chemicals Co. Inc., Tokyo, Japan; CHF_2Br from PCR Inc., Gainesville FL; other chemicals from the Aldrich Chemical Co., Milwaukee WI. Typically, the samples consisted of 350 mm^3 of a solution of C_{60} in a suitable solvent (see Table 1), to which had been added ≈ 25 µM of the alkyl bromide or, if available, iodide. The latter component was added either in a glove-box continuously flushed with dry argon, or by standard vacuum techniques. The samples were contained in 5 mm inner diameter, 6 mm outer diameter Suprasil™ quartz tubes fitted with greaseless stopcocks.

The EPR spectrometer had a Varian E-102 microwave bridge, a 12 inch magnet, and the usual accessories for monitoring the microwave frequency and the magnetic field strength. The microwave cavity was equipped with a Suprasil™ insert (Wilmad Glass Co., Buena NJ) and a Lake Shore Cryotronics Inc. (Westerville OH) model 805 temperature controller. The spectrometer was also equipped with a signal-averaging accessory by Scientific Software Services (Bloomington IL). The samples could be photolyzed in situ using the focused light of a Schoeffel 1000 W Hg/Xe arc filtered through a 5 cm column of water and an Oriel Corp. (Stratford CT) infra-red filter.

Table 1
Hyperfine interactions (mG) of methyl- and fluoromethyl-C_{60} radicals [a]

Radical	^{1}H hfi	^{19}F hfi	Temp. (K)
CH_3C_{60} [b]	3H = (−)35		300
CH_2FC_{60} [c]	2H = (−)230	1F = (+)780	400
CHF_2C_{60} [d]	1H = (−)150	2F = (+)240	300
CF_3C_{60} [e]		3F = (−)74	285
		1F = (+)630	180
		2F = (−)280	180

[a] All g-factors lay in the range 2.0021–2.0023. Errors ±5 in the last digit given. Sign-information inferred [3,6].
[b] Photolysis of CH_3Br in toluene:C_{60}.
[c] Photolysis of CH_2FBr in tert-butylbenzene:C_{60}.
[d] Photolysis of CHF_2Br in tert-butylbenzene:C_{60}.
[e] Photolysis of CF_3I in methylcyclohexane:C_{60}.

3. Results and discussion

3.1. EPR data for CH_3C_{60}, CH_2FC_{60}, CHF_2C_{60} and CF_3C_{60}

It is now well established for CH_3C_{60} and CF_3C_{60} that a proton or fluoron in the symmetric position ($\Theta = 0°$, or over the pentagon) has a *positive* hyperfine interaction, whereas a proton or fluoron in the asymmetric position ($\Theta = \pm 120°$, or over one of the hexagons) has a smaller (in magnitude) and *negative* hyperfine interaction (Table 1) [3,6]. In the case of CH_3C_{60}, this was the explanation offered for the surprisingly small hyperfine interactions observed at 300 K, at which temperature the individual values were averaged by rotation about the CH_3–C_{60} bond [3].
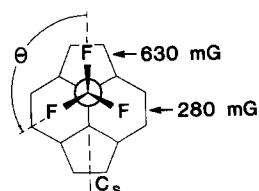
For CF_3C_{60}, however, distinct hyperfine interactions were observed at 180 K for fluorines at $\Theta_F = 0$ and $\pm 120°$ (Fig. 1a). At 300 K, this hyperfine structure collapsed to a much narrower one, behaviour which confirmed opposite signs for the hyperfine interactions of ^{19}F nuclei in the two positions. ROHF/MNDO calculations [7] [1] on the molecules CH_3C_{60} and CF_3C_{60} indicated that it was the nucleus at $\Theta = 0°$ which had a positive hyperfine interaction (Table 1).
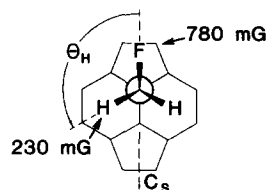
We turn now to the spectrum of CH_2FC_{60} (Fig. 1b). Its hyperfine pattern is clearly that of two equivalent nuclei with spin $I = 0.5$ (the protons), plus another nucleus (the fluoron) also with spin $I = 0.5$ but a
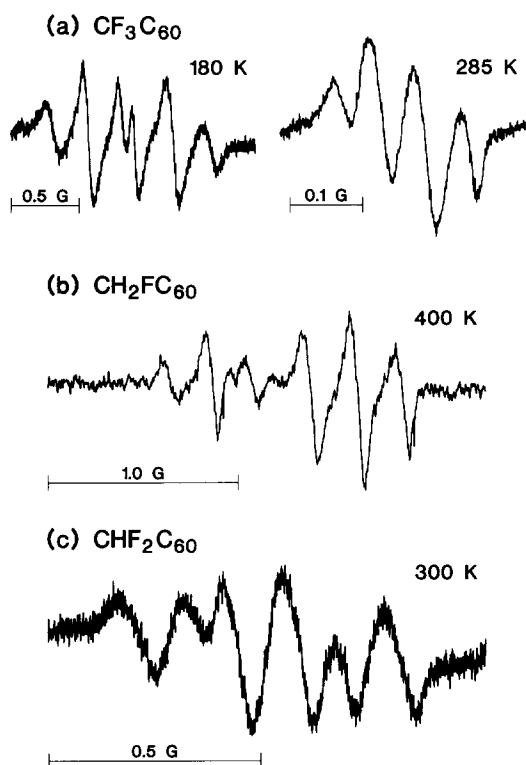
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[1] See footnote 7 of Ref. [6].

(a) CF_3C_{60}

(b) CH_2FC_{60}

(c) CHF_2C_{60}

Fig. 1. (a) The EPR spectrum of CF_3C_{60} at 180 and 285 K; (b) the EPR spectrum of CH_2FC_{60} at 400 K; (c) the EPR spectrum of CHF_2C_{60} at 300 K.

much larger hyperfine interaction. The magnitude of the latter (780 mG) is reasonable for a fluoron at $\Theta_F = 0°$, when compared with the unique fluoron in CF_3C_{60} at 180 K (630 mG). As regards the hyperfine interactions of the protons, which must lie in the $\Theta_H = \pm 120°$ region, there can be little doubt that their hyperfine interactions are negative in sign (see above). However, there being no data from alkyl-C_{60} radicals on the hyperfine interactions of protons in the $\Theta_H = \pm 120°$ region, we compare the proton hyperfine interactions in CH_2FC_{60} (230 mG) with those of the equivalent protons in $CH_2(OH)C_{60}$ (175 mG) and $CH_2(CO_2H)C_{60}$ (330 mG) [8]. In all three cases the third ligand, being more electronegative than the hydrogen atoms, lies over the pentagon. The proton hyperfine interaction in such situations appears to vary widely, ranging between 420 mG for $C_6H_5CH_2C_{60}$ [1] and 175 mG in $CH_2(OH)C_{60}$. We assume this variation is due to the sensitivity of the proton hyperfine interactions to the nature of the

substituent and the angle Θ_H between the C–H bonds and the symmetry plane [7].

It is a remarkable fact that CH_2FC_{60} is frozen into the symmetric configuration on the EPR time-scale, even at 400 K. This is in contrast to CH_3C_{60}, for which the 'frozen' configuration could not be observed, even at 180 K [3]. Clearly, there is an interaction between the fluorine atom in CH_2FC_{60} and the pentagon on the C_{60} surface which leads to a marked preference for the symmetric configuration.

We have also observed the spectrum of CHF_2C_{60} (Fig. 1c). The hyperfine interaction of the proton is even smaller (in magnitude) than those of the protons of CH_2FC_{60}, but not as small as those of CH_3C_{60}. We conclude that the equilibrium configuration of CHF_2C_{60} is asymmetric. In such a situation there is no symmetry requirement that Θ_H be 120° (as would be the case for CH_3C_{60}, for example). Proton hyperfine interactions in these systems being strongly Θ_H-dependent, a value of $(-)$ 150 mG is not unreasonable. An asymmetric equilibrium configuration introduces the possibility of exchange between the enantiomers, as observed for $CH_3CH_2C_{60}$ [3] and $(CF_3)_2CFC_{60}$ [6]. In the case of CHF_2C_{60}, enantiomeric exchange explains both the equivalence of the ^{19}F hyperfine interactions, and their small magnitudes. From the data for CF_3C_{60} at 180 K (Table 1) a prediction of the average hyperfine interaction of the exchanging ^{19}F nuclei may be obtained: $0.5 \times (630 - 280) = (+)175$ mG. Unlike CF_3C_{60}, however, there is no requirement in CHF_2C_{60} that Θ_F be 0° and 120°. In view of the known variation of the ^{19}F hyperfine interaction with Θ_F [7] the observed value of 240 mG at 300 K supports the hypothesis of enantiomeric exchange in CHF_2C_{60}.

The CHF_2C_{60} molecule, therefore, eschews the symmetric configuration which would have placed both fluorines over hexagons and the hydrogen over the pentagon.
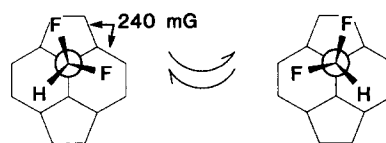
Clearly, the preference of fluorine atoms for the pentagon, and/or the hydrogen atom for the hexagons, is an important factor in determining the rela-

tive energies of the symmetric and asymmetric configurations in both CH_2FC_{60} and CHF_2C_{60}. Similar conclusions can be drawn from the configurations of perfluoroalkyl-C_{60} radicals [6] concerning the relative preference for the pentagon-position of CF_3 groups and F atoms, and also for CH_3 groups relative to H atoms from the EPR spectra of alkyl-C_{60} radicals [3]. Compare, for example, the equilibrium configurations of $CF_3CF_2C_{60}$ (symmetric) and $(CF_3)_2CFC_{60}$ (asymmetric) [6], or $(CH_3)_2CHC_{60}$ (symmetric) and $CH_3CH_2C_{60}$ (asymmetric) [3]. These considerations clearly imply that the preference for the pentagon-position is as follows: $CF_3 > F$ and $H > CH_3$. The present work has established that $F > H$ in its preference for the pentagon-position, so that we have the overall sequence $CF_3 > F > H > CH_3$.

3.2. Conformational analysis

In order to establish the factors which favour the experimentally observed structures, we have computed energies and charge distributions for CH_2FC_{60} and CHF_2C_{60} radicals in each of the two possible conformations, symmetric (C_s) and asymmetric (C_1). The two geometrical structures of each radical were optimized by the MNDO/UHF method [9]. To obtain the energy difference between the two structures we used, in addition to MNDO, the CNDO and INDO semi-empirical Hamiltonians as well as the ROHF/STO-3G ab initio method. The latter calculations were performed with the GAUSSIAN 92 program [10]. Atomic charge distributions were also computed for each conformer. These are presented in Table 2.

All theoretical methods predict very small energy differences (≈ 1 kcal/mol) between the two conformers of the radicals CH_2FC_{60} and CHF_2C_{60}. Of the methods employed, however, only the INDO Hamiltonian predicted the most stable conformers to be those identified as carriers of the EPR spectra. It seems that the greater stability of these conformers is the overall result of several rather small, opposing interactions between the highly polarizable electronic clouds of the fluorine atom(s) and charges on the C_{60} cage. Indeed, it is well known that the correct sign of the energy difference between the conformers of molecules as simple as the fluoro-ethanes [11] can only be obtained with very sophisticated calculations, in-

cluding large basis sets with diffuse functions which account for the larger polarizability of fluorine. Thus, it is not surprising that our semi-empirical methods give only a qualitative description of the large and complex systems studied here.

To gain a simpler insight into the higher stability of conformers in which a fluorine atom lies over the pentagon, we have examined the atomic charge distributions presented in Table 2. These indicate that the fluorine-induced Coulombic interactions, which are different in the two conformers, give a reasonable explanation of the higher stability of those observed experimentally. In fact these interactions must contribute considerably to their relative stability, since steric interactions for the two conformers are almost the same. The following discussion relates to the INDO-predicted charge distributions, since only this Hamiltonian successfully predicted the correct equilibrium configuration of both radicals.

In the case of CH_2FC_{60}, it is seen that most of the charge lies on carbon C9 and the fluorine, with relatively little charge on the C_{60} cage. The effect of the fluorine atom, which is negatively charged and much more polarizable than the hydrogen atom which it has replaced, is to induce a different charge distribution on the cage for the two conformers. It will be seen from Table 2 that C1 always bears the most negative charge, with C5 and C5' having some negative charge in the asymmetric (least stable) conformer. It is clear from the charge distributions that the conformer of CH_2FC_{60} with the fluorine atom over the pentagon is subject to smaller repulsions than the conformer in which the fluorine atom is over one of the hexagons. Indeed, an important interaction in the case of the symmetric conformer of CH_2FC_{60} may well be the attraction between the negative charge on the fluorine atom and the positive charge on atoms C8 and C8'.

Similar considerations lead to the conclusion that the asymmetric conformer of CHF_2C_{60} is also subject to weaker repulsions, or stronger attractions. The fluorine atom over the pentagon is near positive charges on C8 and C8', and the other fluorine is near positive charges on positions 2', 3', 4' and 5'. The diagrams in Scheme 1 show the charge distribution in the more stable configurations of the two radicals.

It is interesting to note that INDO calculations predict a much larger charge on the fluorine atoms than does MNDO. The better performance of INDO in

Table 2
Atomic charge distribution for the two conformers of CH_2FC_{60} (upper half) and CHF_2C_{60} (lower half) radicals

Atom	C_s symmetry			C_1 symmetry		
	MNDO	INDO	MNDO [a]	MNDO	INDO	MNDO [a]
C1	−0.07	−0.023	−0.34	−0.05	−0.014	−0.32
C2	−0.01	0.005	0.11	0.00	0.010	0.12
C2′				−0.01	0.007	0.11
C3	0.02	0.002	−0.15	0.03	0.005	−0.15
C3′				0.01	−0.005	−0.16
C4	−0.01	0.002	0.03	0.00	0.008	0.04
C4′				−0.01	0.003	0.04
C5	−0.02	0.000	−0.07	−0.03	−0.002	−0.07
C5′				−0.04	−0.004	−0.08
C6	0.05	0.003	0.12	0.05	0.004	0.12
C7	−0.01	0.000	−0.04	−0.01	0.000	−0.03
C7′				−0.01	−0.007	−0.03
C8	0.01	0.012	0.02	0.00	0.008	0.01
C8′				0.00	0.004	0.01
H	0.02	−0.035	0.01	0.02	−0.035	−0.01
H				0.02	−0.035	0.00
F	−0.23	−0.307	−0.26	−0.23	−0.306	−0.24
C9	0.29	0.341	0.24	0.26	0.342	0.25

Atom	C_s symmetry			C_1 symmetry		
	MNDO	INDO	MNDO [b]	MNDO	INDO	MNDO [b]
C1	−0.06	−0.004	−0.31	−0.07	−0.014	−0.33
C2	0.01	0.010	0.13	0.00	0.004	0.12
C2′				0.01	0.013	0.13
C3	0.02	0.004	−0.15	0.01	0.001	−0.16
C3′				0.03	0.005	−0.14
C4	0.01	0.010	0.06	−0.01	0.004	0.04
C4′				0.00	0.006	0.05
C5	−0.05	−0.004	−0.09	−0.04	−0.002	−0.08
C5′				−0.02	0.010	−0.06
C6	0.05	−0.030	0.12	0.05	−0.031	0.12
C7	−0.01	0.001	−0.04	−0.01	0.001	−0.04
C7′				−0.01	−0.007	−0.04
C8	0.00	0.009	0.01	0.01	0.015	0.02
C8′				0.01	0.007	0.02
H	0.05	−0.058	0.02	0.05	−0.057	0.03
F	−0.23	−0.320	−0.24	−0.23	−0.320	−0.25
F	−0.23	−0.320	−0.24	−0.23	−0.320	−0.24
C9	0.44	0.640	0.42	0.44	0.640	0.42

[a] $CH_2FC_{60}^-$. [b] $CHF_2C_{60}^-$.

predicting energy differences might well be related to this increased charge on the fluorines, and hence to an increased sensitivity to the different charge distributions that characterize the pentagon or the hexagon on the C_{60} cage. To further check the effectiveness of charge distribution in determining the relative

stability of the conformers, we computed energy differences for the negatively charged C_{60} derivatives $CH_2FC_{60}^-$ and $CHF_2C_{60}^-$. The resulting charge distributions, computed with MNDO, are also listed in Table 2. For the anionic derivatives we found that increased repulsion between the negative charge on
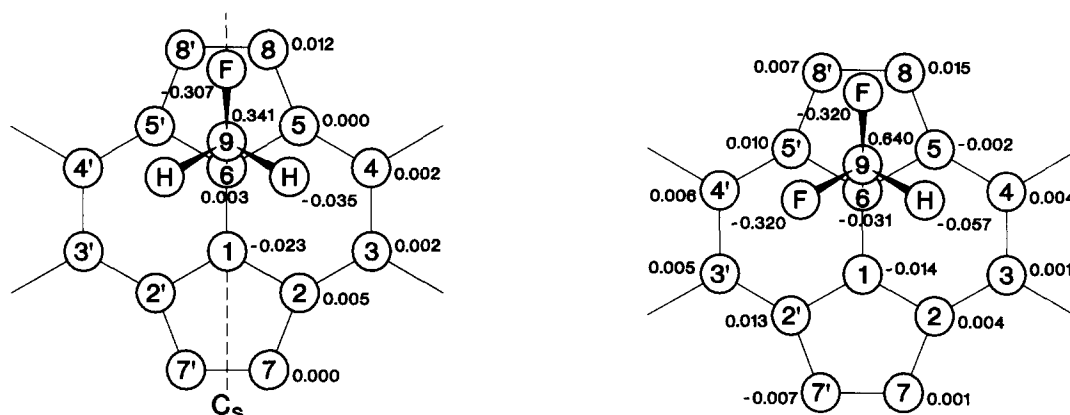
Scheme 1.

the fluorine(s) and on the C_{60} cage leads to a markedly increased stabilization of the conformers in which a fluorine atom lies over the pentagon.

With these anions we have altered the balance among the various interactions, resulting in an enhanced repulsion between the negative charges on the fluorine(s) and those on the C_{60} cage. The result of the calculations on the anions indicated an increased preference for conformers analogous to those experimentally observed. This leads us to suspect that both MNDO and INDO underestimate the importance of repulsive interactions between negative charges in the neutral radicals because of their inherently imperfect description of the polarizability of fluorine electronic clouds.

4. Conclusions

A most surprising feature of our observations on these simple C_{60} derivatives is the very existence of rotational isomers. The uncluttered surface of the C_{60} framework might have led one to expect little or no hindrance to such motion, contrary to the evidence of the present experiments. The present work clearly implies the existence, in the case of fluorine-containing radicals, of significant electronic interactions between the incoming radical and the C_{60} cage. These interactions contribute to the increased barrier to R–C_{60} rotation and the consequent existence of energetically different rotational isomers.

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