# PROGRESS REPORT

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UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

AND

THE UNIVERSITY OF TENNESSEE

PERIOD

SEPTEMBER 15, 1976 TO SEPTEMBER 15, 1977

Title of Project

# RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATION CHEMISTRY

Principal Investigator

T. Ffrancon Williams
Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37916
(Telephone No. 615-974-3144)

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A. Personnel

(1) Dr. T. Ffrancon Williams: Professor of Chemistry and Alumni Distinguished Service Professor.

(2) Dr. Akinori Hasegawa: Postdoctoral Research Associate on leave from the Faculty of Science, Hiroshima University, Hiroshima 730, Japan. Dr. Hasegawa completed his appointment on October 8, 1976 after approximately 1-1/2 years with the project.

(3) Dr. Masaru Shiotani: Postdoctoral Research Associate on leave from the Faculty of Engineering, Hokkaido University, Sapporo 060, Japan. Dr. Shiotani completed his appointment on March 31, 1977 after approximately 1-1/2 years with the project.

(4) Dr. Hisao Murai: Postdoctoral Research Associate. Dr. Murai received his doctorate from the Tokyo Institute of Technology, Tokyo, Japan. He joined the project on October 1, 1976 and will probably complete his appointment during the summer of 1978.

(5) Dr. Moon Bin Yim: Postdoctoral Research Associate. Dr. Yim received his Ph.D. degree from the University of Connecticut, Storrs, Connecticut. He joined the project on February 1, 1977.

(6) Mr. Reggie L. Hudson: Graduate Teaching Assistant and Research Assistant. Mr. Hudson is a candidate for the Ph.D. degree in Chemistry (with a major in Physical Chemistry) at the University of Tennessee.

(7) Mr. Robert I. McNeil: Graduate Teaching Assistant and Research Assistant. Mr. McNeil is a candidate for the Ph.D. degree in Chemistry (with a major in Physical Chemistry) at the University of Tennessee.

(8) Mr. Ashok M. Adur: Graduate Teaching Assistant. Mr. Adur is a candidate for the Ph.D. degree in Chemistry (with a major in Polymer Chemistry) at the University of Tennessee.

## B. Employment

Dr. Williams devoted 25% of his time during the 1976-77 academic year to this research project, this being a University contribution to this Contract. He was also employed full-time for three months during the summer of 1977. The Postdoctoral Research Associates were employed full-time during their appointment periods, as specified above. Mr. Hudson was employed as a Research Assistant from March 1, 1977 to August 31, 1977. Mr. McNeil was employed as a Research Assistant from June 1, 1977 to August 31, 1977.

## C. Facilities and Equipment

This research project relies heavily on three major pieces of equipment consisting of an ESR spectrometer system, a 1.5 kilocurie cobalt-60 γ-irradiation source, and various cryogenic devices including a liquid helium transfer refrigerator system. These items have been described in earlier progress reports. The ESR spectrometer system (acquired in 1966) was essentially in daily operation throughout the past year and the only downtime period (ca. 1 week) was caused by a water-cooling problem in the power-supply unit. This problem seems to have been solved by repeated flushing of the passages in the cooling circuit.

The cobalt-60 Gammacell was out of operation from January 19 to February 3, 1977. A problem developed whereby the sample drawer, which is operated electrically, repeatedly jammed in the "up" position and had to be loosened manually before it could be re-lowered into the irradiation position. A related problem had been experienced in March, 1976 (see last year's progress report ORO-2968-105) but it now appears that the underlying fault was not diagnosed at that time. In the recent breakdown, the problem was eventually traced to a faulty electrical relay system. This system was thoroughly overhauled and the positions of the microswitches were adjusted. Since resumption of the Gammacell use in February, 1977, there have been no further problems in the operation of the drawer.

The main equipment acquisitions during the past year consisted of a high-quality analytical balance and an "explosion-proof" refrigerator for the storage of volatile and heat-sensitive chemicals.

## D. Outline of Progress and Publications

Considerable progress has been made in our ESR studies of fluorocarbon radicals and this continues to be a fertile field of investigation. Since last year's progress report, we have obtained the ESR spectrum of the hexafluorocyclopropane radical anion to complete the series of perfluorocycloalkane radical anions from $\underline{c}$-$C_3F_6^-$ through $\underline{c}$-$C_6F_{12}^-$. A detailed report of this work was presented at the Faraday Discussion on "Radiation Effects in Liquids and Solids" held in March, 1977 and will shortly appear in the printed account of the meeting; a preprint of our paper is included in this progress report. This paper also summarizes our work on the radical anions of the Freons, including $CF_3Cl^-$, $CF_3Br^-$, $CF_3I^-$, and $CF_2Cl_2^-$. All these negative ions are characterized as "hypervalent" species, i.e. they possess more electrons than can be accommodated by valence-bond structures based on the Lewis octet rule. There is therefore much interest in the electronic structure of these novel species. The ESR results for the perfluorocycloalkane radical anions indicate that the unpaired electron is delocalized over the ring in an orbital of high symmetry, whereas in the $CF_3X^-$ anions the unpaired spin density is largely concentrated in the $\sigma^*$ antibonding orbital between carbon and the unique halogen. ESR studies have also shown that, as expected, the $CF_3X^-$ radicals dissociate to give the $CF_3$ radical.

In addition to our work on radical anions derived from saturated fluorocarbons and halocarbons, we have been successful in obtaining the ESR spectra of several perfluoroalkene radical anions, including the tetrafluoroethylene radical anion. During the course of our ESR studies on the $C_2F_4^-$ species, we obtained evidence for the noval cycloaddition of neutral $C_2F_4$ to $C_2F_4^-$ resulting in the formation of the octafluorocyclobutane radical anion. Further work is presently in progress on other fluoroalkene radical anions. Two papers describing our studies on $C_2F_4^-$ have been accepted for publication and are appended to this report. Another paper on the ESR spectra of perfluorocycloalkene radical anions ($\underline{c}$-$C_4F_6^-$, $\underline{c}$-$C_5F_8^-$, and $\underline{c}$-$C_6F_{10}^-$) will be submitted shortly.

Although much of our recent ESR work has been concerned with fluorine-containing radicals, there has been a continuing effort to identify the intermediate radicals produced by irradiation of compounds such as dimethyl carbonate, trimethyl phosphite, tetramethyl orthosilicate, and trimethyl borate. The main interest here is in the generation and characterization of radicals formed by electron attachment and/or electron loss processes, since these processes are widely believed to be primary steps in the chemical effects of high energy radiation. A particularly detailed study has been made of the dimethyl, diethyl, and di-n-propyl carbonates. In each case it has been possible to identify the electron-gain center (radical anion) and to trace the formation of the secondary radical produced from this primary center. This is illustrative of how the ESR method can be used to distinguish between the primary and secondary reactions in radiation chemistry.

A particular highlight of the work on methyl derivatives of inorganic acids is the recent detection of the dimer radical anion of trimethyl borate (Document ORO-2968-110, accepted for publication in J. Am. Chem. Soc.). As far as we are aware, this is the first unambiguous example of a $\sigma$ radical with a one-electron bond, and it serves as a model for isostructural electron-deficient species, such as $C_2H_6^+$, which are of considerable interest in many areas of chemistry. In general, radicals of this type are extremely elusive to ESR detection on account of their great reactivity. For example, it is significant that unambiguous ESR spectra have not yet been reported for the positive ions of saturated hydrocarbons. Therefore, it is of interest to know that the structure of the $[(MeO)_3B{\cdot}B(OMe)_3]^-$ radical, as deduced from its ESR spectrum, is in accord with theoretical expectations for the $C_2H_6^+$ species, the common feature being that the semi-occupied $\underline{a}_{1g}$ molecular orbital is σ bonding between the two central atoms.

Studies have also continued on the problem of hydrogen-atom abstraction reactions at low temperatures, especially with a view to evaluating the contribution from quantum-mechanical tunneling. Recently, we published results showing that the reaction rate constant for hydrogen-atom abstraction by methyl radicals in methanol glasses reaches a limiting value below 40 K (R. L. Hudson, M. Shiotani, and F. Williams, Chem. Phys. Letters, **48**, 193 (1977)). These results can be regarded as convincing evidence for quantum tunneling. Very similar findings have just been reported for a hydrogen atom transfer reaction in irradiated crystals of dimethylglyoxime (K. Toriyama, K. Nunome, and M. Iwasaki, J. Am. Chem. Soc., **99**, 5823 (1977)), and a similar conclusion was drawn about the importance of tunneling. Additional kinetic studies have been carried out in our group on methyl radical reactions in ethanol, these results providing further support for the role of tunneling in hydrogen-atom transfer reactions at very low temperatures.

Finally, we describe some exploratory experiments involving pulse radiolysis studies of radical anions which were carried out at the Center for Fast Kinetics Research at the University of Texas at Austin during the week of June 13 to June 17, 1977. The aim of this work was to complement our ESR and optical studies on solids by kinetic measurements at higher temperatures. Although intermediates in solids frequently have the desirable feature of being long-lived so that they can be studied at leisure, the very nature of the matrix-isolation technique makes it less suitable for detailed kinetic studies. From a number of systems that were investigated, positive results were obtained in at least two cases. Firstly, the dimer radical anion of acetonitrile was detected as a transient in the upper crystalline phase at -50°C by its absorption at 450-550 nm. This absorption decayed by first-order kinetics with a half-life of *ca.* 300 μsec at -50°C, in contrast to the indefinitely long lifetime observed for this center at -196°C. Secondly, a spectrum of the perfluorobenzene radical anion was detected by pulse radiolysis of a $C_6F_6$ solution in tetrahydrofuran, the transient absorption ($\lambda_{max}$ at 380 nm) agreeing with the spectrum obtained by γ irradiation of a solution of $C_6F_6$ in a rigid methyltetrahydrofuran glass. Kinetic measurements indicated that the transient decayed by first-order kinetics with a half-life of 3 μsec. On the other hand, transient spectra were not detected in some systems (*e.g.* tetrafluoroethylene solutions) for which characteristic spectra have been obtained by irradiation at low temperatures. Negative results in pulse-radiolysis experiments can be attributed to a number of possible factors, such as a weak absorption spectrum and a short lifetime for the transient. In general, it seems that pulse radiolysis studies of this type will be most successful for radical anions which have intense optical absorption bands.

During the course of this year five papers were issued (Reports ORO-2968-106 through ORO-2968-110) and all of these have been accepted for publication. A listing of these current reports and their abstracts is given below in Section 1. Also, all of last year's current reports have been published (Reports ORO-2968-100 through ORO-2968-104) and the titles are included in the present compilation under Section 2. This summary of our activities in the past year concludes with a list of conference presentations in Section 3. Preprints and reprints of the above papers are appended to this report.

## SECTION 1 - CURRENT REPORTS

I. [CRO-2968-106] ELECTRON SPIN RESONANCE STUDIES OF ELECTRON ATTACHMENT TO FLUOROCARBONS AND RELATED COMPOUNDS (A. Hasegawa, M. Shiotani, and F. Williams, Faraday Discussions Chem. Soc., No. 63, 000 (1977), in press).

ABSTRACT: Radical anions of three perfluorocycloalkenes and several halofluoromethanes have been detected and identified by e.s.r. studies following γ irradiation at 77 K of solid solutions containing up to 5 mole % of the parent compound in neopentane or tetramethylsilane. The isotropic e.s.r. spectra of $\underline{c}$-$C_3F_6^-$, $\underline{c}$-$C_4F_8^-$ and $\underline{c}$-$C_5F_{10}^-$ are photobleached by visible light and show the second-order structure characteristic of 6, 8, and 10 equivalent fluorines, respectively, the total $^{19}F$ coupling being approximately the same value (1170 ± 20 G) in each case. Identical e.s.r. spectra were generated in photoionization experiments using tetramethyl-$\underline{p}$-phenylenediamine, confirming the radical anion identifications. The equivalence of the fluorines indicates that the unpaired electron is delocalized over the entire molecular framework in an orbital of high symmetry. The e.s.r. spectra of the $CF_3X^-$ radical anions (X = Cl, Br, I) were anisotropic and showed clear evidence for axially symmetric hyperfine interactions with three equivalent fluorines and the unique halogen. On this basis, a matrix diagonalization program was used to calculate the line positions and the best-fit e.s.r. parameters obtained. Confirmation of the $CF_3X^-$ identifications was achieved by parallel photoionization experiments and by studies showing that the decay of the $CF_3X^-$ spectrum in neopentane above 100 K was accompanied by a growth in the spectrum of the $CF_3$ radical. The spin density distributions calculated from the e.s.r. parameters of these congeneric radical anions suggest that the unpaired electron resides in an $\underline{a}_1$ ($\sigma^*$) antibonding orbital which is composed largely of the $\underline{p}$ orbitals from carbon and the unique halogen which lie along the $\underline{C}_{3v}$ symmetry axis of the radical anion. Consistent with this proposal, the spin densities in the $\underline{s}$ and $\underline{p}$ orbitals of the unique halogen increase along the

series Cl, Br, I, which is the order expected for the effect of decreasing halogen electronegativity.

II. [ORO-2968-107] HYDROGEN ATOM ABSTRACTION BY METHYL RADICALS IN METHANOL GLASSES AT 15-100 K: EVIDENCE FOR A LIMITING RATE CONSTANT BELOW 40 K BY QUANTUM-MECHANICAL TUNNELING (Reggie L. Hudson, Masaru Shiotani, and Ffrancon Williams, Chem. Phys. Letters, **48**, 193 (1977)).

ABSTRACT: Rate constants for hydrogen atom abstraction by methyl radicals in methanol glasses have been measured from 100 to 15 K. The Arrhenius plot is nonlinear and the reaction rate constant appears to reach a limiting value below 40 K. The results are discussed in terms of simple models for quantum-mechanical tunneling in the solid state at low temperatures. Assuming that the methyl group rotation in methanol brings about a merging of the energy level distribution at the potential barrier, the observation of temperature-independent rate constants below 40 K may be attributable to a freezing out of this rotation such that tunneling occurs only from the zero-point vibrational level.

III. [ORO-2968-108] THE ISOTROPIC AND ANISOTROPIC EPR SPECTRA OF THE TETRAFLUOROETHYLENE RADICAL ANION (Robert I. McNeil, Masaru Shiotani, Ffrancon Williams, and Moon B. Yim, Chem. Phys. Letters, in press).

ABSTRACT: The tetrafluoroethylene radical anion has been generated in solid solutions by electron addition to the parent molecule. Both its isotropic and anisotropic EPR spectra have been observed, including the isotropic $^{13}C$ satellite lines in natural abundance. The isotropic EPR parameters are $a_F = 94.3$ G, $a_C = 48.7$ G, and $g = 2.0027$. Two possible geometries, planar and chair, are discussed for this radical anion. The magnitude of the $^{19}F$ and $^{13}C$ hyperfine coupling constants are consistent with a planar ($D_{2h}$) structure provided that the unpaired electron occupies the $5b_{1u}$ ($\sigma^*$) rather than the $2b_{1g}$ ($\pi^*$) molecular orbital which is predicted by ab initio calculations to be the LUMO of the parent molecule. On the other hand, the EPR parameters do not rule out a chair ($\underline{C}_{2h}$) structure if the bending of the $CF_2$ groups introduces only a small distortion from planarity.

IV. [ORO-2968-109] NOVEL CYCLOADDITION OF TETRAFLUOROETHYLENE TO THE TETRAFLUOROETHYLENE RADICAL ANION AT 95 K: DIRECT OBSERVATION BY EPR STUDIES (Robert I. McNeil, Masaru Shiotani, Ffrancon Williams, and Moon B. Yim, *Chem. Phys. Letters*, in press).

ABSTRACT: The novel cycloaddition reaction $C_2F_4^- + C_2F_4 \rightarrow \underline{c}\text{-}C_4F_8^-$ has been observed directly by EPR spectroscopy in organic glasses at 80 - 95 K. According to the frontier orbital theory, the concerted reaction is symmetry allowed irrespective of whether the interaction is SOMO-LUMO or SOMO-HOMO, the SOMO of $C_2F_4^-$ being the $5\underline{b}_{1u}$ ($\sigma^*$) orbital suggested by EPR studies. The assignment of $C_2F_4^-$ as a $\sigma$ radical also suggests that a concerted [2 + 2] suprafacial mechanism should be considered for the thermal cycloaddition reaction between two neutral $C_2F_4$ molecules.

V. [ORO-2968-110] ELECTRON SPIN RESONANCE SPECTRUM OF $[MeO)_3B\cdot B(OMe)_3]^-$. A NOVEL σ-RADICAL WITH A ONE-ELECTRON BOND (Reggie L. Hudson and Ffrancon Williams, *J. Am. Chem. Soc.*, in press).

ABSTRACT: The γ irradiation of crystalline trimethyl borate at 77 K gives an ESR spectrum which is assigned to the dimer radical anion $[(MeO)_3B\cdot B(OMe)_3]^-$. The hyperfine pattern shows the presence of two anisotropically equivalent boron atoms with axially symmetric hyperfine tensors, the spectral parameters being $\underline{A}_{//}(^{11}B) = 59.3$ G, $\underline{A}_{\perp}(^{11}B) = 39.8$ G, $\underline{g}_{//} = 2.0020$, and $\underline{g}_{\perp} = 2.0043$. The spin distribution is accounted for by a $D_{3d}$ structure with a one-electron bond between the two boron atoms.

## SECTION 2 - UPDATE OF PREVIOUS REPORTS

VI. [ORO-2968-100] ELECTRON SPIN RESONANCE SPECTRUM OF THE PERFLUOROCYCLOBUTANE RADICAL ANION (Masaru Shiotani and Ffrancon Williams, J. Am. Chem. Soc., **98**, 4006 (1976)).

VII. [ORO-2968-101] RADIATION - INDUCED CATIONIC POLYMERIZATION OF ISOBUTYLENE - ISOPRENE SYSTEMS. ADVANTAGES AND DISADVANTAGES COMPARED TO CATALYTIC INITIATION (Ffrancon Williams, Akihiro Shinkawa, and Joseph P. Kennedy, J. Polymer Sci., Symposium No. 56, 421 (1976)).

VIII. [ORO-2968-102] THE ESR SPECTRUM AND STRUCTURE OF $BF_3^-$ (Reggie L. Hudson and Ffrancon Williams, J. Chem. Phys., **65**, 3381 (1976)).

IX. [ORO-2968-103] ESR SPECTRA AND STRUCTURE OF THE $CF_3Cl^-$, $CF_3Br^-$, and $CF_3I^-$ RADICAL ANIONS (Akinori Hasegawa and Ffrancon Williams, Chem. Phys. Letters, **46**, 66 (1977)).

X. [ORO-2968-104] THE ANISOTROPIC ESR SPECTRUM OF THE $SF_5$ RADICAL (Akinori Hasegawa and Ffrancon Williams, Chem. Phys. Letters, **45**, 275 (1977).

## SECTION 3 - CONFERENCE PRESENTATIONS

Two contributed papers were presented at the Eighth Southeastern Magnetic Resonance Conference (Wake Forest University, Winston-Salem, NC, October 7-8, 1976) and also at the Southeastern Regional Meeting of the American Chemical Society (Gatlinburg, TN, October 27-29, 1976). The abstracts of these papers are given below.

ESR SPECTRA OF PERFLUOROCYCLOALKANE RADICAL ANIONS. Masaru Shiotani[†] and

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[†] On leave from Faculty of Engineering, Hokkaido University, Sapporo 060, Japan.

Ffrancon Williams, Department of Chemistry, University of Tennessee, Knoxville, TN 37916

The novel octafluorocyclobutane and decafluorocyclopentane radical anions have been identified by means of their isotropic ESR spectra in a tetramethylsilane matrix, the radicals having been generated by γ irradiation at 77K of a solid solution containing 5 mol% of the perfluorocycloalkane. Their ESR spectra are photobleached by visible light and show the expected second-order structure characteristic of radicals possessing eight and ten equivalent fluorines, the parameters being $a_F$ = 148 G, g = 2.0021 and $a_F$ = 115 G, g = 2.0030 for the <u>c</u>-$C_4F_8^-$ and <u>c</u>-$C_5F_{10}^-$ radicals, respectively. The identity of the <u>c</u>-$C_4F_8^-$ radical anion was confirmed by the generation of an identical ESR spectrum in photoionization experiments using tetramethyl-p-phenylenediamine as an electron donor. It is proposed that the unpaired electron occupies either $a^*_1$ or $b^*_1$ group molecular orbitals which are derived from combinations of the localized C-F σ orbitals in $C_{2v}$ local symmetry. For <u>c</u>-$C_4F_8^-$ in $D_{4h}$ symmetry, the representations of these orbitals become $a^*_{1g}$ and $a^*_{2u}$, respectively.

THE ESR SPECTRUM AND STRUCTURE OF $BF_3^-$. Reggie L. Hudson and Ffrancon Williams, Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916.

An isotropic ESR spectrum observed in a γ-irradiated solid solution of $BF_3$ in tetramethylsilane at 80-100K has been assigned unequivocally to the $BF_3^-$ radical anion. Although this radical was previously reported [<u>Chem. Phys. Lett.</u>, **18**, 112 (1973)] to be one of the paramagnetic centers in an irradiated single crystal of $NaBF_4$, the ESR parameters appeared to be anomalous since they indicated that the radical was nearly planar. In the present work, the ESR spectrum was analyzed as a quartet of quartets originating from hyperfine interaction with three equivalent $^{19}F$ (I = 1/2) nuclei and a single $^{11}B$

(I = 3/2) nucleus, the parameters being $\underline{a}_{19}$ = +178 G, $\underline{a}_{11}$ = +153 G, and g = 2.0021. All the lines were easily photobleached thereby providing evidence for the anionic nature of the radical. Due to the large $^{19}F$ hyperfine couplings, second-order splittings were observed giving the appropriate number of line components with the expected relative intensities. The line positions were fitted by a matrix diagonalization computer program which accurately reproduced the variation in the second-order splittings across the spectrum. The ESR parameters are entirely consistent with those of the isoelectronic radicals $CF_3$, $NF_3^+$, and $F_2NO$, the results showing that $BF_3^-$ has a pyramidal geometry with a 2s spin density of 0.21 on the boron atom.

Invited papers were presented at the Faraday Discussion on Radiation Effects in Liquids and Solids (University of Leicester, Leicester, England, March 23-25, 1977) and at the Sixth International Symposium on Magnetic Resonance (Banff, Alberta, Canada, May 21-27, 1977). The abstract of the Faraday paper has been given in Section 1. Also, a Foreign Travel Report was submitted by Dr. Williams in connection with his attendance at this meeting and his other travel in the United Kingdom. At the Banff Symposium, Dr. Williams presented one of the "keynote" lectures entitled "ESR Studies of Hypervalent Radical Anions". The abstract of this talk is given below.

## ESR STUDIES OF HYPERVALENT RADICAL ANIONS

F. Williams, A. Hasegawa, K. Nishikida and M. Shiotani

Radicals possessing more electrons than can be accommodated by valence-bond structures based on the Lewis octet rule are termed hypervalent. Although many examples of such radicals are known where the central atom is a second-row element (e.g. $SiF_4^-$, $PF_4$, $SF_6^-$, $ClF_6$), the only known hypervalent radicals derived from first-row elements consisted until recently of the venerable

$V_k$-center $F_2^-$ and $F_3^{2-}$. In photoionization and γ-irradiation studies of electron attachment to a variety of *saturated* fluorine-containing compounds at low temperatures, several novel hypervalent radicals in which nitrogen or carbon is the central atom have been discovered by ESR spectroscopy, including $F_3NO^-$, $CF_3X^-$(X=Cl, Br, I), $CF_2Cl_2^-$, $CFCl_3^-$, $CCl_3Br^-$, *c*-$C_3F_6^-$, *c*-$C_4F_8^-$ and *c*-$C_5F_{10}^-$. For $F_3NO^-$, the isotropic couplings to the three fluorines are equivalent and there is a large spin density (0.27) in the nitrogen 2s orbital suggesting that the radical adopts $C_{3v}$ symmetry and that the unpaired electron occupies an $a_1^*$ orbital. The $CF_3X^-$ anions also adopt $C_{3v}$ symmetry and the unpaired electron appears to be largely localized in a $\sigma^*$ antibonding orbital between carbon and the unique halogen. In the *c*-$C_nF_{2n}^-$ series, the 2n fluorines are equivalent and the total $^{19}F$ coupling has approximately the same value (1170 ± 20 G) for each radical anion. These results indicate that the unpaired electron is delocalized over the perfluorocycloalkane ring in an orbital of high symmetry.

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