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The Octafluorocyclooctatetraene Radical Anion. Identification and Proof of Aromaticity by Electron Spin Resonance

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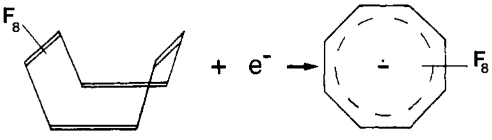
Abstract: The octafluorocyclooctatetraene radical anion has been generated by γ irradiation of a solid solution of the parent compound in a 2-methyltetrahydrofuran glass at 77 K. Its isotropic ESR spectrum is observed on warming the matrix to 145 K, the pattern consisting of nine lines in an approximately binomial intensity distribution with the parameters a (8F) = 10.92 G and g = 2.0049. The equivalence of the eight fluorines suggests a planar D_{8h} structure and INDO calculations for this geometry assign the unpaired electron to one of the doubly degenerate nonbonding E_{2u} (π) orbitals such that the spin density ρ is distributed uniformly around the ring and is mostly concentrated in the $2p_z$ orbitals of the carbon atoms. This model of a simple aromatic π radical anion is strongly supported by comparison of the $Q^{\rm F}{}_{\rm eff}$ value, defined by $a/\rho_{\rm C}$ ($2p_z$), for $C_8F_8^-$ with the corresponding values derived for perfluoroaromatic radical cations. In spite of the negative charge, $C_8F_8^-$ can be considered electron deficient in terms of Hückel's $4n + 2$ rule, thus affording a theoretical basis for the comparison with the perfluoroaromatic radical cations.

Introduction

ESR studies have shown that the structure of a perfluorinated organic radical may differ drastically from that of its hydrogen-containing counterpart.[1] For example, CF_3 is pyramidal whereas CH_3 is planar.[2] Also, $C_6F_6^-$ is thought to be a σ^* rather than a π^* radical analogous to $C_6H_6^-$ even though both species are presumed to have D_{6h} symmetry.[3] In view of the recent synthesis of octafluorocyclooctatetraene (OFCOT),[4] it was therefore of interest to generate the radical anion and compare its structure with that of the cyclooctatetraene (COT) radical anion, the latter having already been studied exhaustively by electrochemical and ESR methods more than two decades ago.[5,6] Since both of these neutral molecules adopt a tub conformation, the C_8 ring of OFCOT being only slightly more flattened than that of COT,[7] the basic question to be answered is whether or not the radical anion of OFCOT can assume planarity and become aromatic like its hydrogen-containing analogue.[8]



Attempts to observe the OFCOT radical anion by reduction of the neutral compound with alkali metals and with sodium naphthalenide in fluid solution met with failure.[9] Considering the difficulties encountered in the generation of perfluorinated aromatic radical anions[3a] by the use of alkali metal or electrolytic reduction,[10,11] this negative result is not altogether surprising. Resort was therefore made to the technique of γ irradiation of rigid solutions since several studies over the past decade have demonstrated the utility of this method for the generation of a wide variety of fluorocarbon radical anions in aprotic organic solvents.[3,12,13]

As described below, the OFCOT radical anion has been identified unambiguously by its isotropic ESR spectrum in 2-methyltetrahydrofuran (MTHF) solution at ca. 145 K following γ irradiation of the sample in the glassy state at 77 K. Similar experiments using rigid matrices of hexamethylethane, tetramethylsilane, and methylcyclohexane were unsuccessful, possibly owing to a lower solubility of OFCOT in these polycrystalline solids. It should be stressed, however, that radical generation is not the only factor involved and that rather stringent motional and kinetic requirements must also be satisified to observe the *isotropic* ESR spectra of radicals in γ-irradiated solids,[13c] a point that is in fact clearly illustrated by the present study.

Experimental Section

Dilute solutions (ca. 0.1 mol %) of OFCOT in MTHF were prepared in Spectrosil ESR tubes on a vacuum line, the MTHF (Aldrich) being introduced from a storage vessel after it had been degassed and subjected to trap-to-trap distillation. Blank samples of MTHF were also prepared under the same conditions. The samples were irradiated at 77 K with γ rays from a ^{60}Co source (Gammacell 200, Atomic Energy of Canada Ltd.) for doses up to 0.5 Mrad (5×10^3 J kg^{-1}) and transferred to a variable-temperature dewar insert mounted in the cavity of an ESR (Bruker ER 200 D SRC) spectrometer. Spectra were recorded at temperatures between 80 and 150 K as the samples were progressively annealed.

Results

ESR Studies. The ESR spectrum of a γ-irradiated pure MTHF glass recorded at 82 K and low microwave power is shown in the

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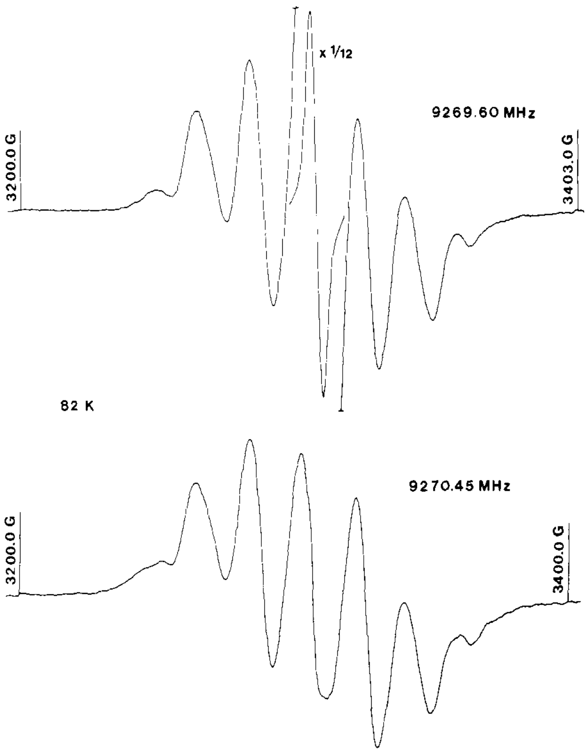

Figure 1. First-derivative ESR spectra of samples of pure MTHF (upper spectrum) and of a 0.1 mol % solution of OFCOT in MTHF (lower spectrum) recorded under the same conditions at low microwave power (55 dB) and 82 K after exposure to ^{60}Co γ radiation for identical doses (0.5 Mrad) at 77 K.

upper portion of Figure 1. As expected, this spectrum consists of the superimposition of an intense sharp singlet due to the solvent-trapped electron on a broad seven-line hyperfine pattern which has been assigned to the neutral MTHF radical formed by loss of a hydrogen atom from the C-2 position.[14,15] In comparison, the lower spectrum of the rigid OFCOT solution obtained under identical conditions of γ irradiation and ESR measurement shows virtually no signal from the solvent-trapped electron, indicating that OFCOT is an excellent electron scavenger. This conclusion is reinforced by the observation that the rigid OFCOT solution turned magenta instead of dark blue on γ irradiation, the latter color being characteristic of trapped electrons in MTHF.[16]

In spite of the above circumstantial evidence that OFCOT captures electrons, there is almost no difference between the outer portions of the spectra in Figure 1 except perhaps for a broader underlying envelope absorption in the spectrum of the OFCOT sample. That is, outside the center region, both spectra at 82 K are dominated by the spectrum of the neutral MTHF radical. Since this radical is probably produced as the result of a reaction involving the positive hole,[14-16] it is understandable that the presence of the OFCOT should have little or no effect on its radiation chemical yield, as is clearly observed in Figure 1.

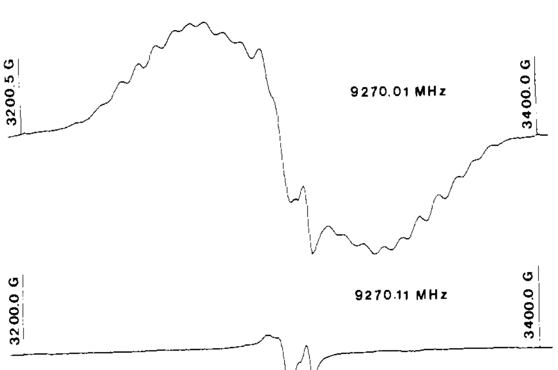

Figure 2. First-derivative ESR spectra of γ-irradiated samples of a 0.1 mol % solution of OFCOT in MTHF (upper spectrum) and of pure MTHF (lower spectrum) recorded under the same conditions (microwave power of 10 dB) at 82 K after the samples had been treated identically to thermal annealing at 103 K and recooled.

It was only on subsequent annealing of the samples that evidence was revealed for the formation of a product radical from OFCOT. The signal from the solvent-trapped electron in the pure MTHF sample disappeared at 95 K while at slightly higher temperatures (100–103 K) the spectrum of the neutral MTHF radical decayed completely in both samples. The samples were then recooled to 82 K and the pertinent spectra are shown in Figure 2. A very broad absorption envelope extending over 200 G with traces of structure is now present in the spectrum of the OFCOT sample whereas there are only residual signals from the γ-irradiated Suprasil tube in the spectrum of the pure MTHF sample. Evidently this broad anisotropic resonance associated with the OFCOT sample is buried under the spectrum of the neutral MTHF radical in the lower spectrum of Figure 1.

A gradual improvement in spectral resolution occurred on raising the temperature of the OFCOT sample above 100 K. The signal amplitude increased dramatically from 100 to 110 K, and at 120 K many of the lines from the complex anisotropic pattern began to coalesce into a simpler multiplet. Incidentally, the sample became distinctly "lossy" above 120 K and the microwave power had to be reduced from 10 to 22 dB. Above 142 K the spectrum became essentially isotropic and the lines sharpened up considerably to reveal a simple nine-line binomial pattern as exemplified by the first-derivative and second-derivative presentations shown in Figure 3. Both of these spectra were recorded at 145 K, which seemed to be the optimum temperature for achieving good resolution without appreciable thermal decay of the radical. This decay became quite rapid at 150 K so that the window of observation for the isotropic spectrum is restricted to the relatively narrow range of temperature between 142 and 150 K.

Figure 3 also shows that the second-derivative isotropic spectrum is satisfactorily simulated by means of the parameters $a(8\text{F})$ = 10.92 G and g = 2.0049 with a line width of 4.0 G. The fit is excellent except for the relative intensities of the lines, but this small discrepancy is understandable since the simulation did not allow for a likely dependence of the line width on the M_I value of the line.

INDO Calculations. Using the INDO program,[17] calculations were performed for the OFCOT radical anion assuming a regular octagonal (D_{8h}) geometry with C–F and C–C bond lengths of 1.35 and 1.38 Å, respectively. These parameters correspond to the C–F bond length and to the average of the C–C and C═C bond lengths in the neutral molecule.[7] The results of the calculations were found to be relatively insensitive to small changes in bond lengths from this standard geometry.

According to these INDO calculations, the unpaired electron occupies one of the (nearly) doubly degenerate E_{2u} nonbonding π orbitals in the OFCOT radical anion, the other E_{2u}-type orbital lying immediately below the SOMO. Reflecting the π symmetry and the nonbonding character of the SOMO, the spin density is found to be uniformly distributed in $2p_z$ orbitals around the ring with a strong bias in favor of the carbon orbitals, ρ_C ($2p_z$) being 0.116 whereas ρ_F ($2p_z$) is only 0.009. Thus, more than 90% of the π spin density is located on the eight carbon atoms. Only very small spin densities are predicted to reside in the 2s orbitals of carbon and fluorine, the low values obtained for ρ_C (2s) = 0.0029 and ρ_F (2s) = 0.0002 again reflecting the π symmetry of the SOMO.

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Table I. Compilation of $Q^F{}_{eff}$ Values[a] for Perfluoroaromatic Radical Cations and the Octafluorocyclooctatetraene Radical Anion

parent compound	radical ion	ring position	$\rho_C{}^b$	$a_F{}^c$/G	$Q^F{}_{eff}$/G	ref
perfluorobenzene	$C_6F_6{}^+$		0.124	15.9	128.2	19
perfluoronaphthalene	$C_{10}F_8{}^+$	1 (4)	0.178	18.5	103.9	19
			0.195	19.0	97.4	21
		2 (4)	0.048	4.6	95.8	19
			0.050	4.8	96.0	21
perfluoroanthracene	$C_{14}F_{10}{}^+$	1 (4)	0.089	9.2	103.4	19
		2 (4)	0.035	3.6	102.9	19
		9 (2)	0.212	19.0	89.6	19
perfluoropyrene	$C_{16}F_{10}{}^+$	1 (4)	0.142	13.8	97.2	19
		2 (2)	−0.034	(−)3.4	100.0	19
		4 (4)	0.084	7.0	83.3	19
perfluorocyclooctatetraene	$C_8F_8{}^-$		0.1159	10.92	94.2	*d*

[a] $Q^F{}_{eff}$ is defined in the text. [b] Spin densities on carbon calculated by the McLachlan method for the radical cations[19,21] and by the INDO method for $C_8F_8{}^{-d}$. [c] Experimental fluorine hyperfine coupling constants. [d] This work.

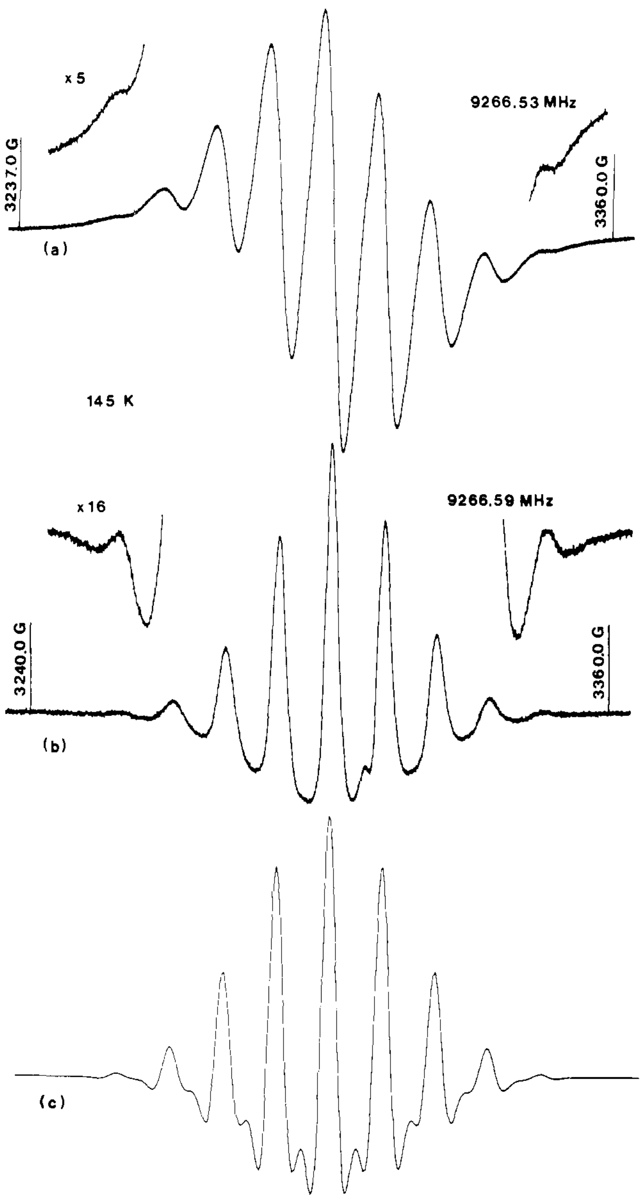

Figure 3. First-derivative (a) and second-derivative (b) ESR spectra of a solid solution of 0.1 mol % OFCOT in MTHF recorded at 145 K after γ irradiation (dose of 0.5 Mrad) at 77 K. The second-derivative spectrum (c) was obtained by computer simulation using the parameters in the text and a linewidth of 4 G.

Table II. Isotropic *g* Values for Perfluorinated Aromatic Radicals

radical	*g* value	ref
C_5F_5	2.0041	22
$C_8F_8{}^-$	2.0049	*a*
$C_{10}F_8{}^+$	2.0045	19
	2.0042	21
$C_{14}F_{10}{}^+$	2.0041	19
$C_{16}F_{10}{}^+$	2.0046	19

[a] This work.

Discussion

The ESR results obtained with the MTHF matrix demonstrate that electrons are scavenged by the dissolved OFCOT and that the radical product of this reduction[18] possesses a nine-line isotropic spectrum with a nearly binominal intensity distribution. The equivalence of the eight fluorines already provides strong prima facie evidence that the OFCOT radical anion is planar, but a more compelling argument for this conclusion will now be given based on the magnitude of the fluorine hyperfine coupling and the calculated spin distribution.

Hückel's $4n + 2$ rule, where $n = 2$, predicts that OFCOT$^-$, like COT$^-$,[5,6] is one electron short of the full complement for aromaticity. Thus it can be argued that the electronic structure of OFCOT$^-$ is closely analogous to the radical *cations* of fluorinated aromatic molecules. This similarity is strongly supported by the INDO calculations which predict that in D_{8h} symmetry, OFCOT$^-$ is a simple π radical with most of the spin density on the carbons, just as is the case for the radical cations of perfluorobenzene, perfluoronaphthalene, and perfluoroanthracene.[19-21] It should be noted in passing that, as mentioned in the Introduction, the radical anion of perfluorobenzene is almost certainly not a simple π radical of this type. Therefore, here we wish to stress the specific comparison between $C_8F_8{}^-$ and (say) $C_6F_6{}^+$, whereas for the perprotiated species, $C_8H_8{}^-$ has been compared to $C_6H_6{}^-$ as well as $C_6H_6{}^+$.[8] This latter comparison is valid only because both of the benzene radical ions are clearly established as π radicals.

Since most of the spin density for the "electron-deficient" aromatic species $C_8F_8{}^-$, $C_6F_6{}^+$, $C_{10}F_8{}^+$, and $C_{14}F_{10}{}^+$ resides on the carbon atoms, perhaps the most useful equation for relating the observed isotropic fluorine coupling to the calculated spin distribution assumes the very simple McConnell form:[19-21]

$$a_F = Q^F{}_{eff}\rho_C$$

It follows that the constancy of the parameter $Q^F{}_{eff}$ from one radical to another can be used to relate isostructural species. Using calculated McLachlan spin densities and observed hyperfine

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(18) Cyclic voltammetric reduction of OFCOT in 0.1 M tetrabutylammonium perchlorate/acetonitrile at a vitreous carbon electrode produced waves at −1.57 ± 0.02 and −1.96 ± 0.02 V vs. an Ag/0.1 M $AgNO_3$/acetonitrile electrode. Though detailed interpretation of this irreversible voltammogram is open to question, it is noteworthy that the first reduction step is 0.5 V anodic of that for the parent hydrocarbon measured in a similar medium. C. McDade, Senior Fellowship Thesis, Dartmouth College, 1980.

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splittings,[19-21] Q^F_{eff} values (in G) were calculated for four perfluoroaromatic radical cations and the results are given in Table I. Bearing in mind that appreciable errors may be introduced in the computation for positions of low spin density, the spread of calculated Q^F_{eff} values is remarkably small and most of them are clustered between 90 and 104 G. Other authors have made estimates of 93.1 G[21] and 107.4 G[19] for this parameter from data on both perfluorinated and partially fluorinated aromatic radical cations.

Also included in Table I are the results of this work on $C_8F_8^-$ which yields a Q^F_{eff} value of 94.2 G. The good agreement between this value and the results derived from the perfluoroaromatic radical cations is striking. Moreover, a recent study of the neutral C_5F_5 radical indicates a very similar value of 98.2 G,[22] further supporting the idea that Q^F_{eff} is sensibly constant for electron-deficient aromatic π radicals, irrespective of the electric charge on the radical. The isostructural character of these species is also confirmed by the fact that their isotropic g values (Table II) are grouped in a narrow range with a small positive shift from the free-spin value. We conclude, therefore, that the ESR parameters for $C_8F_8^-$ are strongly supportive of a planar aromatic radical.

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Registry No. Octafluorocyclooctatetraene radical anion, 88211-63-6.

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Nuclear Spin Relaxation and Ring-Current Shifts in Chlorophyll Dimers

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Abstract: ^1H spin–lattice relaxation (SLR) times and chemical shifts of various protons in chlorophyll *a* monomer, the "special pair" (SP) dimer and the (Chl $a)_2$ dimer have been determined at 100 MHz. The SLR times can be related to the geometry of the particular dimer by applying a rotational diffusion model. Due to the limited number of protons suitable for SLR experiments, this comparative study provides a check on previously proposed dimer structures but cannot define entirely new geometries. An independent check on these geometries is provided by the experimental ring-current shifts. Calculations employing either SLR data or ring-current shifts yield very similar geometries for both types of dimers. In particular, the signs and relative magnitudes of the ring-current shifts turn out to be sensitive to the dimer structure. Both macrocycles in the (Chl $a)_2$ dimer are found to be perpendicular, corresponding to a rotation over the Eulerian angles (90°, 90°, 135°); their centers are displaced by the vector (7.5, −0.65, 0) (Å) in an axis system fixed to one of the monomers; the rotational diffusion tensor elements are $D_{xx} = 0.6$, $D_{yy} = 3$, $D_{zz} = 2$ ($\times 10^9$ s^{-1}). Experimental results for the ethanol-linked SP dimer confirm the Shipman–Katz geometry, defined by the relative translation (7.7, −0.13, 3.6) (Å) and rotation (0°, 180°, 180°); the rotational diffusion tensor elements are $D_{xx} = 0.5$, $D_{yy} = 0.5$, $D_{zz} = 3$ ($\times 10^9$ s^{-1}). For both dimers, the average diffusion constant is found to be approximately half that of the monomer, as expected. However, the relative magnitudes of the separate components of the rotational diffusion tensor of both dimers cannot be simply rationalized by an anisotropic hydrodynamic model.

During the last decade various chlorophyll species in vivo and in vitro have been extensively studied.[1-7] The occurrence of various forms of chlorophyll in vitro depends on the nature of their environment and has provided proposals for the structure of chlorophyll complexes in vivo.[4a,b] In particular the Chl *a* dimer (Chl $a)_2$ and the Chl *a* "special pair" (SP) (Chl $a{\cdot}L)_2$, where L is a ligand (e.g., H_2O), have been suggested to be important in photosynthesis.[4a,b]

To assess to what extent these complexes may serve as models for the photosynthetic apparatus, it is important to know their geometry as precisely as possible, since that will largely determine such properties as the absorption spectrum and ionization potential, which make some chlorophyll complexes suited for their role in photosynthesis.

For the SP dimer, IR[8] and ESR[9] data suggest that two Chl *a* molecules are held in a plane-parallel orientation via two ligands with both electron-donor and electron-acceptor properties.[4a,b,10] From CD[11] and NMR[12] studies it was concluded that the two macrocycles in (Chl $a)_2$ are ~40° tilted relative to each other, but this geometry has not generally been accepted.[13]

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