MO study of the effect of substituents on the properties of localized organic and organometallic radicals

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Abstract: *Ab initio* UMP2/DZP calculations on localized organic and organometallic radicals reproduce very well the experimental hyperfine splitting (hfs) constants and show that substituents largely influence spin distribution. In α-substituted alkyl, silyl and phosphonyl radicals there is no relation between the magnitude of the hfs constant and the geometry at the radical center as generally accepted. The sizeable variations observed experimentally in the hfs constant at the radical center upon α-substitution are due to the electronic effect of the α-substituents rather than to structural changes at the radical center. In β-substituted alkyl radicals adopting the eclipsed conformation electronegative substituents reduce sizeably the spin density at β-hydrogens so that the unexpectedly low β-proton splittings observed experimentally are due to the electronic effect of the β-substituents rather than to an asymmetric bridging as generally recognized.

INTRODUCTION

Localized organic and organometallic radicals play an important role in organic synthesis. Knowledge of their structural and conformational properties is very useful for predicting their reactivity. Structural information on such reactive species are usually obtained from the experimental hyperfine splitting (hfs) constants (1). The local radical geometry is determined from the s-character of the orbital containing the unpaired electron (SOMO) as estimated by dividing the experimental hfs constant per the value (A_0) computed for a unitary s-population. The preferred conformation of β-substituents is determined from the β-proton hfs constant taking advantage of its angular dependence. The use of experimental hfs constants for obtaining structural information is based on the assumption that in localized radicals the spin distribution is little affected by the electronic nature of α- and β-substituents. Thus, the effect of α- and β-substituents on the structural and electronic properties of localized radicals has been investigated by means of *ab initio* calculations to establish whether reliable structural information can be obtained from experimental hfs constants.

THE EFFECT OF SUBSTITUENTS

α-Substituent effect

The magnitude of the experimental hfs constant at the radical center (a_{exp}) in α-substituted alkyl (2), silyl (3) and phosphonyl (4) radicals was found to increase with increasing electronegativity of the α-substituents. This was interpreted in terms of an increasing pyramidalization at the radical center causing the increase of s-character of the SOMO.
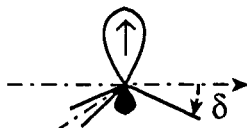
Hence, it was concluded that the degree of pyramidalization at the radical center increases as the α-substituent becomes more electronegative. Electronegative substituents were also found to favour the bent structure (σ-type radical) in α-substituted vinyl radicals, whereas the linear structure (π-type radical) was observed with electropositive substituents (5).

σ-type   π-type

The structures of alkyl (6), silyl (7,8), acyl, vinyl, and phosphonyl radicals have been determined by high level *ab initio* calculations. Geometries have been optimized at the unrestricted Hartree Foclk (UHF) level of theory employing the triple-ζ 6-311G** basis set supplemented with polarization function (TZP), except for silyl radicals where the less flexible Dunning/Huzinaga double-ζ basis set (DZP) has been employed. However, in this case correlation energy estimated at the second order Moller-Plesset perturbation theory (UMP2) has been also taken into account. Geometries at the radical center and experimental hfs constants do not display the same trend as a function of the electronegativity of the α-substituents. For example, Fig. 1 shows that in symmetrically α-substituted silyl radicals $Y_3Si^\bullet$ no correlation exists between the trend of the out-of-plane angle δ and that of $a_{exp}(^{29}Si_\alpha)$. The arrangement of atoms around silicon is essentially tetrahedral in all the radicals except when the α-substituent is a strongly electron-releasing group such as trimethylsilyl. By contrast, $a_{exp}(^{29}Si_\alpha)$ increases largely with increasing electronegativity of the α-substituents.
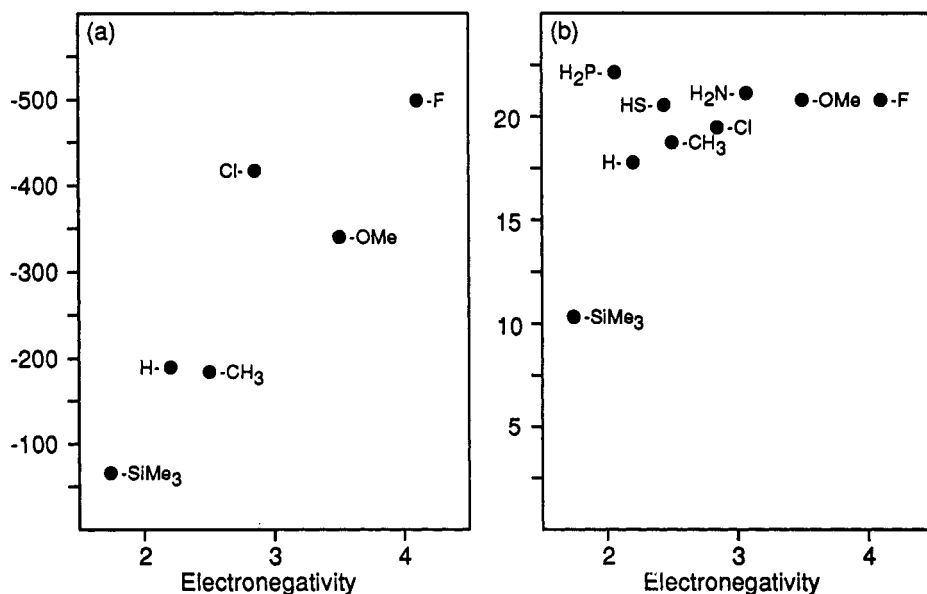

Fig. 1 a) $a_{exp}(^{29}Si_\alpha)$ (G) and b) optimum out-of-plane angle δ (degree) at the UMP2/DZP level as a function of the Allred-Rochow electronegativity of the α-substituents in $Y_3Si^\bullet$ radicals

Data presented in Table 1 confirm that a large discrepancy exists between the optimum values of the out-of-plane angle δ for silyl and alkyl radicals with those based on a_{exp}.

TABLE 1. Optimum out-of-plane angles δ (degrees) of $Y_3X^\bullet$ radicals along with values estimated from $a_{exp}(X_\alpha)$

X	C			Si		
Y	UHF/TZP	A	B	UMP2/DZP	A	B
H	0.0	7.5	4.4	17.7	15.6	13.1
H_3C	8.5	8.5	6.3	18.7	15.4	13.0
MeO	16.3	14.7	17.7	20.8	20.5	21.0
F	17.5	19.3	22.2	20.8	24.4	24.2
Me_3Si	6.1	6.5	4.5	10.6	9.3	5.2
MeS	8.8	8.9	12.6	-	-	-
Cl	10.3	12.9	16.7	19.4	22.5	25.8

The out-of-plane angle δ has been estimated from the s-character in the SOMO at the central atom X assuming complete orbital following (9) (*i.e.* that the nuclear coordinates follow the interorbital angles)

$$\delta = \text{arc } \cos[2/(s+2)]^{1/2} \qquad (1)$$

Two different approximations have been used to estimate the s-character. In approach A, the s-character has been computed directly from a_{exp} (the values of A_0 have been taken from HF atomic calculations (10))

$$s = a_{exp}/A_0 \qquad (2)$$

In this crude but widely used approach, one assumes that spin-polarization (a_{pol}) and spin-delocalization contributions in equation (3) are negligible (ρ represents the electron density in the SOMO at the radical center)

$$s = (a_{exp} - a_{pol})/A_0\rho \qquad (3)$$

In approach B, these contributions have been estimated by means of accurate *ab initio* calculations (UMP2/DZP) since for silyl radicals a reliable estimate of the polarization term a_{pol} can not be obtained from experiment. In fact, silyl radicals are non-planar while a_{pol} is usually taken as the value of a_{exp} in a planar radical where the direct contribution vanishes.

It should be noted that the discrepancy is smaller in the crude approach A, possibly because effects operating in opposite direction are neglected.

Hfs constants have been computed at the UMP2/DZP level at optimum geometries. This level of theory gives hfs constants in excellent accord with experiment as shown in Fig. 2. Vibrational effects estimated averaging the computed hfs constants over the thermally populated vibrational states of the pyramidal inversion mode (umbrella mode) were found to be important only for planar radicals such as methyl (6). The excellent accord between theory and experiment indicates that the computed local radical geometries are reliable. This confirms that there is not a direct relation between a_{exp} and geometries at the radical center.
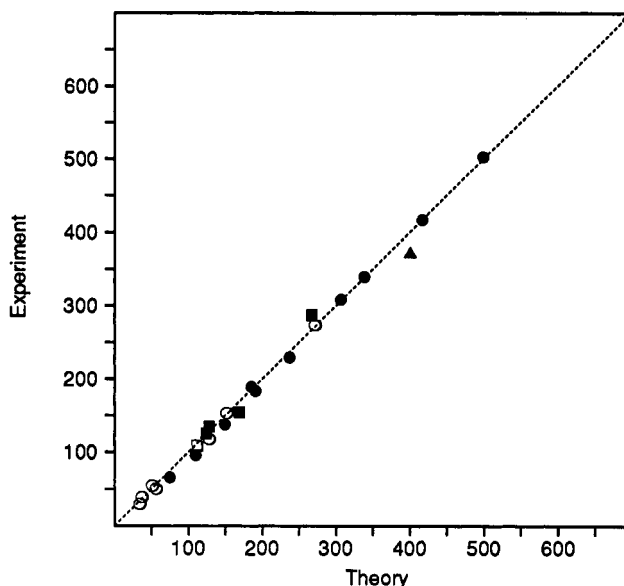
Fig. 2 Plot of $a_{exp}(X_\alpha)$ vs. UMP2/DZP values (Gauss) for alkyl ○, silyl ●, phosphonyl ▲, vinyl □, and acyl ■ radicals

Indeed, computations demonstrate that in the constrained tetrahedral structure (which should corresponds to sp^3 hybridization) the s-population in the SOMO of alkyl and silyl radicals increases dramatically with increasing electronegativity of the α-substituents. In silyl radicals, it ranges from a value (0.04 for Y = SiH_3) expected for a nearly planar structure to that (0.42 for Y = F) expected for a structure much more bent than tetrahedral (0.25). This trend was interpreted in terms of an increasing mixing of the p pure AO of the radical center with the lowest symmetric X-Y antibonding MO (σ^*_{X-Y}) that has a large s-character (6,7). According to one-electron perturbation molecular orbital (PMO) theory the extent of their mixing in the tetrahedral structure is inversely proportional to their energy difference ($\Delta E_{p-\sigma^*(X-Y)}$) in the planar form. Indeed, Fig. 3 shows that in $Y_3Si^\bullet$ radicals $\Delta E_{3p-\sigma^*(Si-Y)}$ decreases with increasing electronegativity of the α-substituents. This MO interaction should also dictate the trend of the inversion barriers E_{inv} since they display the same trend as the s-population in the tetrahedral structure. Indeed, an analogous trend observed in AY_3 molecules was explained invoking this MO interaction (11).

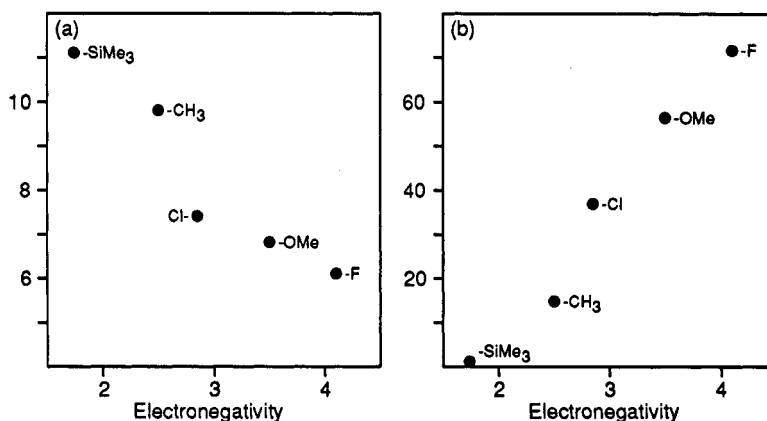Fig. 3 a) $\Delta E_{3p-\sigma^*(Si-Y)}$ (eV) in the planar structure and b) inversion barriers E_{inv} (kcal/mole) as a function of the Allred-Rochow electronegativity of the α-substituents in $Y_3Si^\bullet$ radicals

However, a_{exp} does not strictly depend on the electronegativity of the α-substituent. Its value for elements from third-row is larger than that expected only on the electronegativity basis as displayed in Fig. 1. This finding was attributed to a contraction of the valence s orbital containing the unpaired electron towards the nucleus (7).

On the other hand, the existence of linear relations between the hfs constants at the radical center X (X = C, Si, P) and the J(X-H) coupling constants from the NMR spectra of the protic parents (3,4,12) supported the hypothesis that the magnitude of a_{exp} is essentially related to the geometry at the radical center. In fact, the values of a (X) and J(X-H) are related to the s-population at the atom X since both these constants depend on the Fermi contact interaction. The small deviations from the straight line were interpreted in terms of slight delocalization of the unpaired electron onto α-substituents (3). However, it was suggested that such linear correlations have a physical meaning only inside a family of compounds. For example, two different linear correlations were found between the s-character of the SOMO and that of the σ(X-H) bond for the $(Me_3Si)_{3-n}Me_nSi^•$ and $Cl_{3-n}Me_nSi^•$ radicals (13). The magnitude of the angular coefficients was interpreted in terms of capability of a substituent to produce a change at the radical center. However, it should be emphasized that this relation predicts an sp hybridization in the Si-H bond of $HSiCl_3$, which has no chemical meaning. It has been demonstrated that in this case the successive replacement of the methyl group with the chlorine atom affects only spin distribution, whereas the structure at silicon remains unchanged (8). The existence of a good correlation implies only that the structures of radicals and their protic parents are similar, whereas deviations from correlation are mainly due to structural changes at the radical center upon homolysis of the X-H bond.

Vinyl and acyl radicals have been computed to have a bent structure (σ-type radicals). Also in these radicals $a(^{13}C_\alpha)$ and E_{inv} decrease with decreasing electronegativity of the α-substituents. In vinyl radicals E_{inv} is very small with strongly electropositive α-substituents such as the silyl group. The presence of two silyl groups in the β position favours the π-type structure in accord with ESR experiment (14).

These theoretical results can be useful for understanding and projecting reactions involving localized organic and organometallic radicals as reactive intermediates. In fact, the preference for retention of configuration at the radical center depends both on the degree of pyramidality at the radical center and on the height of the barrier to inversion.

β-Substituent effect

Third-row β-substituents were found to exert stereochemical control in free-radical reactions involving localized organic radicals such as β-substituted alkyl (15) and vinyl (16) radicals. This stereochemical control was supposed to occur via an asymmetric bridging between the radical center and the β-substituent (Fig. 4). There was no evidence for bridging from second-row elements.

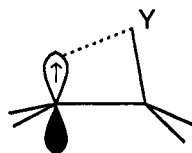Fig. 4 Hypothesized asymmetric bridging structure for eclipsed β-substituted alkyl radicals.

ESR investigations on β-substituted ethyl radicals $YCH_2CH_2^•$ supported the asymmetric bridging hypothesis (17). Second-row β-substituents were found to rotate freely about the C_α-C_β bond with a flat minimum in the staggered conformation since the β-proton splittings are greater than the free-rotation limit ($a_{H\beta}$ = A + B/2 = 27 G) for ethyl with positive temperature dependence. Third-row β-substituents were found to be locked in the eclipsed conformation (Fig. 5) by an asymmetric bridging since $a_{H\beta}$ are significantly lower than the minimum value ($a_{H\beta}$ = A + B/4 = 15 G) expected for the ethyl radical according to

the semiempirical equation suggested by Heller and McConnell (18)

$$a_{H\beta}(\theta) = A + B\cos^2\theta; \quad A \cong 3\,G\,, B \cong 48\,G \tag{4}$$

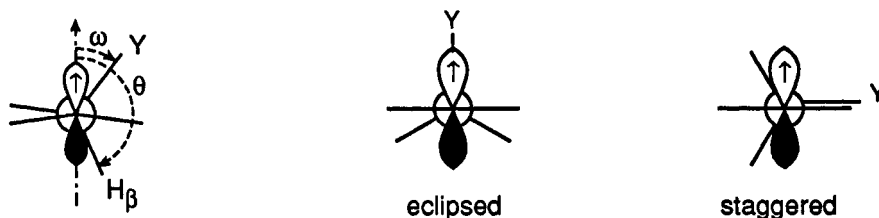**Fig. 5** Dihedral angles and rotamers in β-substituted alkyl radicals.

The β-hydrogens move away from the radical center and close to the nodal plane of the orbital containing the unpaired electron, thus reducing the β-proton splittings.

By contrast, *ab initio* UHF/DZP calculations performed on β-substituted ethyl radicals as a function of the dihedral angle θ showed that the electronic effect of the β-substituent cannot be neglected. Therefore, a third term was added to equation (4) to correctly describe the angular dependence of $a_{H\beta}$ (19).

$$a_{H\beta}(\theta) = A + B\cos^2\theta + C\cos\theta\,\sin\theta \tag{5}$$

A and B were found to be nearly constant, whereas C increases with increasing electronegativity of the β-substituent. Figure 6 shows that the influence of the β-substituent has a maximum in the eclipsed conformation and decreases upon rotation, becoming almost negligible in the staggered conformation. Thus, it follows the variation of the overlap between the orbital containing the unpaired electron and those of the β-substituent.
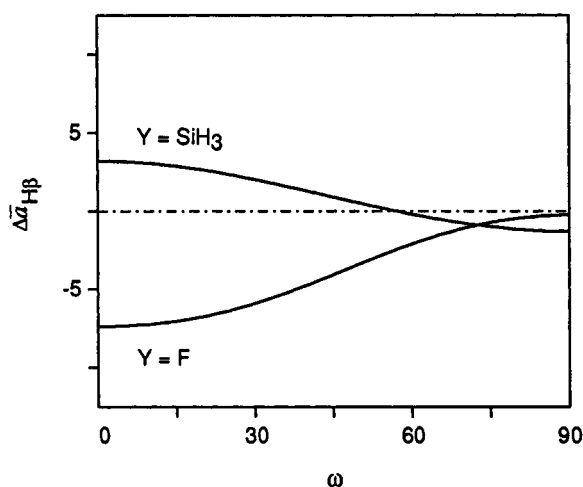

Fig. 6 Variation in the mean value of $\alpha_{H\beta}$ (Gauss) produced by the β-substituent Y as a function of the rotational angle ω.

The unexpected low values of β-proton splitting observed in most of substituted alkyl radicals adopting the eclipsed conformation were therefore attributed to electronic interactions (electronic hypothesis).

The electronic hypothesis was experimentally challenged, since no correlation was found between the β-proton splittings and the group electronegativity of substituents bearing second-row elements in β-substituted 1,1- diphenylethyl radicals; here the β-substituents were supposed to be locked in the eclipsed conformation because of steric hindrance around the radical center (20).

The structure of rotamers in β-substituted ethyl radicals, the rotational barriers and the β-proton coupling constants averaged over the rotational states were determined with *ab initio* UMP2/DZP calculations (21). The asymmetric bridging hypothesis was clearly ruled out since the arrangement of atoms around C_β is essentially tetrahedral in all the radicals. The radical center is slightly pyramidal with an out-of-plane angle of about 10-15°. The shape of the computed rotational barriers is consistent with experiment. For radicals containing second-row substituents the rotation is nearly free, whereas a barrier of about 2 Kcal/mole constrains β-substituents from third row in the eclipsed conformation. An inversion about the radical center occurs during the rotation about the C_α-C_β bond.

In third-row β-substituted radicals the rotational barrier arises owing to the largely stabilizing interaction occurring between the SOMO and the $\sigma^*(C_\beta$-Y) MO which lies low in energy only for third- and higher row substituents as established by means of the ETS spectroscopy and continuum MSXα calculations on *tert*-butyl halides (22).

UMP2/DZP calculations contributed also to rationalize experimental findings previously interpreted in contradictory manner in the literature. For example, the rotationally averaged value of the β-proton splitting for Y = H_3Si has been computed to be higher than the corresponding value for the ethyl radical. This trend agrees nicely with experiment and it is due to the lower electronegativity of silicon with respect to hydrogen. On the contrary, this apparently anomalous result was interpreted in terms of a tilt of the substituent in the opposite side away from the radical center (23). However, on the basis of kinetic studies, the same group envisaged an asymmetric bridging assistance by silicon in order to explain the preferential formation of β-silyl alkyl radicals in hydrogen-abstraction reactions from tetralkylsilanes (24). An asymmetric bridged structure was also invoked in order to explain the low values of the β-proton splittings observed in β-oxygen alkyl radicals when the β-substituent is constrained in the eclipsed conformation because of steric hindrance (25). This is in contrast with the hypothesis that the strong interaction occurring between the SOMO and the vacant *d* orbitals (26) is the driving force to bridging. On the contrary, the unexpectedly low β-proton splittings are due to the high electronegativity of the oxygen atom (19).

The influence of the shape of the rotational potential on the magnitude of rotationally averaged values of $a_{H\beta}$ was also investigated. The lack of correlation between the β-proton splittings and the group electronegativity of substituents containing second-row heteroatoms in substituted 1,1-diphenylethyl radicals was explained in terms of deviation of the energy minima from the eclipsed conformation (21).

The stereochemical control exerted by third- and higher-row elements in free-radical reactions was also explained with a dynamic asymmetric bridging (15).
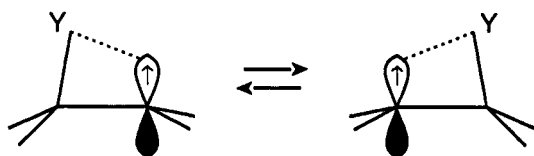

Fig. 7 Shuttle motion between two asymmetric bridged structures.

In the model shown in Fig. 7 the substituent is envisaged to oscillate rapidly between the two carbon atoms. UMP2/DZ+BF calculations showed that the shuttle motion is less favoured with respect to the rotoinversion motion about the C_α-C_β bond, resulting in a likely process only for the chlorine atom (21). For the fluorine atom, a large barrier to shuttling and a nearly free rotation about the C_α-C_β bond make

the shuttle motion highly unlikely. For others substituents exerting stereochemical control (SiR$_3$, SR) the shuttle motion is impossible because the symmetric bridged structure is computed to dissociate into ethylene plus Y$^\bullet$. Hence, the stereochemical control can be explained with the change in the rotoinversion energy surface on going from second- to third-row elements.

CONCLUSIONS

Ab initio calculations have shown that the electronic effect of the α- and β-substituents influences largely the magnitude of the hfs constants in localized organic and organometallic radicals. Thus, structural information previously obtained from experimental hfs constants without taking into account this factor have been demonstrate to be incorrect. In particular, it has been shown that the geometry at the radical center can not be reliably estimated from the experimental hfs constant of the α-nucleus and that the conformation of β-substituents can be obtained from the β-proton splittings only if the electronic effect of the β-substituent is taken into account by adding a third term (the second order sine term in a Fourier series expansion) to the generally used Heller-McConnell equation.

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