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Spin Polarization, Delocalization, and the Effect of Nonplanarity in Hyperfine Coupling Constants of Perfluorinated Alkyl Radicals

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Density functional calculations are presented on the structure and magnetic parameters of the perfluorinated ethyl and *n*-propyl radicals and compared with the non-fluorinated analogs. It is found that fluorine substitution leads not only to nonplanarity at the radical center but to delocalization of spin density onto the F^{α} atoms and to spin polarization effects that both lead to pronounced anomalies in the anisotropic contribution to the hyperfine tensor. The nonplanar radicals do not obey the traditional McConnell relations. They serve as model systems for similar species that are observed in perfluorinated polymers.

1. Introduction

Fluorinated radicals are of relevance in fluoropolymers and important for example when polymer films are radiation grafted to produce proton conducting polyelectrolyte membranes for use in low-temperature fuel cells.[1−3] Also, polymer degradation frequently involves transient radicals. For an identification of these radicals one needs to distinguish features from *g* and hyperfine anisotropy to obtain the corresponding tensors and analyze the local structure. It is therefore important to understand the relation between geometry and hyperfine coupling parameters. There does not seem to have been significant theoretical work for more than three decades after the early INDO calculations by Morokuma.[4] Meanwhile, theoretical methods have made vast progress in the prediction of magnetic resonance parameters,[5] and only recently have these methods been applied in computational studies of electron spin resonance parameters of perfluorinated alkane and alkene radical anions.[6,7] Here we show, on the basis of density functional calculations, that pronounced spin polarization and delocalization effects lead to unexpected behavior of the hyperfine anisotropy of small neutral perfluorinated radicals. It is demonstrated by comparison of the parameters of $CF_3{}^{\bullet}CF_2$, both in its fully optimized nonplanar and in a forced planar conformation at the radical center, with those of the analogous non-fluorinated and essentially planar $CH_3{}^{\bullet}CH_2$ radical. The study is extended briefly to the fluorinated and the non-fluorinated 1-propyl radicals.

Magnetic nuclei are sensitive probes of molecular electronic structure. Magnetic resonance methods have therefore become the standard methods for structure determination of organic molecules and even of proteins. In nuclear magnetic resonance the parameters of interest are the chemical shift and dipolar spin−spin coupling tensors, and the isotropic *j*−*j* coupling constants. In a completely analogous way, electron spin resonance derived dipolar nuclear hyperfine coupling (hfc) and *g* tensors, and isotropic (Fermi contact) hfc constants, are being used for local structural and conformational analysis near the unpaired electron of organic radicals. Decades ago, McConnell established two important relations,[8] the first one describing the proportionality of the isotropic hfc a^{α} of nuclei that are directly bound to a planar radical center carrying a π-type electron spin population ρ_{π},

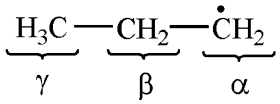
$$a^{\alpha} = Q^{\alpha}\rho_{\pi} \tag{1}$$

and the second one for β nuclei that are separated by two bonds from a radical center,

$$\langle a^{\beta}\rangle = \rho_{\pi}[A + B\langle\cos^{2}(\theta - \theta^{0})\rangle + C\langle\cos(\theta - \theta^{0\prime})\rangle] \tag{2}$$

The notation of the nuclei uses Greek letters, starting with α for the nominal radical center and its hydrogen or halogen substitutents, the group one bond further remote is labeled β, and the next one is labeled γ, as shown in Scheme 1.

SCHEME 1



$$\underbrace{H_3C}_{\gamma}-\underbrace{CH_2}_{\beta}-\underbrace{\dot{C}H_2}_{\alpha}$$

A in eq 2 was described as a spin polarization term that for protons is usually small and often negligible compared with a hyperconjugative contribution *B* that transmits spin density to the β-nucleus with an angular dependence relating to the dihedral angle θ between the C−X bond of the β-nucleus X (measured relative to its equilibrium value θ^{0}) of interest and the direction of the p_z orbital that carries most of the unpaired electron spin density. For the case of planar radical centers *C* equals 0, which is the standard assumption in this McConnell relation, but in the present case this is not always obeyed. For β methyl groups, due to their local C_3 symmetry, $\langle\cos^{2}(\theta - \theta^{0})\rangle = 1/2$, the angular dependence gets lost in the average over three protons, and eq 2 can be written in a more compact form as

$$a^{CH_3} = Q^{CH_3}\rho_{\pi} \tag{3}$$

Q^{α} and Q^{CH_3} are proportionality constants that adopt typical values for given classes of radicals.[9] A value of unity is assigned to ρ_{π} of the ${}^{\bullet}CH_3$ radical, but by spin polarization or hyperconjugation some of the spin population at the central carbon

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transfers onto each substituent other than H and diminishes ρ_π. $\langle \cos^2(\theta - \theta^0) \rangle$ stands for the expectation value that represents a Boltzmann average over ground and excited states of the degree of freedom of internal rotation about the $C^\alpha - C^\beta$ bond, described by θ, which is what is measured experimentally. When there is extensive averaging, it is not appropriate to solve $\langle \cos^2(\theta - \theta^0) \rangle$ for θ, but for rigid conditions at low temperatures it is reasonable to use θ for conformational analysis.

The above McConnell relations were derived and routinely used for proton coupling constants,[8,9] but occasionally the treatment was extended to other nuclei like ^{13}C or ^{14}N. Furthermore, it is sometimes tacitly assumed that it holds also for ^{19}F because F is a single valence atom and therefore a formal substitute for H.[10,11] Although alkyl substitution affects the planarity at the radical center only slightly, it has long been known that fluorine substitution at the radical center leads to severe nonplanarity and pronounced pyramidal geometry for the $^{\bullet}CF_3$ radical.[12] Furthermore, it was shown that F can induce strong and sometimes counterintuitive charge polarization in molecules,[13] so it may be expected that related phenomena apply to spin polarization.

The 2-fold ($\cos^2 \theta$) rotation symmetry with 180° periodicity in eq 2 has its origin in the square of the hyperconjugative overlap integral of the C−X bond orbital with the half-filled p_z orbital hosting the unpaired electron density at the radical center. For increasing nonplanarity at the radical center the half-filled orbital adopts more and more s-character, eventually resulting in sp^3 hybridization for tetrahedral-like local geometry. In representations of the rotational dependence of the isotropic β hfc, nonplanarity can be accounted for by adding the $\cos(\theta - \theta^{0\prime})$ term in eq 2. ρ_π is no longer well-defined so that the new coefficients are just phenomenological. Furthermore, in the present theoretical work we have not performed any averaging over the vibrational wave functions or Boltzmann populations. We report the accurate calculated angular dependence at zero absolute temperature and in the absence of zero-point vibration. We therefore omit the symbols for the expectation values:

$$a^\beta = a_0^{\ \beta} + b^\beta \cos^2(\theta - \theta^0) + c^\beta \cos(\theta - \theta^{0\prime}) \qquad (4)$$

Also related to symmetry but based on a somewhat different origin is the potential to internal rotation, $V(\theta)$, which is periodic and may be written as a sum of terms V_i with periodicity index i. As a consequence of the local C_3 symmetry of the methyl group and the C_2 symmetry at the radical center, V_6 is the only nonzero periodic term for $CH_3{}^{\bullet}CH_2$, whereas V_1 comes in for nonplanar radicals:

$$V(\theta) = V_0 + \frac{V_1}{2}\cos(\theta - \theta_1^0) + \frac{V_6}{2}\cos(6\theta - \theta_6^0) \qquad (5)$$

V_0 provides a constant offset. $V(\theta)$ determines the wave function for the internal rotational motion that is responsible for $\langle a^\beta \rangle$.

The dipolar contribution to the electron−nuclear hyperfine interactions scales as $\langle (3 \cos^2 \theta - 1)/r^3 \rangle$. The expectation value is calculated over the electron−nuclear distance r as the integral over the orbital containing the unpaired electron. The angular dependence defines a double cone with an opening angle that is twice the magic angle, i.e., 109.4°. The orientation of the double cone (centered at the nucleus) that can accommodate the largest fraction of the electron spin density distribution in the section around the symmetry axis of the cone defines the positive axis of the anisotropy tensor.[14] Spin polarization creates a significant amount of negative spin density at other atoms and can therefore complicate the simple picture.

TABLE 1: Comparison of Experimental and Calculated Isotropic Hyperfine Couplings (A_{iso}) and Components of Dipolar Hyperfine (B_{ii}) and g Tensors for the $^{\bullet}CF_3$ Radical for the Purpose of Validation of the Method

	component	experimental values[a]/G	theoretical values/G
^{13}C hfc	B_{zz}	+47	+44.6
	B_{yy}	−33	−22.3
	B_{xx}	−14	−22.3
	A_{iso}	+271	+271
^{19}F hfc	B_{zz}	+108	+136
	B_{yy}	−53	−66
	B_{xx}	−57	−69
	A_{iso}	+145	+136
g	g_{zz}	2.0024	2.0019
	g_{yy}	2.0046	2.0043
	g_{xx}	2.0038	2.0043
	g_{iso}	2.0036	2.0035

[a] Reference 18.

2. Theoretical Methods

All calculations were performed with the Gaussian 03 package.[15] The optimized geometries of the radicals and the energies were obtained in DFT calculations using the UB3LYP hybrid functional and a 6-311+G** basis set.[16] The dihedral angle θ is defined between the axis of the $2p_z$ or hybrid orbital hosting the unpaired electron at the C^α atom and the plane containing the C^α, C^β, and $F^\beta(H^\beta)$ atoms. In some separate calculations the C^α, C^β, and the two $F^\alpha(H^\alpha)$ atoms were constrained to the same plane to enforce planarity at the radical center.

Hyperfine coupling constants were obtained from single point calculations using the UB3LYP/EPR-II option.[15] For the g tensors the MAG program from the University of Würzburg was used.[5]

There are relatively few data available in literature that are suitable for a validation of the hyperfine and g tensors. The most complete and reliable set is the one for the $^{\bullet}CF_3$ radical.[17] It is given in Table 1 and compared with the corresponding set of calculated values. The agreement for the hfcs of ^{13}C is quite remarkable, considering that only the standard method with no special choice of basis set was used. It gives confidence in particular in the extent of nonplanarity at the radical center. For ^{19}F the agreement is still within ca. 20% for the individual components, and better for the isotropic value. The positive components of the ^{13}C and ^{19}F hyperfine tensors are parallel within error in the experiment[18] and nearly parallel in the calculation. The nonaxiality of the experimental ^{13}C hfc tensor was ascribed to interfering lines from a superimposed spectrum of a minority species.[18] Slightly, this also affects the experimental g tensor, whereas the calculated one is axial as expected, and the isotropic value (i.e., the average of the three components) is in excellent agreement with observation. The component along the symmetry axis is slightly below the value of the free electron, $g_e = 2.00232$ (see also section 3.2).

3. Results and Discussion

3.1. Energies. Both the forced planar fluorinated ethyl radical (Figure 1a) and the non-fluorinated ethyl radical (not shown) exhibit a nearly negligible 6-fold potential ($V_6 \approx 0.1-0.2$ kJ

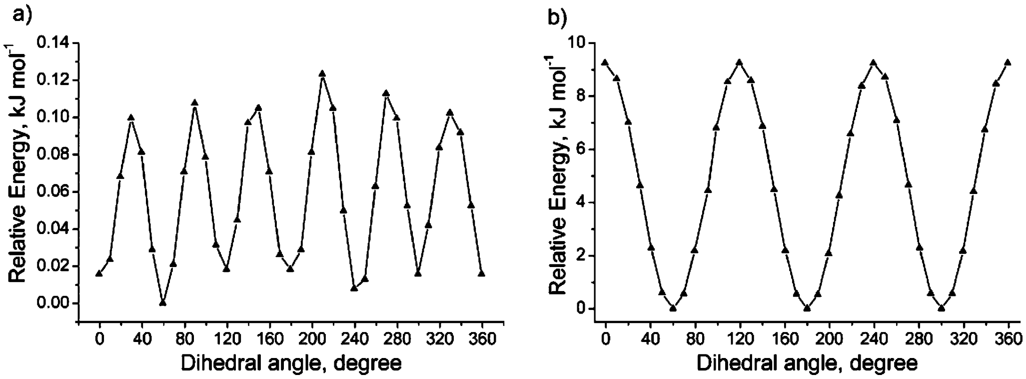


Figure 1. Relative energies as a function of the dihedral angle θ for rotation about the $C^{\alpha}-C^{\beta}$ bond of the forced planar (a) and optimized (b) $CF_3^{\bullet}CF_2$.

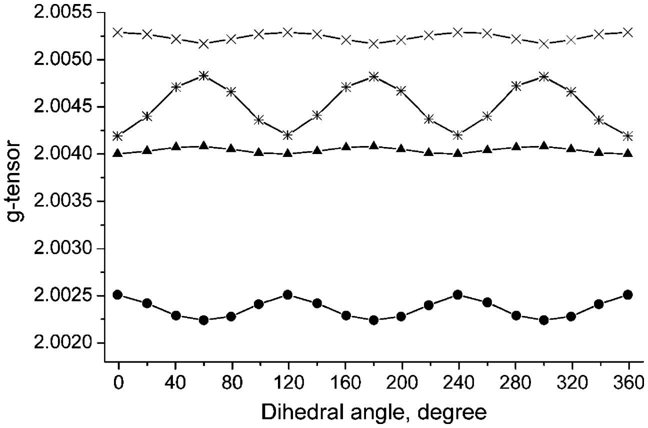
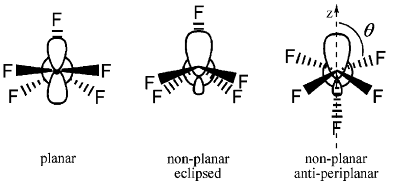


Figure 2. g tensor components along the C−C axis (×), eclipsed with the hybrid orbital containing the unpaired electron (●), and perpendicular to these two (∗) and the isotropic g value (▲) of the optimized $CF_3^{\bullet}CF_2$ structure as a function of the dihedral angle θ.

SCHEME 2



mol^{-1}) that hinders internal rotation about the $C^{\alpha}-C^{\beta}$ bond. In both cases the energy minimum is calculated to be for $\theta = 0$, which points to a slight stabilizing hyperconjugative effect due to the overlap of the C−H(F) bond with the half-filled p_z orbital in the eclipsed conformation (see first entry of Scheme 2). Admitting nonplanarity for the radical center of $CF_3^{\bullet}CF_2$ leads to a stabilization by 26 kJ mol^{-1}, but the 3-fold potential for internal rotation with all other parameters fully relaxed amounts to $V_3 = 9.3$ kJ mol^{-1} (Figure 1b). In the latter motion the radical center does not invert. The energy minimum is now obtained for the conformation in which a C−F bond is antiperiplanar to the major lobe of the sp^3-like semi-occupied atomic orbital at the radical center (Scheme 2, third entry).

Substitution of one of the β-H(F) atoms by a $CH_3(CF_3)$ group leads to a somewhat more complex potential that, however, amounts to only on the order of 1 kJ mol^{-1} for the planar species, whereas it remains at 9−10 kJ mol^{-1} for fully optimized $CF_3CF_2^{\bullet}CF_2$.

3.2. *g* Tensors. The g tensor of $CF_3^{\bullet}CF_2$ shows a nearly constant component (see Figure 2) with a high value near 2.00525 in a direction roughly along the C−C bond and two out-of-phase oscillating components, the one in the direction parallel to the p_z-like hybrid orbital is near the free electron value ($g_e = 2.0023$). The resulting isotropic value is nearly independent of the rotation angle θ and adopts a value of 2.0040. The predicted anisotropy of 0.14% is sizable, nearly 4 times that of the non-fluorinated ethyl radical and can lead to a line splitting of ca. 5 G in X-band ESR spectroscopy, which may be essential for the interpretation of solid-state spectra. In many cases the σ character of the orbital containing the unpaired electron at a nonplanar radical center is expected to lead to $g < g_e$, as predicted for $^{\bullet}CF_3$ (see Table 1) and observed for $H^{\bullet}CO$ ($g = 2.0009$), $CH_3O^{\bullet}CO$ ($g = 2.0002$), $H_2{=}C^{\bullet}CN$ ($g = 2.000$), and also phenyl ($^{\bullet}C_6H_5$, $g = 2.00227$).[9,17] In the present case a slight relativistic contribution of F that is a heavier atom than H may compensate this effect of nonplanarity so that $g > g_e$.

TABLE 2: Isotropic hfc of $^{13}C^{\alpha}$ and $^{13}C^{\beta}$ Nuclei Represented by the Coefficients of Eq 6 for the Fully Optimized and Forced Nonplanar Non-fluorinated and Perfluorinated Ethyl Radicals

	a_0/G		a_1/G (θ^0)	
	$^{13}C^{\alpha}$	$^{13}C^{\beta}$	$^{13}C^{\alpha}$	$^{13}C^{\beta}$
$CH_3^{\bullet}CH_2$ (planar)	28.96	−11.85	0.00	0.00
$CH_3^{\bullet}CH_2$ (optimized)	29.84^a	−11.74^a	0.85^a (0°)	0.11^a (0°)
$CF_3^{\bullet}CF_2$ (planar)	34.30	−17.57^a	0.00	0.05^a (0°)
$CF_3^{\bullet}CF_2$ (optimized)	147.63	+14.38	5.28(−100°)	1.81 (−130°)

^{a} $a^i = a_0{}^i + a_1{}^i \cos(6\theta + \theta^0)$.

TABLE 3: Isotropic hfc of H^{α} and F^{α} Nuclei Represented by the Coefficients of Eq 6 for the Fully Optimized and Forced Nonplanar Non-fluorinated and Perfluorinated Ethyl Radicals

	a_0/G		a_1/G (θ^0)	
	$^{1}H^{\alpha}$	$^{19}F^{\alpha}$	$^{1}H^{\alpha}$	$^{19}F^{\alpha}$
$CH_3^{\bullet}CH_2$ (planar)	−22.06		0.34 (−90°)	
$CH_3^{\bullet}CH_2$ (optimized)^a	−21.82		0.37 (−90°)	
$CF_3^{\bullet}CF_2$ (planar)		+48.55		1.26 (−90°)
$CF_3^{\bullet}CF_2$ (optimized)		+77.23		2.73 (−60°)

^{a} $a^i = a_0{}^i + a_1{}^i \cos(3\theta + \theta_0) + 0.22\ \mathrm{G} \times \cos(6\theta)$.

3.3. Hyperfine Couplings. The dependence of the isotropic hfcs as a function of the dihedral angle θ is relatively small for the $^{13}C^{\alpha,\beta}$ and the F^{α} and H^{α} nuclei. For ethyl radicals it is represented well by an expression

$$a^i = a_0^i + a_1^i \cos(3\theta + \theta^0) \tag{6}$$

These coefficients are given in Tables 2 and 3.

For the F^{β}, H^{β}, and $^{13}C^{\gamma}$ nuclei the dependence is much more pronounced. It is collated in the form of the coefficients of eq

TABLE 4: Isotropic hfc of H^β and F^β Nuclei Represented by the Coefficients of Eq 4 for the Non-fluorinated and Perfluorinated Ethyl Radicals (Rotation about the $C^\alpha-C^\beta$ Bond)

	a_0/G	b/G (θ^0)	c/G ($\theta^{0\prime}$)
$CH_3{}^\bullet CH_2$ (planar)	0.2	55.8 (60°)	0.0
$CH_3{}^\bullet CH_2$ (optimized)	−0.3	56.6 (60°)	0.0
$CF_3{}^\bullet CF_2$ (planar)	−1.6	70.0 (60°)	0.0
$CF_3{}^\bullet CF_2$ (optimized)	−1.3	27.5 (60°)	8.2 (60°)
$CH_3CH_2{}^\bullet CH_2$ (optimized)	−0.3	53.1 (60°)	0.0
$CF_3CF_2{}^\bullet CF_2$ (planar)	−1.1	105.9 (80°)	0.0
$CF_3CF_2{}^\bullet CF_2$ (optimized)	−0.7	44.9 (70°)	1.4 (80°)

TABLE 5: Isotropic hfc of $^{13}C^\gamma$ Nucleus Represented by the Coefficients of Eq 4 for the Non-fluorinated and Perfluorinated 1-Propyl Radicals (Rotation about the $C^\alpha-C^\beta$ Bond)

	a_0/G	b/G (θ^0)	c/G ($\theta^{0\prime}$)
$CH_3CH_2{}^\bullet CH_2$ (optimized)	−0.2	33.1 (−60°)	0.0
$CF_3CF_2{}^\bullet CF_2$ (planar)	−1.4	20.4 (−60°)	0.0
$CF_3CF_2{}^\bullet CF_2$ (optimized)	−0.5	9.9 (−60°)	6.3 (−60°)

4 in Tables 4 and 5. The behavior of the anisotropic contribution will be discussed for selected conformations.

$^{13}C^\alpha$. The isotropic $^{13}C^\alpha$ hfc is a sensitive indicator of nonplanarity at the radical center. For planar radicals with pure p_z character of the half-occupied orbital one finds values on the order of $\rho_\pi \times 35$ G, which arise from spin polarization of the s-orbitals by p_z. Nonplanarity contributes further s character to this orbital, which enhances the spin density at the nucleus and therefore the coupling constant. This is well-known since the work of Fessenden,[18] and it is verified in Table 2 where this hfc amounts to ca. 30 G for the non-fluorinated radicals and 34 G for the planar fluorinated radicals but close to 150 G when nonplanarity is admitted so that the geometry is more pyramidal (the sum of the three bond angles at the radical center amounts to 341° as compared to 329° for a fully tetrahedral and 360° for a planar geometry). The magnitude of the dipolar contribution is given by the principal values of the diagonalized tensor, $B_{xx}/B_{yy}/B_{zz}$. It amounts to ca. −25/−25/+50 G for $CH_3{}^\bullet CH_2$ and for all conformations of the fully optimized structure of $CF_3{}^\bullet CF_2$ and to ca. −30/−30/+60 G for its forced planar geometries. As expected, the positive component of this axial tensor is directed parallel to the p_z orbital of the unpaired electron.

$^{13}C^\beta$. This hfc arises from spin polarization through the bond to C^α and is therefore negative for the planar geometries (ca. −12 G for the non-fluorinated and −18 G for the fluorinated radicals). However, in the nonplanar case it changes sign and adopts values of ca. +14 G for the perfluorinated ethyl radical, whereas it becomes strongly θ dependent, with values between +26 and −3 G, for the perfluoro-1-propyl radical. Partly this is a consequence of the changing hybridization at C^α, but a comparison of calculated values for the planar perfluorinated and non-fluorinated radicals shows that it is mostly an effect of fluorine substitution.

For species with planar radical center the dipolar contribution at C^β is small, with components ≤1 G, but in the nonplanar case they increase to about −2/−2/+4 G, with the positive component along the C−C bond.

F^α and H^α. The isotropic H^α hfc of the non-fluorinated radicals is −22 G. For F^α it becomes θ dependent and oscillates by ±1 to ±3 G about a value of +48.5 G for the planar and +77 G for the nonplanar structures (Figure 3). Thus, the hfc is predicted to be positive for F, also in the planar case, which is not compatible with a mechanism that is dominated by spin polarization of the C−F bond by the unpaired electron at C^α. For the nonplanar case it was demonstrated long ago in the beautiful work by Fessenden,[18] who suggested that even the H^α hfc of $^\bullet CHF_2$ may be positive. This has been confirmed here in a calculation of $^\bullet CHF_2$: the ^{13}C hfc is predicted at +147.7 G (experimental value: 148.8 G), revealing a similar degree of nonplanarity as the perfluoroethyl radical, whereas +75.1 G (84.2 G) is predicted for F and +24.3 G (22.2 G) for H, in good agreement with experiment.[19]

For the non-fluorinated radical the dipolar contribution to the H^α hfc tensor is of planar symmetry (one component close to zero) and amounts to −14/0/+14 G with the positive component along the C−H bond and the zero component parallel to the p_z-orbital. The orientations of two of the principal hfc tensor axes are indicated with arrows in Figure 4a.

For the planar fluorinated radicals the tensor changes to −85/−70/+155 G, which is much larger than in the non-fluorinated case, and most remarkably the positive component of this near-axial tensor is now parallel to the p_z orbital (Figure 4b,c). There is a slight oscillation of the latter values by ca. ±2 G for the different conformations. For the nonplanar fluorinated radicals we calculate −79/−71/+150 G with very little variation for the different conformations or additional CF_3 substitution. The large values of the dipolar contributions mean that the effective hfc (the sum of isotropic plus dipolar contributions) can vary in a rigid system, depending on orientation with respect to the applied magnetic field, between nearly zero and +227 G, which is not unexpected but can pose a challenge for the observation and assignment of experimental spectra.

Both the large positive isotropic hfc and the unexpected orientation of the anisotropy tensor with its positive component having the same orientation for F^α as for the neighboring C^α can be explained by spin delocalization from the radical center to the F^α nuclei, as represented by the mesomeric structures in Scheme 3.

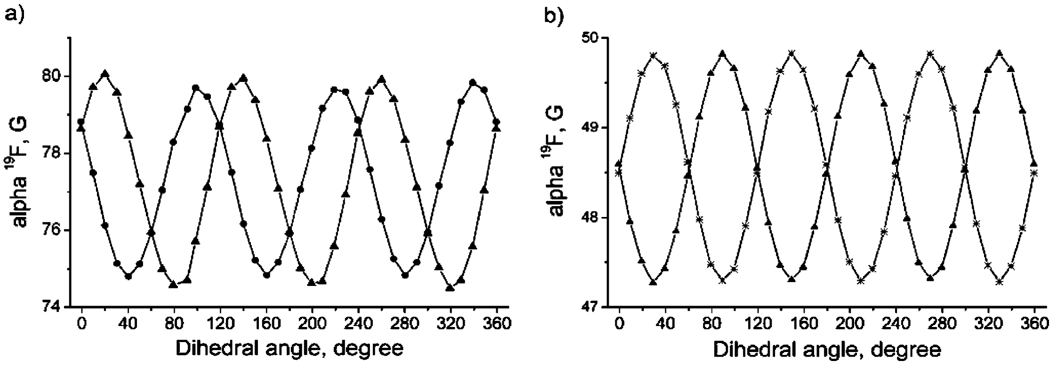


Figure 3. F^α hfc as a function of the dihedral angle θ for fully optimized (a) and forced planar (b) $CF_3{}^\bullet CF_2$.

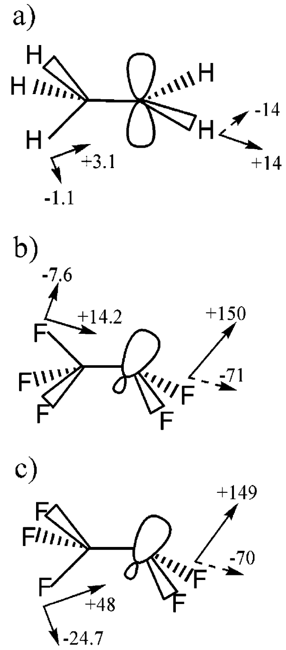
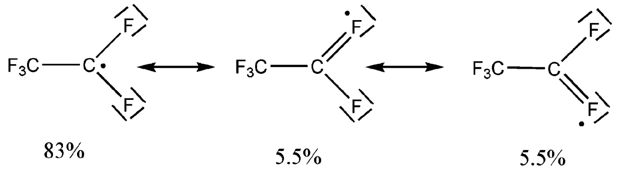


Figure 4. Side-on view of the optimized geometry of the planar $CH_3^{\bullet}CH_2$ radical (a) and of the $CF_3^{\bullet}CF_2$ radical with one F^{β} in the eclipsed (b) and in the antiperiplanar (c) conformation with respect to the main lobe of the hybrid orbital containing the unpaired electron. The arrows indicate the directions of two principal axes of the fluorine dipolar hyperfine tensors. These are in the paper plane for H^{β} and F^{β}. For H^{α} the positive component is along the C−H bond and the zero component parallel to the p_z-orbital, whereas the positive component of F^{α} is approximately parallel to the direction of the hybrid orbital at C^{α} and the negative component approximately in the direction of the C−F bond. The third component that is not shown is determined by the condition that the dipolar tensor is traceless so that the sum of the three components equals zero.

SCHEME 3



This is supported by the calculated Mulliken total atomic spin populations. For the planar ethyl radical these are +1.050 for C^{α}, +0.087 for the sum of the three H^{β}, −0.051 for C^{β}, and −0.027 for each of the two H^{α}. For the planar perfluoroethyl radical they are all positive: +0.828 for C^{α}, +0.025 for the sum of the three F^{β}, +0.037 for C^{β}, and +0.055 for each of the two F^{α}. A spin population of 5.5% on each of the F^{α} might seem small, but because both the isotropic hfc (calculated for 100% s-character of the unpaired electron) and the dipolar hfc (100% spin population in 2p of F) are predicted to be a factor 15 larger for F than for C,[20,21] this relatively small spin population on F^{α}, which is almost entirely of π character, dominates the hyperfine anisotropy. This partial delocalization influences also the bond length, which amounts to 1.314 Å for $C^{\alpha}-F^{\alpha}$ as compared to 1.361 Å in the average for $C^{\beta}-F^{\beta}$, indicating partial double bond character for the $C^{\alpha}-F^{\alpha}$ bond. Regarding the orientation of the dipolar hfc tensor of the F^{α} nuclei the present calculations confirm the results of a detailed analysis of the $CO_2^-CF_3^{\bullet}CFCO_2^-$ radical in an electron irradiated single crystal of sodium perfluorosuccinate.[10]

F^{β} and H^{β}. The isotropic hfcs of β-nuclei of $CH_3^{\bullet}CH_2$ and planar $CF_3^{\bullet}CF_2$ are both good fits to the McConnell relation. In the form of eq 4 a_0^{β} is close to zero and c^{β} is equal to zero, whereas b^{β} amounts to 57 G for the non-fluorinated and 70 G for the fluorinated species (Figure 5). Surprisingly, b^{β} increases to 105 G for planar $CF_3CF_2CF_2^{\bullet}$, although it remains essentially unchanged for the non-fluorinated analogue. Nonplanarity at the radical center leads to an expected nonzero c^{β}, but the total variation of the F^{β} hfc reduces to 35 G for $CF_3^{\bullet}CF_2$ and to 45 G for $CF_3CF_2^{\bullet}CF_2$, with the largest value in the antiperiplanar conformation ($\theta = 180°$). Thus, nonplanarity leads to a net increase of the isotropic hfc at F^{α}, but a decrease at F^{β}. Figure 5 demonstrates that the frequent assumption that the standard form of the McConnell relation for β-nuclei (eq 2, with $C = 0$) holds also for fluorine is valid only for the forced planar structure but clearly not for the more realistic nonplanar structure.

Because the dipolar contribution scales with the inverse cube distance of the nucleus from the unpaired electron, $\langle r^{-3}\rangle$, it is expected to be much smaller for β- than for α-nuclei. As expected, we find near axial values with a dominant positive contribution of ca. 3.1 G for the non-fluorinated radicals (Figure 4a). However, for the fluorinated species the hyperfine anisotropy is enhanced by a large factor. The tensor is also axial, but the dominant positive contribution has increased to 56 G for F^{β} in the eclipsed or antiperiplanar conformation of the planar radical, and it is still 22 G for F at a θ of 120°. In the fully optimized nonplanar case the positive dipolar hfc component of F^{β} amounts to 14 G for F in the eclipsed position (Figure 4b, 22 G for the atoms at $\theta = 120°$), but this increases to 48 G for F in the antiperiplanar position (Figure 4c, 5 G at 120°).

In the *n*-perfluoropropyl radical with a planar radical center the dipolar component of the eclipsed F^{β} increases even further to ca. 71 G. Because the nuclear moment of F is slightly less than that of H and the distance of these β-nuclei cannot be

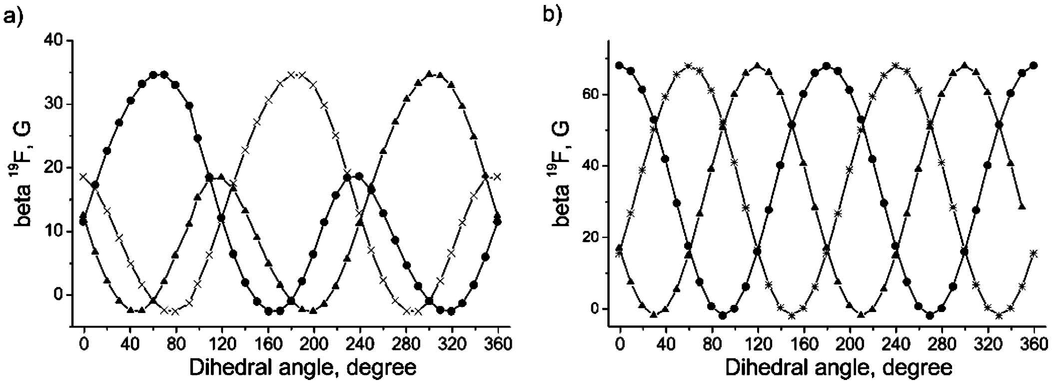


Figure 5. F^{β} hfc as a function of the dihedral angle θ for fully optimized (a) and forced planar (b) $CF_3^{\bullet}CF_2$.

TABLE 6: Isotropic hfc of F^γ (H^γ) Nuclei Represented by the Coefficients of Eq 4 for the Non-fluorinated and Perfluorinated 1-Propyl Radicals[a)]

	a_0/G	b/G (θ^0)	c/G ($\theta^{0'}$)
$CH_3CH_2{}^\bullet CH_2$ (optimized)	−0.9	6.4 (−60°)	0.0
$CF_3CF_2{}^\bullet CF_2$ (planar)	−0.8	15.0 (−60°)	0.0
$CF_3CF_2{}^\bullet CF_2$ (optimized)	+1.7	5.8 (−60°)	7.6 (−60°)

[a] Eq 4 holds only for the γ-atom in the zigzag ("W-plan") conformation; the other two γ-atoms vary less and are not discussed here.

greatly different, the spectacular increase of the dipolar component by a factor of 20 and more over that of the non-fluorinated radical cannot be explained by a through-space interaction of the nuclear point dipole with the unpaired electron in an atomic orbital localized at the radical center but must reflect the effect of large through-bond spin polarization, which leads to a significant delocalization of the spin density distribution.

$^{13}C^\gamma$. This nucleus is located two bonds from the radical center and behaves therefore in an analogous way as F^β and H^β, with a strong dependence of the isotropic hfc on the dihedral angle θ. This is verified in Table 5 where it is seen that the b coefficients are a factor of 2 lower than those for H^β. On the basis of the $^1H/^{13}C$ relative magnetic moments alone, one should have expected a factor 4, so there is some spin polarization involved. The dipolar contributions amount to little more than 1 G at maximum.

H^γ and F^γ. These nuclei are at a distance three bonds away from the radical center. In the zigzag ("W-plan") conformation the isotropic hfcs are nevertheless predicted to vary with the rotation angle about the $C^\alpha-C^\beta$ bond with an amplitude of 6.0 G for the non-fluorinated and 14.8 G for the *n*-perfluoropropyl radicals (Table 6). It has been known since the early work by Ellinger that a planar conformation in which the $H^\gamma-C^\gamma-C^\beta-C^\alpha-p_z$-orbital are arranged in a zigzag ("W-plan") conformation is particularly suitable to induce sizable γ-couplings.[22] Also the dipolar contributions can be a few Gauss for the non-fluorinated and up to 7 G for the fluorinated species.

3.4. Comparison with Experimental Values. Our calculated value of the isotropic g factor of 2.0040 for $CF_3{}^\bullet CF_2$ agree well with literature data,[17] but for the $ROCF_2{}^\bullet CF_2$ radical a value of only 2.0025 with a small anisotropy, both more typical for non-fluorinated species, was reported.

In small fluorinated radicals typical values for $a_{iso}(F)$ are large, in the range of 60−90 G for α-fluorine (except for $^\bullet CF_3$ for which it is 145 G) and 11−70 G for β-fluorine.[10,17] Further fluorine hyperfine splittings of 170 G for F^α and 16 G for F^β were quoted for the end-chain radical, $-CF_2{}^\bullet CF_2$, in γ-irradiated poly(tetrafluoroethylene), PTFE.[23] The end-chain radical $RCF_2{}^\bullet CF_2$ was formed by UV irradiation of Nafion and Dow perfluorinated membranes.[11] The principal values of the ^{19}F hyperfine tensors were determined, obtained by simulation of the ESR spectrum from the $RCF_2{}^\bullet CF_2$ radical, and the F^α hfcs were found to be compatible with the corresponding values for the propagating end-chain radical in PTFE or perfluorinated polyethers, but the F^β hfcs were different compared to those observed with PTFE.[11]

4. Conclusions

DFT calculations predict distinctly different behavior in the hyperfine coupling parameters of the perfluoroethyl radical compared with its non-fluorinated analog. The first difference is in the anisotropic contribution to the F^α nuclei, which is extremely large and oriented parallel to that of the carbon atom at the radical center. Also the F^β nuclei exhibit a very large anisotropy that furthermore depends strongly on the conformation of the radical. Most of these differences are attributed to the nature of the F atom which other than H can polarize bonds and conjugate with orbitals at the neighboring carbon atom. Also, the nonplanarity at the F-substituted radical center plays a role. The original McConnell relations, which hold well for non-fluorinated species, fail and need extension with further angularly dependent terms.

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