MO study of the effect of α-substituents on the ^{13}C hfs constants of acyl radicals: an electronic rather than structural effect

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The experimental ^{13}C hyperfine splitting (hfs) constants of the acyl radicals Y–C$^\bullet$=O, (Y = H, Me, OBu^t, NH_2 and F) have been well reproduced by *ab initio* calculations at the UMP2/DZP//UHF/6-311G level of theory. The large increase observed experimentally in $a(^{13}C)$ as the electronegativity of the α-substituents increases is due to the electronic influence of the α-substituents rather than to an increase in bending at the radical centre as previously suggested. There is a large breakdown in orbital following in the singly occupied molecular orbital (SOMO) which strongly depends on the electronegativity of the α-substituents. This confirms still further that in localized radicals reliable structural information cannot be obtained by taking into account the trend in the experimental isotropic hfs constants at the radical centre.**

From the magnitude of the experimental ^{13}C hyperfine splitting (hfs) constants it is well established that the radical centre in α-substituted acyl radicals Y–C$^\bullet$=O is bent.[1–3] The large variations observed experimentally in $a(^{13}C)$ were exclusively attributed to structural changes at the central carbon.[1,2] Hence, on the basis of the trend in $a(^{13}C)$ Griller and Roberts[2] concluded that the geometry at the radical centre becomes more bent as the electronegativity of the α-substituent increases. By contrast, we have recently shown by means of *ab initio* calculations that in α-substituted methyl,[4] silyl[5,6] and phosphonyl[7] radicals there is not a strict relation between the magnitude of the experimental hfs constant and the geometry at the radical centre. In symmetrically α-substituted silyl and phosphonyl radicals the large variations observed in the magnitude of the hfs constant for the central atom are exclusively due to the electronic effect of the α-substituents, the radical centre remaining nearly tetrahedral, except for the tris(trimethylsilyl)silyl radical, *i.e.* in the presence of strongly electropositive α-substituents such as the trimethylsilyl groups, whereas in symmetrically substituted methyl radicals both structural and electronic factors are operative in determining the variations in $a(^{13}C)$. Thus, *ab initio* calculations have been carried out on α-substituted acyl radicals to verify the reliability of the structural information obtained directly from the experimental ^{13}C hfs constants and to establish to what extent the electronic effects of the α-substituents contribute to the large variations observed experimentally in $a(^{13}C)$.

Computational details

Ab initio unrestricted Hartee–Fock (UHF) calculations have been performed on the acyl radicals Y–C$^\bullet$=O (Y = H, Me, OBu^t, NH_2 and F) with the GAUSSIAN92 system of programs[8] running on a RISC-6000 IBM computer. Geometries have been optimized employing the valence-triple-ζ 6-311G** basis set supplemented with polarization functions.[9,10] ^{13}C hfs constants in Gauss units have been computed at the optimized geometries from the Fermi contact integrals $Q(0)$ in atomic units which are related by eqn. (1)[11] where g_e is

$$a(^{13}C) = (8\pi/3)g_e\beta_e g_C\beta_C Q(0) \equiv C_C Q(0) \qquad (1)$$

the electronic g factor, β_e is the Bohr magneton, g_C and β_C are the analogous values for the carbon nucleus. A C_C value of 400.4 G au^{-1} has been used.[12] The Fermi contact integrals, *i.e.* the spin densities at the carbon nucleus, have been computed from the generalized density matrices corresponding to the second-order Møller–Plesset perturbation (UMP2)[13] energies obtained with the Z-vector method.[14,15] In these calculations the Dunning–Huzinaga full double-ζ basis set (DZ)[16] augmented with polarization functions (P), p functions on hydrogens and d functions on heavy atoms[10] has been employed. This level of theory (UMP2/DZP//UHF/6-311G**) provided hfs constants at the radical centre in excellent agreement with experiment in localized radicals where the doublet state was found to be little contaminated by higher spin multiplets[4,6,7] as in the present calculations, the expectation value of S^2 being *ca.* 0.76. Good agreement with experiment was obtained with the UMP2 method also employing the 6-311G** basis set.[17]

Table 1 Optimum θ bond angles (degrees) at the UHF/6-311G** level in Y–C$^\bullet$=O radicals. The values estimated from a^C_{exp} using eqns. (2), (3) and eqns. (2,) (4), (5) are also reported

	θ/degrees		
Y	UHF/6-311G**	Eqns. (2), (3)	Eqns. (2), (4), (5)
H	126.6	141.8	129.9
Me	129.4	143.0	133.2
NH_2	130.8	137.3	126.7
OBu^t	128.6	135.8	123.0
F	128.1	126.2	111.8

Results and discussion

The structures at the radical centre of acyl radicals determined by means of reliable *ab initio* calculations have been compared with those obtained from the experimental $a(^{13}C)$ constants and the factors which contribute to the observed differences have been examined in detail.

The values of the ∠YCO bond angle, θ, optimized at the UHF/6-311G** level are reported in Table 1. All investigated acyl radicals are computed to be bent at the radical centre, the value of θ being *ca.* 128°, *i.e.* slightly larger than that expected for an sp^2 hybridized carbon atom (θ = 120°). Interestingly, substitution of the α-proton produces only a small decrease in the deviation from linearity which does not depend on the electronegativity of the α-substituents, the variations displaying a random trend. This finding is in contrast to the conclusion reached on the basis of the EPR data. Cochran *et al.*[1] concluded that the large increase in $a(^{13}C)$ observed experimentally in

Table 2 Theoretical (UMP2/DZP//UHF/6-311G**) and experimental ^{13}C hfs constants (G) of Y–C$^{\bullet}$=O radicals

Y	a/G Theory	a/G Experiment	Ref.
H	127.2	133.9	24
Me	123.0	124.6	25
NH_2	167.3	170.0	26
OBu^t	183.2	183.5	2
F	271.6	286.6	1

passing from H–C$^{\bullet}$=O (134 G) to F–C$^{\bullet}$=O (286 G) is due to an increase in the C-2s population in the singly occupied molecular orbital (SOMO) associated with a decrease in θ. The radical centre was estimated to be slightly less bent than trigonal ($\theta = 125°$) in formyl and nearly tetrahedral ($\theta = 110°$) in fluoroformyl. Later, Griller and Roberts[2] suggested that the degree of bending at carbon should, in general, increase with increasing electronegativity of the α-substituents since they found an intermediate value of $a(^{13}C)$ (183.5 G) in the presence of the *tert*-butoxy substituent that has an intermediate electronegativity between those of hydrogen and fluorine.

The computed bond angles θ are compared in Table 1 with the values estimated from the experimental ^{13}C hfs constants, a^{C}_{exp}, following the approach generally used by EPR spectroscopists. This is based on the assumption that the interorbital angles in the SOMO follow the nuclear coordinates (complete orbital following).[18] The bond angle θ has been determined from the C-2s character, s, in the SOMO by means of eqn. (2) assuming that the σ C–Y and C–O bonding orbitals

$$\theta = 2\arccos\{[s/(1+s)]^{1/2}\} \quad (2)$$

are equivalent sp^n hybrid orbitals.[1,19] The estimate of the s character in the SOMO has been obtained by dividing a^{C}_{exp} by the value A_0 computed for a unitary C-2s population ($\rho_{C\text{-}2s} = 1$)[20,21] [eqn. (3)]. An A_0 value of 1115.4 G has been used for

$$s \equiv \rho_{C\text{-}2s} = a^{C}_{exp}/A_0 \quad (3)$$

carbon.[21,22] The values of θ estimated from a^{C}_{exp} decrease with increasing electronegativity of the α-substituents. This confirms the qualitative conclusion reached by Griller and Roberts,[2] but it is in contrast to the structural information obtained with *ab initio* UHF/6-311G** calculations. Besides, the estimated values of θ are much larger than those computed at the UHF/6-311G** level except for fluorine. UHF/6-311G** calculations are known to provide reliable structural parameters, especially bond angles.[23] The reliability of the structural information obtained from the *ab initio* calculations has been confirmed by comparing experimental and theoretical ^{13}C hfs constants. In fact, Table 2 shows that the values of $a(^{13}C)$ computed at the optimized geometries are in good accord with the experimental ones. Furthermore, the optimized values of θ for formyl and fluoroformyl are close to those estimated from photon spectroscopy (125.0° for Y = H[27] and 127.3° for Y = F[28]) being only *ca.* 1° larger. Interestingly, the value of θ for formyl is found to be slightly smaller than that for fluoroformyl both at the UHF/6-311G** level and by means of photon spectroscopy. Thus, the discrepancy between the values of θ obtained from a^{C}_{exp} and those determined at the UHF/6-311G** level could be due either to a large breakdown in orbital following in the SOMO which would depend strongly on the electronegativity of the α-substituents or to an increase in the total spin density on the central carbon with increasing electronegativity of the α-substituents. In this latter case, it is likely that the C-2s population increases proportionally to the increase in the total spin density so that the C-2s character and hence the geometry at the central carbon should not change significantly with α-substitution. This would also explain why the values of θ estimated directly from a^{C}_{exp} are much larger than those computed at the UHF/6-311G** level. Indeed, eqn. (3), which is currently utilized by EPR spectroscopists,[29,30] holds when the spin-polarization (a_{pol}) and spin-delocalization contributions are negligible. In general, the s population in the SOMO should be estimated by subtracting the spin-polarization contribution from the value of the experimental hfs constant [eqn. (4)] and the s character should be determined by

$$\rho_{C\text{-}2s} = (a^{C}_{exp} - a^{C}_{pol})/A_0 \quad (4)$$

normalizing the s population to the total electron density in the SOMO on the radical centre (ρ_C) [eqn. (5)] so that the s

$$s = \rho_{C\text{-}2s}/\rho_C \quad (5)$$

character is larger than the s population. The spin-polarization contribution is usually approximated by the value of the hfs constant in a π-electron radical where the direct contribution vanishes, *i.e.* in a linear configuration for radicals localized at a trivalent atom. Unfortunately, all acyl radicals are bent, thus the spin-polarization contribution has been estimated by computing the ^{13}C hfs constant of the investigated acyl radicals in their linear configuration since the calculations reproduce very well the experimental ^{13}C hfs constants. Note that the spin-polarization contribution depends on the configuration at the radical centre. In this case it is expected to decrease slightly on bending.[12] Table 3 shows that the correction to the s population due to spin-polarization is small, the estimated values of a^{C}_{pol} being of the order of 13 G. On the other hand, the total spin density at carbon (ρ_C), computed according to the Mulliken population is about half that expected for a completely localized radical, the unpaired electron being mainly delocalized to the α-oxygen. Thus, the C-2s character in the SOMO is twice as large as the C-2s population. The resulting values of θ are hence much lower than those estimated using eqn. (3). Interestingly, the values estimated for the formyl and fluoroformyl radicals are close to those determined by Cochran *et al.*[1] from the ^{13}C hyperfine tensor. Indeed, both spin-polarization and spin-delocalization effects were correctly taken into account in their approach. However, the trend in θ does not change even with computing correctly the C-2s character. Indeed, Table 3 shows that the total electron density in the SOMO on carbon, ρ_C, remains nearly constant with α-substitution ranging from 0.52 to 0.56 so that the trend in the C-2s character parallels that in the C-2s population. The difference between the value of θ estimated correctly from experiment and that computed at the UHF/6-311G** level is small for formyl, but it increases with increasing electronegativity of the α-substituents so that the value of θ for Y = F is particularly underestimated with respect to the *ab initio* value. This discrepancy is due to a large breakdown in orbital following in the SOMO rather than to an increase in the total spin density on the central carbon. Indeed, the C-2s population $\rho_{C\text{-}2s}$ increases largely with increasing electronegativity of the α-substituents both when computed by *ab initio* calculations and when estimated from a^{C}_{exp}. This confirms that in localized radicals the relation between the magnitude of the isotropic hfs constant for the central atom and the geometry at the radical centre does not, in general, hold.

It has been shown that the large variations observed experimentally in $a(^{13}C)$ upon α-substitution are due to the electronic effect of the α-substituents rather than to structural changes at the radical centre. The same behaviour was previously found in phosphonyl radicals[7] and was ascribed to the large difference in electronegativity between the central

Table 3 C-2s population $\rho_{C\text{-}2s}$ and C-2s character s in the SOMO of Y–C$^{\bullet}$=O radicals computed by *ab initio* calculations and estimated from a^{C}_{exp}. Total atomic electron densities ρ in the SOMO are also reported

	UHF					Exp		
Y	$\rho_{C\text{-}2s}$	s	ρ_C	ρ_O	ρ_Y	$\rho_{C\text{-}2s}$ [eqn. (3)]	$\rho_{C\text{-}2s}$ [eqn. (4)]	s
H	0.12	0.22	0.53	0.36	0.11	0.12	0.11	0.22
Me	0.13	0.26	0.53	0.29	0.18	0.11	0.10	0.20
NH_2	0.21	0.40	0.56	0.34	0.10	0.15	0.14	0.26
OBu^t	0.24	0.48	0.52	0.28	0.20	0.17	0.15	0.30
F	0.28	0.54	0.54	0.36	0.10	0.25	0.24	0.50

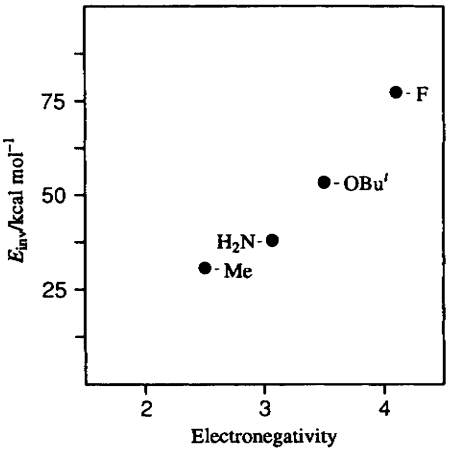

Fig. 1 Inversion barriers E_{inv}/kcal mol^{-1} of Y–C$^{\bullet}$=O radicals *versus* the Allred–Rochow electronegativity[32] of the α-substituents computed at the UHF/6-311G** level

atom and the α-oxygen. This finding is in contrast to the conclusion reached on the basis of the perturbation molecular orbital (PMO) theory according to which the degree of bending at the radical site should increase as the α-substituent becomes more electronegative.[31] Note that the PMO theory also predicts that the barrier to inversion at the radical site should increase with increasing electronegativity of the α-substituents. Indeed, Fig. 1 displays the expected trend for this property as previously found for α-substituted silyl,[33] methyl[4] and vinyl[34] radicals. On the other hand, our studies on the effect of α-substituents on the properties of localized radicals indicate that the degree of bending at the radical centre increases with increasing electronegativity of the α-substituents as expected only when the inversion barriers at the radical site are small (E_{inv} < 10 kcal mol^{-1}), *i.e.* when the difference in electronegativity between the central atom and the α-substituents is small as in α-substituted methyl[4] and vinyl[34] radicals, whereas it is little influenced by the electronic nature of the α-substituent when the inversion barrier is high, *i.e.* when the difference in electronegativity between the central atom and α-substituents is large such as in α-substituted silyl,[5,6] phosphonyl[7] and acyl radicals. This is probably due to the steric repulsion between the negatively charged α-substituents which counterbalances the electronic effect.[35]

Conclusions

The ^{13}C hfs constants of the acyl radicals Y–C$^{\bullet}$=O are well reproduced by UMP2/DZP//UHF/6-311G** calculations. The central carbon in these species is computed to be nearly sp^2 hybridized, the degree of bending at carbon being little influenced by the substituents Y as previously found in phosphonyl radicals because of the presence of the α-oxygen which is much more electronegative than the central carbon atom. Hence, the large variations observed experimentally in $a(^{13}C)$ are due to the electronic influence of the substituents Y rather than to a structural change at carbon as previously established on the basis of the EPR data. Thus, also in this case the magnitude of the hfs constant for the central atom is not strictly related to the geometry at the central atom as usually accepted by EPR spectroscopists.

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