temperatures (zero-point effect) and for low barriers to inversion. Curve 7 (two vibrational states below the barrier top) no longer displays a negative temperature coefficient.[17] The latter is thus a *sufficient but not necessary* symptom of bent radical structure. The ratio of eq 7 is not constant and is greater than 2.330 which is approached asymptotically as E_0 increases. Our complete least-squares calculations indicate that reduced potentials with $E_0 \leq 10$ (curves 4 through 7) cannot be used to fit the experimental points for *tert*-butyl (Figure 2). In that case, the use of 2.330 rather than the appropriate quantum mechanical value involves an error of less than 3% justifying our further use of the classical approximation.

The simplest least-squares fitting (classical theory) involves the approximation of a quadratic $a(\alpha)$ (V_0 = 640 cal/mol) and $a(T) = a_0 + a_2\alpha_m^2F_2(T)$ in which $F_2(T)$ can be easily calculated (Figure 1). The least-squares fit to Wood's data gives a_0 = 8.8 G and $a_2\alpha_m^2$ = 44.9 G (Figure 2). The resulting value of the ^{13}C coupling for a nonvibrating planar *tert*-butyl (8.8 G) is low compared to the INDO calculations.[18] The latter can be fitted for $0 \leq \alpha \leq 30°$ with a root mean square deviation of 4 G by $a(\alpha) = 38.9 + 0.150\alpha^2 = 820.1\ (0.0475 + 1.835 \times 10^{-4}\alpha^2) = A^C\rho^C(\alpha)$ (α in degrees). The second expression is obtained by extracting the empirical proportionality constant built into the INDO program[19] (A^C = 820.1 G) relating the ^{13}C coupling to the unpaired C 2s spin density. A comparison of the least-squares results with the INDO quadratic $\rho^C(\alpha)$ gives A^C = 185 G and α_m = 36° in this approximation.

The INDO results indicate the importance of the *quartic* term since they can be fitted much better by $a(\alpha) = 34.0 + 0.211\ \alpha^2 - 8.846 \times 10^{-5}\alpha^4$ (root mean square (dev) = 0.7 G). Unfortunately, there are now too many parameters for a meaningful least-squares treatment. A systematic variation of V_0 and α_m using the INDO quartic $\rho^C(\alpha)$ followed by a least-squares determination of A^C indicates that reasonable root mean square deviations between theory and experiment can be obtained only for $450 \leq V_0 \leq 700$ cal/mol and $17° \leq \alpha_m \leq 22°$ leading to $375 \leq A^C \leq 489$ G ($15.6 \leq a_0 \leq 20.3$ G). The curve for V_0 = 550 cal/mol, α_m = 19.5° (tetrahedral angle), and A^C = 435 G (Figure 2) shows that the effect of the quartic term is to make the minimum shallower and to move T_{min} toward higher values. The discrepancy between our range for A^C and the INDO A^C is noteworthy and can no doubt be attributed to the neglect of zero-point effects, which can be appreciable even for shallow double-minimum potentials (Figure 1), in the INDO parametrization.[19] The details of this study as well as further applications (e.g., the CF_3 radical) will be reported elsewhere.

Acknowledgments. We are grateful to Professor D. O. Harris (Santa Barbara) for his symmetric oscillator computer program and useful advice.

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An Electron Spin Resonance Study of the Substituent Effects Causing Nonplanarity in Alkyl Radicals. Electronegativity vs. π-Conjugative Destabilization

Sir:

The geometries of simple organic radicals ($\dot{C}XYZ$) are strongly substituent dependent. Thus, while the methyl radical is planar or nearly so,[1] the trifluoromethyl[2] and *tert*-butyl[3] are pyramidal albeit with different barriers to inversion. Pauling[4] has explained these structural variations in free radicals in terms of electronegativity concepts, noting that the s character of the singly occupied orbital on carbon, and hence the nonplanarity of the radical, should increase as the polarity of the $\dot{C}$–X bond increases in the direction C^+–X^-. Recently, Bingham and Dewar[5] have presented theoretical arguments which demonstrate that conjugative destabilization associated with the presence of two or three donor dominant substituents should also give rise to nonplanar geometries.[5b] This latter proposal receives considerable support from the observation that two donor substituents induce pyramidality to a far greater extent than would be expected on the basis of the effect of one alone.[6] We report now the ESR data for several radicals derived from fluoroacyl halides which, taken together with published results, clearly show that conjugative destabilization and not electronegativity is the primary electronic factor which gives rise to nonplanar radical structures.

Ultraviolet irradiation in the ESR cavity of dilute solu-

Table I. ESR Parameters for Fluorinated Alkyl Radicals

Radical	Temp, °C	Hyperfine splittings, G			g
		$a(\alpha\text{-}F)$	$a(X)$	$a(^{13}C)$	
$\dot{C}H_3$[a]	−177		−23.0(H)	38.5	2.0026
$\dot{C}FH_2$[a]	−188	64.3	−21.1(H)	54.8	2.0045
$\dot{C}F_2H$[a]	−188	84.2	22.2(H)	148.8	2.0041
$\dot{C}F_3$[a]	−188	142.4		271.6	2.0031
$\dot{C}H_2CH_3$[b]	−178		−22.38(α-H)	39.07	2.0026
			26.87(β-H)	−13.57(α-C)	
$\dot{C}(CH_3)_3$[c]	−182		22.2(β-H)	49.5	
$\dot{C}(CH_3)_3$[d]	−128		22.76(β-H)	−12.3(α-C)	
$\dot{C}F(CF_3)_2$	+25	70.29	19.77(β-F)		2.0031
$\dot{C}F_3OC(CF_3)_2$[e]	−40		18.80(β-F)	−12.59(α-C)	2.0026
$\dot{C}(CF_3)_3$	+26		18.69(β-F)	44.3	2.0020
				−14.6(α-C)	
$\dot{C}F_2CF_3$[f]	−94	87.64	11.35(β-F)		2.0037
$\dot{C}F_2CH_3$[f,g]	−78	94.01	13.99(β-H)		2.0036
$Et_3SiO\dot{C}F(CF_3)$[f]	−47	88.22	14.03(β-F)		2.0034
$Et_3SiO\dot{C}F(CH_3)$[f]	−45	95.11	13.80(β-H)		2.0032
$Et_3SiO\dot{C}F[CF(CF_3)_2]$	+30	86.55	28.86(β-F)	3.74(γ-F)	2.0032
$CF_3O\dot{C}F(CF_3)$[e,f]	−63	91.85	12.21(β-F)		2.0035
$CF_3O\dot{C}F(CF_2CF_2SiBu_3)$[f,h]	−21	91.20	12.23(β-F)		2.0032
$HO\dot{C}F(CH_3)$[f]	−83	110.59	13.74(β-H)	5.59(OH)	2.0034
$Et_3SiO\dot{C}F_2$[i]	−86	147.6			
$\dot{C}Cl_2CF_3$[g]	−81	4.14(Cl)	18.56(β-F)		2.0080
$\dot{C}Cl_2CH_3$[g]	−108	4.34(Cl)	19.70(β-H)		2.0073
$Et_3SiO\dot{C}Cl(CF_3)$[f]	−97	6.97(Cl)	17.72(β-F)		2.0048
$Et_3SiO\dot{C}Cl(CF_2CF_3)$[f]	−25	6.02(Cl)	28.22(β-F)	3.71(γ-F)	

[a] Reference 2a. [b] Reference 1b. [c] D. E. Wood and R. F. Sprecher, *Mol. Phys.*, **26**, 1311 (1973). [d] Reference 3b. [e] Fluoromethoxy $a(F) < 0.05$ G. [f] Selective line broadening due to hindered internal rotation. [g] Reference 10. [h] Reference 8. The structural formula for this radical and its g value were wrongly transcribed. [i] Reference 8.

tions of fluoroacyl fluorides in inert fluorocarbons (CF_2Cl_2, c-C_4F_8, perfluoro-1,2-dimethylcyclobutane) gives rise to the spectra of the fluoroalkyl radicals formed by the cleavage of the R_F–COF bonds (Figure 1).

$$R_FCOF \overset{h\nu}{\rightleftarrows} [R_FCOF]^* \rightarrow \dot{R}_F + (\dot{C}OF) \quad (1)$$

$$R_F = CF_3, C_2F_5, i\text{-}C_3F_7, t\text{-}C_4F_9, CF_3O\dot{C}F(CF_3), CF_3O\dot{C}(CF_3)_2$$

The spectrum of the fluoroformyl radical is not observed.[7] Radical concentrations increase with temperature, and the best spectra are obtained above room temperature.

If small amounts of trialkylsilanes are also present, intense spectra of siloxy radicals II are obtained instead.

$$R_FCOF \overset{h\nu}{\rightleftarrows} [R_FCOF]^* \xrightarrow{R_3SiH} R_F\dot{C}F(OH)\ (I) + R_3Si\cdot \quad (2)$$

$$R_3Si\cdot + R_FCOF \rightarrow R_3SiO\dot{C}FR_F\ (II) \quad (3)$$

Analogous chlorosiloxy radicals can be generated from fluoroacyl chlorides. The radical formed by initial photoreduction (I) could be observed only with CH_3COF. The same radical, together with $(CH_3)_2\dot{C}OH$, is produced by photoreduction of CH_3COF in the presence of isopropyl alcohol. Perfluoroacyl fluorides did not undergo ready photoreduction, since the spectra of $R_F\dot{C}F(OH)$ could not be obtained under similar conditions, in contrast to the behavior of perfluoro ketones.[8] The magnitudes of the α fluorine splittings in these radicals (Table I), the anomalous sign of their temperature coefficients (vide infra), together with the restricted rotation of α-CF_3[9] and α-CH_3[10] groups inferred from severe selective line broadening in the corresponding quartets at low temperatures (<−50°) indicate pronounced nonplanarity at the radical sites.

According to elementary ESR theory, the isotropic couplings associated with the trigonal carbon atoms as well as with the α atoms (H, F, Cl, etc.) become more positive as the departure of the radical from planarity increases. These couplings could be used as indicators of local radical geometry were it not for the different spin withdrawing abilities of various α substituents. The latter could vary, furthermore, with the geometry at the trigonal carbon. For planar radicals, the INDO[11] unpaired positive spin density in the 2 p_z orbital at the central carbon provides guidance. For $\dot{C}H_3$, $\dot{C}(CF_3)_3$, $\dot{C}F_3$, and $\dot{C}(CH_3)_3$, $\rho_{INDO}{}^{2p_z}$ = 100, 86.73, 81.74, and 80.54% indicating 0, 4.42, 6.09, and 6.49% positive spin withdrawal by each H, CF_3, F, and CH_3, respectively.[12] For bent structures, the INDO results do not afford similar information directly. However, a total spin density on the central carbon can be estimated from $\rho_c = \rho_c{}^{2p_z} + \Delta\rho_c{}^{2s} + \Delta\rho_c{}^{2p_x} + \Delta\rho_c{}^{2p_y}$, where each $\Delta\rho$ is the increment in unpaired spin populations of the corresponding carbon atomic orbitals relative to the values for the planar radical.[13] The resulting $\rho_c(\alpha)$ (Figure 2) reveal that the spin withdrawing abilities of CF_3 and CH_3 groups are rather insensitive to the local structure (contrary to the withdrawals by α-H and F atoms) and that the *CF_3 group always removes less spin density than the CH_3 group.*[14] This conclusion is supported by the β proton splittings for $HO\dot{C}(CH_3)_2$

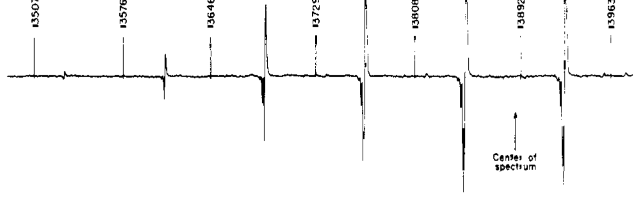

Figure 1. ESR spectrum of the $\dot{C}(CF_3)_3$ radical formed by photolysis of a dilute solution of perfluoropivaloyl fluoride in CF_2Cl_2 at room temperature showing second-order splittings. The proton NMR field markers are in kHz.

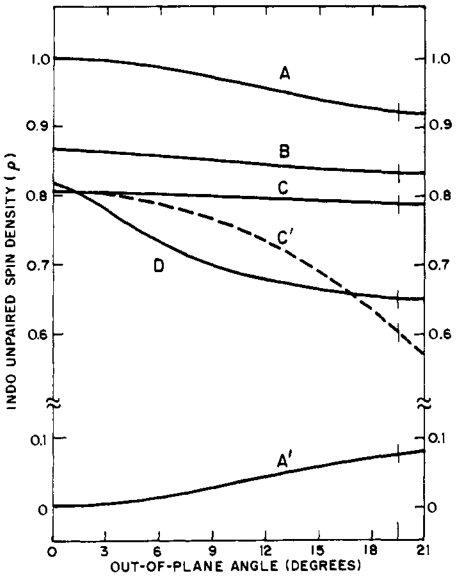

Figure 2. Total unpaired spin density on the trigonal carbons of $\dot{C}H_3$ (A), $\dot{C}(CF_3)_3$ (B), $\dot{C}(CH_3)_3$ (C), and $\dot{C}F_3$ (D) calculated by the INDO method as a function of the out-of-plane angle (19.47° = tetrahedral structure marked with short vertical lines). A′ represents the positive spin density increment on the three hydrogens in $\dot{C}H_3$ ($3\,\Delta\rho_H{}^{1s}$, $A + A' = 1$). Curve C′ for $\dot{C}(CH_3)_3$, calculated using the empirical functional form given in ref 14, deviates markedly from the INDO curve (C).

(19.6 G)[15] and $HO\dot{C}(CH_3)CF_3$ (21.4 G);[8] the larger $a(H\beta)$ for the latter implying a larger spin density at the central carbon.[16]

The data relevant to our discussion are summarized in Table I. The synergistic effect of fluorine substituents in bending the methyl radical geometry is revealed by the disproportionate change in a(H) and $a(^{13}C)$ in going from $\dot{C}FH_2$ to $\dot{C}F_2H$. Significant nonplanarity is indicated only when *two or more* fluorine substituents are present.

The trigonal-^{13}C splittings of $\dot{C}H_2CH_3$ and especially $\dot{C}(CH_3)_3$ are more positive than that of $\dot{C}H_3$ despite the spin withdrawals of α-CH_3 groups which would tend to reduce $a(^{13}C)$.[17] A progressive radical bending attending CH_3 substitution is indicated.[6,18] Indeed, for $(CH_3)_3\dot{C}$ a nearly tetrahedral equilibrium geometry with a barrier to inversion of 600 cal/mol has been determined recently from the anomalous temperature dependence of $a(^{13}C)$ (which decreases with increasing T).[3]

The ^{13}C splitting of $\dot{C}(CF_3)_3$, on the other hand, is smaller than that of $\dot{C}(CH_3)_3$ and has a normal temperature dependence (increases with T) indicating a more planar geometry. *Methyl substituents, therefore, induce more bending than the strongly electronegative CF_3 groups.* The same conclusion emerges from a comparison of α-F (and α-Cl) splittings which are larger for $\dot{C}F_2CH_3$($\dot{C}Cl_2CH_3$) and $Et_3SiO\dot{C}F(CH_3)$ than for their trifluoromethyl analogues despite the greater spin withdrawals by CH_3 compared to CF_3. The magnitudes of a(α-F) also indicate a bending synergism in structures such as -$\dot{C}$F(OR) (R = H, CF_3, R_3Si) entirely analogous to that pointed out for two fluorines and that noted previously for -$\dot{C}(OR)_2$ fragments.[6] The strong pyramidality of such moieties is also revealed by the very small H and F splittings of α-CH_3[6,10] and α-CF_3[9,19] groups, by their restricted rotation (which is quite pronounced in $\dot{C}F_2CF_3$ and $CF_3O\dot{C}FCF_3$ but is not apparent in $CF_3\dot{C}FCF_3$ and $CF_3O\dot{C}(CF_3)_2$ despite the replacement of a bulky CF_3 by a smaller F atom), and by the negative temperature coefficient of a(α-F) (e.g., −11.3 mG/°K for $Et_3SiO\dot{C}FCF_3$ at −20°). Significantly, radical HO-$\dot{C}FCH_3$ (a(F) = 110.59 G) is more bent than F-$\dot{C}FCH_3$ (a(α-F) = 94.01 G) despite the lesser group electronegativity of OH (3.7) relative to F (3.95).[20] A comparison of α-F splittings reveals further that nonplanarity increases in the order $CF_3\dot{C}F_2 < CH_3\dot{C}F_2 < Cl\dot{C}F_2 < F\dot{C}F_2 < Et_3SiO\dot{C}F_2$ which parallels closely the conjugative ability of the unique substituent as measured by $\sigma_R{}^\circ$ constants.[21]

We conclude that the primary cause for strong bending in simple carbon radicals is the presence of at least two α atoms with unshared electron pairs giving rise to the π-conjugative destabilization described by Bingham and Dewar.[5] The bending effect of methyl groups can be rationalized similarly by considering that they interact primarily via their doubly occupied group $(\sigma\pi)_z$ orbitals.[22] In this sense, α-methyl substituents may be regarded as pseudo-electron-pair substituents.

Acknowledgments. We thank Drs. P. R. Resnick and D. C. England for gifts of several fluorinated compounds and Messrs. B. F. Gordon and J. J. O'Reilly for technical assistance.

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Received August 20, 1975