Long-range Proton Hyperfine Couplings in Radical Cations of Carbonyl Compounds

Larry D. Snow and Ffrancon Williams*
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996–1600, U.S.A.

Large non-aldehydic ^{1}H hyperfine couplings in the radical cations of four carbonyl compounds are assigned to long-range hyperfine interactions relayed through a *trans* (W-plan) arrangement of C–C and C–H σ bonds; for example, the two strongly coupled hydrogens in the cyclohexanone radical cation are identified by deuterium substitution as the 'δ' equatorial pair at C-3 and C-5 rather than the 'γ' equatorial pair at C-2 and C-6 assigned previously.

The availability of a simple method for the generation of positive ions by γ-irradiation of dilute solutions of the parent molecules in Freon matrices has sparked off considerable interest in the structure of novel radical cations as revealed

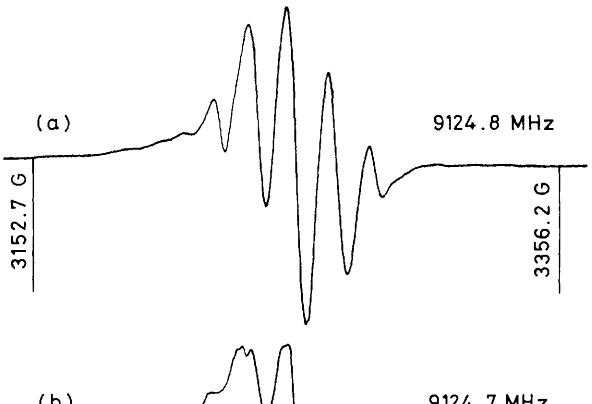
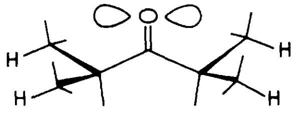


Figure 1. First-derivative e.s.r. spectra of the 2,4-dimethylpentan-3-one radical cation in CFCl$_3$ (a) at 88 K, (b) at 155 K, and (c) on subsequent cooling to 103 K. The cation was generated by γ-irradiation of a 1 mol % solution of the parent compound at 77 K for a dose of 0.5 Mrad.

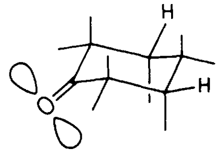
by solid-state e.s.r. spectroscopy.[1–4] Of particular significance is the finding that the SOMOs of radical cations derived from saturated molecules such as alkanes[2–4] and acetals[5,6] are delocalized through multicentre orbitals. In the case of n-alkane cations,[3,4] the σ SOMO is spread out along the C–C bonds so it is not surprising that the strongly coupled hydrogens are those which lie in the plane containing the extended carbon chain. Here we report that in the radical cations of carbonyl compounds where the σ SOMO is nominally confined to the in-plane oxygen p-orbital of the $>$C=O group, large ^{1}H hyperfine couplings can also arise *via* long-range interactions. While the effect is similar to that previously described for the bicyclic semidione radicals,[7] the magnitude of the couplings is very much larger in the present case.

Whereas the e.s.r. spectrum of the acetone radical cation shows no resolvable hyperfine splitting from the methyl hydrogens,[8,9] unusually large ^{1}H hyperfine interactions are observed in the e.s.r. spectra of the 2,4-dimethylpentan-3-one and cyclohexanone radical cations, as described below. These contrasting results immediately raise the possibility that the strongly coupled protons in these cations are remote from the carbonyl group.



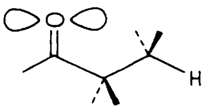
(1)

A(4H) = 15.2G



(2)

A(2H) = 27.5 G



(3)

A(1H) = 12.5 G

For the 2,4-dimethylpentan-3-one radical cation, a strong hyperfine interaction with four equivalent ^{1}H nuclei is evident from the well resolved 1 : 4 : 6 : 4 : 1 pattern in the e.s.r. spectrum taken at 88 K (Figure 1a). Further, the reversible temperature dependence of the spectrum as revealed by the additional spectra (b) and (c) in Figure 1 provides strong evidence that this hyperfine interaction is linked to a preferred conformation of the cation which is present at low temperature (*ca.* 100 K) but not at 150 K, stringent conformational requirements being expected for long-range hyperfine interactions in non-rigid radicals.[10,11] Accordingly, it is proposed that the cation adopts the C_{2v} structure (**1**) at low temperatures wherein the four strongly coupled hydrogens, one from each of the locked methyl groups, occupy the *trans*-positions relative to the C(2)–C(3) or C(4)–C(3) bonds, this arrangement serving to optimise the long-range interaction.[7,10,11]

Unequivocal evidence for the long-range character of the large proton hyperfine couplings in ketone cations also comes from studies of the rigid cyclohexanone system. In previous work on the cyclohexanone cation,[8,12] the two strongly coupled protons were assigned to the 'γ' equatorial pair at C-2 and C-6, the rationale being that these protons are held close to the plane containing the half-occupied p orbital on oxygen. Unfortunately this assignment, which corresponds to an anti-W arrangement,[11] was largely predicated on an interpretation of the e.s.r. spectrum of the acetaldehyde radical cation[8] that has since been shown to be erroneous.[9] That the two interacting protons are not located at C-2 and C-6 is conclusively demonstrated by results showing that the e.s.r. spectra of the non-deuteriated cyclohexanone and 2,2,6,6-tetradeuteriocyclohexanone radical cations are identical except for the slightly narrower lines from the partially deuteriated species. Accordingly, the two strongly coupled protons must surely reside on C-3 and C-5 [structure (**2**)] and the assignment to the equatorial pair accords with previous empirical and theoretical findings.[7,10,11] In fact, the hyperfine coupling of 27.5 G for these protons (Table 1) is the largest ever reported for such long-range interactions[7] and clearly corresponds to a nearly perfect W-plan arrangement[7,11] in a rigid system, as depicted in structure (2).

The e.s.r. parameters for the propionaldehyde and isobutyraldehyde radical cations are also listed in Table 1, hyperfine couplings to one and two hydrogens, respectively, being observed in addition to coupling from the aldehydic

Table 1. E.s.r. parameters for radical cations of ketones and aldehydes in solid $CFCl_3$ solution.

Radical $R^1R^2C{=}O^{+\bullet}$		T/K	g-Factor[a]	Hyperfine splittings/G[a]
R^1	R^2			
Me	Me	88	2.0030	—
Pr^i	Pr^i	88	2.0033	15.2 ($4H_\delta$)[b]
$-[CH_2]_5-$		88	2.0032	27.5 ($2H_\delta$)[c]
$-CD_2[CH_2]_3CD_2-$		88	2.0032	27.5 ($2H_\delta$)[c]
Me	H	130	2.0054[d]	136.2 ($1H_\beta$)[d]
$MeCH_2$	H	120[e]	2.0048	135.1 ($1H_\beta$), 12.5 ($1H_\delta$)
$MeCD_2$	H	120[e]	2.0048	135.3 ($1H_\beta$), 12.5 ($1H_\delta$)
Pr^i	H	120	2.0044	120.3 ($1H_\beta$), 20.4 ($2H_\delta$)

[a] g-Factors and hyperfine splittings are considered accurate to ±0.0005 and ±0.5 G, respectively. [b] The binomial quintet structure was retained to 145 K. [c] The spectra were independent of temperature between 88 and 155 K. [d] Data taken from ref. 9. [e] At lower temperatures the spectra were distorted by a matrix superhyperfine interaction similar to that described for the acetaldehyde radical cation in ref. 9.

hydrogen. Long-range coupling to two equivalent hydrogens from symmetrically disposed methyl groups in the isobutyraldehyde cation is clearly expected on the basis of the previous results for the 2,4-dimethylpentan-3-one cation. Moreover, the coupling to the single non-aldehydic hydrogen in the low-temperature spectrum of the propionaldehyde cation can definitely be assigned to a methyl hydrogen on the basis of the almost identical e.s.r. spectra derived from [2,2-$^2H_2$]propionaldehyde and the non-deuteriated compound. Interestingly, the preferred conformation of the methyl group suggested by our results for $CH_3CH_2CHO^+$ and shown in structure (**3**), in which the four heavy atoms and the strongly coupled methyl hydrogen are coplanar, also corresponds to the equilibrium conformation of the more stable rotamer of the neutral molecule.[13]

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