Measurement of the ^{13}C Hyperfine Tensors for Cubyl and Related Bridgehead Radicals

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^{13}C hyperfine features have been detected by electron paramagnetic resonance (EPR) spectroscopy from a range of bridgehead radicals following γ-irradiation of the corresponding bromides at 77 K. For cubyl and its 4-methoxycarbonyl derivative, both parallel and perpendicular components of the ^{13}C tensor were resolved, but only the parallel components could be detected for the 4-bromo derivative. The full ^{13}C tensors were also obtained for bicyclo[2.2.1]heptyl and tricyclo[3.1.1.0^{3,6}]heptyl radicals, but for bicyclo[2.2.1]hexyl, bicyclo[2.2.2]octyl and bicyclo[1.1.1]pentyl radicals only the parallel components were apparent, the perpendicular regions being obscured by other signals.

A linear correlation is found between $A_{\parallel}$ and the one-bond C—H ($^1J_{C-H}$) coupling in the nuclear magnetic resonance (NMR) spectra of the parent bridgehead alkanes and is used in the estimation of isotropic coupling constants for the bridgehead radicals, even in those cases where $A_{\perp}$ is unknown.

While the configurations of unconstrained alkyl radicals are known to execute out-of-plane vibrations that may be viewed as energetically very shallow inversions about an essentially planar structure, all available evidence suggests that strained bridgehead radicals are forced into a bent geometry at the radical centre.[1] In accord with theoretical calculations, the proton hyperfine coupling constants (hfcc) for these (σ) species take appreciable 'long-range' values,[1] but for positions β to the unpaired electron orbital, where direct overlap with the C–H bond is possible, they are reduced in magnitude relative to those expected from the unconstrained analogues. This effect is most clearly seen in the case of the cubyl radical (**II**) where, although
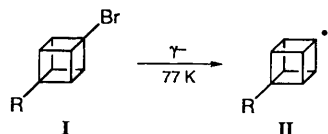
the dihedral angles between the p-type orbital at the 'radical-bearing' carbon atom and the three β-C–H bonds are zero, so that these are fully aligned with the density axis of the orbital giving maximum overlap, the coupling is only 12.4 G (ca. 54 G would be expected for an effectively planar radical).[2]

The most direct evidence for the configuration of a carbon-centred radical is provided by the ^{13}C hyperfine tensor, as measured in a solid environment, because 2s and 2p orbital populations may be estimated from the derived isotropic and anisotropic coupling constants, leading to a further estimation of the average bond angle, at least within the concept of 'complete orbital following'.[3] In the present study, we have succeeded in the detection of ^{13}C hyperfine features for a number of bridgehead radicals, including cubyl and some of its derivatives: the structural significance of which is elaborated in the following.

Results

Both parallel and perpendicular components were detected for cubyl radicals (**II**), R=H, following γ-irradiation of cubyl bromide frozen at 77 K [Fig. 1(a)], and similarly for the 4-

methoxycarbonyl derivative, (**I**) R=MeO$_2$C [Fig. 1(b)]. With 1,4-dibromocubane, (**I**) R=Br, only the parallel features were observed [Fig. 1(c)], since the expected perpendicular regions were obscured by signals from other radicals, but, as is clear from the data in Table 1, there is good accord between the parallel couplings for all three cubyl radicals, and the full ^{13}C tensor components for the first two show a reassuring similarity. The parallel features are very broad for 4-bromocubyl radicals, which is probably a consequence of anisotropic effects stemming from spin density at the bromine atom. The procedure was also appropriate to the formation of the bicyclo[2.2.1]heptyl (**IV**) (Fig. 2) and tricyclo[3.1.1.0^{3,6}]heptyl (**V**) (Fig. 3) radicals from which the full parallel and perpendicular ^{13}C components were similarly detected. In all other cases (**VI–VIII**), only the parallel features were resolved, because the perpendicular regions were obscured by signals from other radicals, or by the 'tail' from the bridgehead radical containing non-magnetic carbon nuclei. The data are displayed in Table 1 along with that for the 1-adamantyl radical (**III**) reported by Mishra and Symons.[4]

Correlations between EPR and NMR Data.—It was first pointed out by Dixon[5] that there should be correlation between EPR isotropic coupling constants in a radical R˙ and NMR isotropic coupling constants in the corresponding molecule RH, since both should be dominated by the Fermi contact interaction. He further suggested that if the configuration of the two 'fragments' (R) were similar in both cases, then a constant ratio of all the couplings (EPR–NMR) would be obtained. He applied this principle to vinyl radicals, but found only a moderately constant ratio: the reason being that vinyl radicals are appreciably less bent than their corresponding ethenes,[6] and this change in configuration influences couplings in different positions by different amounts.

However, it has been shown that, for a given series of compounds, when one coupling is considered, then good linear correlations are obtained for a series of methanes,[7] silanes[8,9] phosphines[10] and aldehydes[11] and the corresponding radicals formed by loss of an H˙ atom. As we discuss later, these relationships hold despite basic structural changes which cause radicals always to take configurations with larger bond angles.
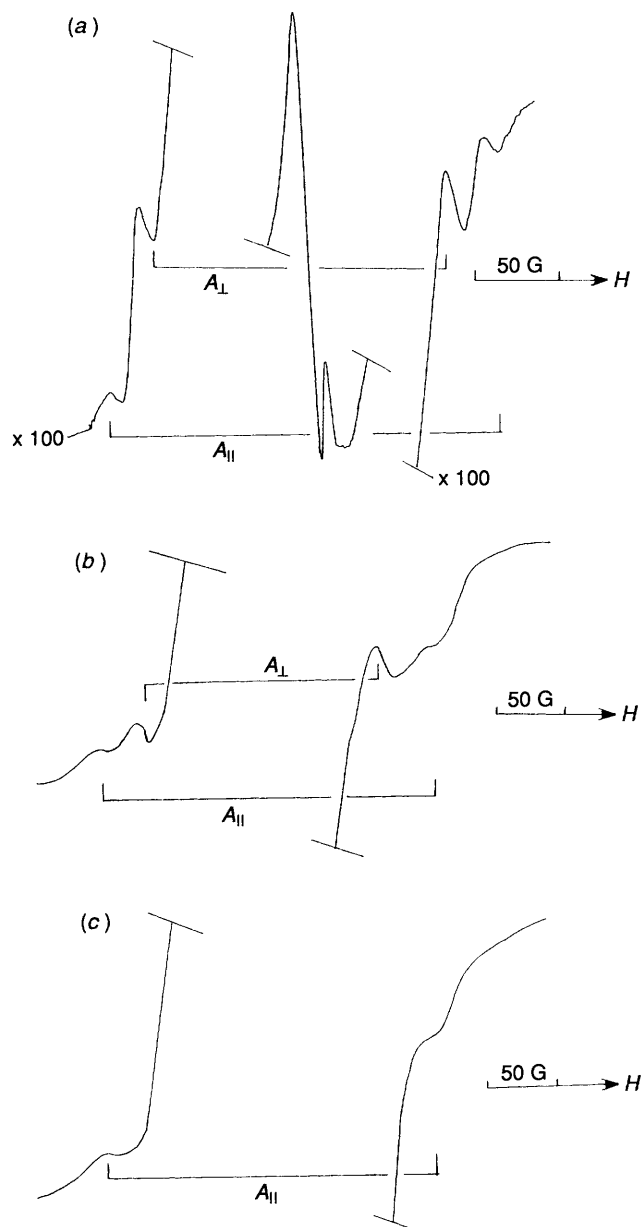
Fig. 1 ^{13}C hyperfine features from cubyl radicals, observed by EPR following γ-radiolysis of the solid cubyl bromide, both at 77 K. (a) Cubyl, (b) 4-methoxycarbonylcubyl, (c) 4-bromocubyl
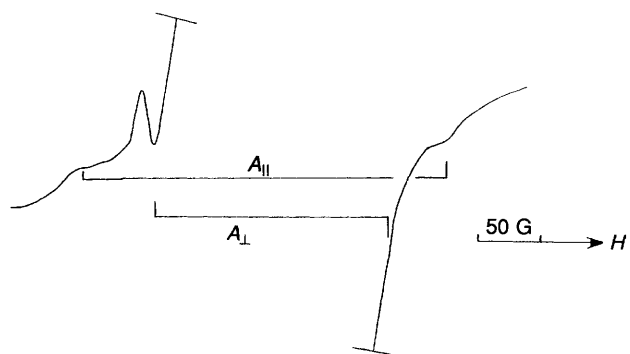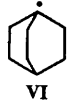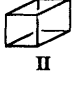

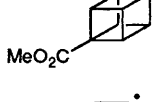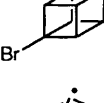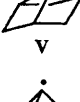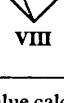Fig. 2 ^{13}C hyperfine features from bicyclo[2.2.1]heptyl radicals, recorded at 77 K, following γ-radiolysis of 1-bromobicyclo[2.2.1]heptane at 77 K

These correlations are always of the form of eqn. (1), and for

$$a = mJ + C \qquad (1)$$

Table 1 ^{13}C hyperfine data (G) and orbital populations for bridgehead radicals

Radical	$A_{\parallel}$	$A_{\perp}$	a	a^a	ρ_{2s}	ρ_{2p}
III[b]	179	110	133	132	0.12	0.70
VI	190	—	—	143		
IV	198	124	149	151	0.13	0.74
VII	220	—	—	174		
II	231	164	186	185	0.17	0.68
MeO$_2$C (bridgehead)	237	168	191	191	0.17	0.70
Br (bridgehead)	240	—	—	194		
V	251	181	204	205	0.18	0.71
VIII	268	—	—	223		

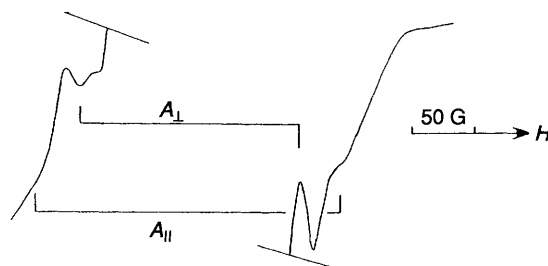^{a} a value calculated from eqn. (6). ^{b} Ref. 4.

Fig. 3 ^{13}C hyperfine features from tricyclo[3.1.1.0$^{3.6}$] heptyl radicals recorded at 77 K following γ-radiolysis of the corresponding bromide at 77 K

the four bridgehead radicals, II–V, a regression equation [eqn. (2)] is obtained, where $^1J_{C-H}$ is in Hz, $A_{\parallel}$ in G and M is a

$$a(^{13}C) = 2.73^1 J_{C-H} - 230.4; r = 0.993 \qquad (2)$$

constant. This is in accord with previous studies on isotropic coupling data. Surprisingly, however, a good straight line (Fig. 4) could be plotted between our parallel bridgehead coupling constants, for which seven points are available, and the isotropic $^1J_{C-H}$ coupling constants for the bridgehead alkanes[12-14] yielding eqn. (3).
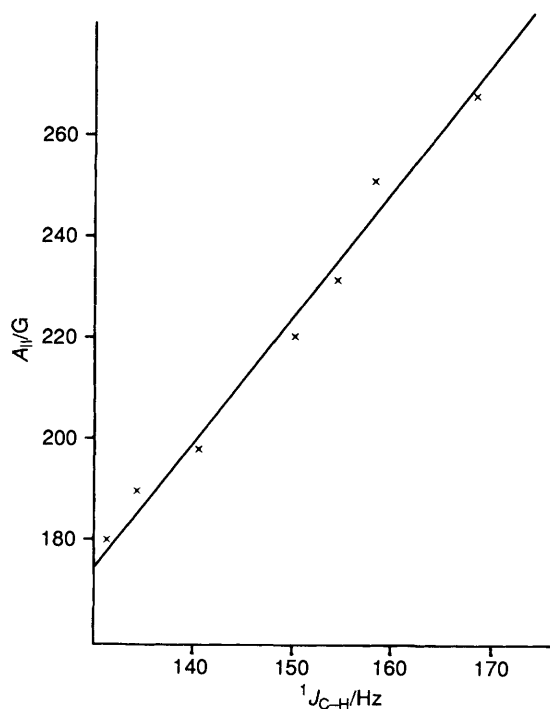
Fig. 4 Plot of $A_{\parallel}$ couplings for bridgehead radicals $vs.$ $^{1}J_{\text{C-H}}$ couplings in the parent bridgehead alkanes

$$A_{\parallel} = 2.48\ ^{1}J_{\text{C-H}} - 147.6;\ r = 0.995 \qquad (3)$$

Physical Significance of Eqn. (3) and Derivation of Isotropic ^{13}C *Couplings.*—To understand the meaning of eqn. (3), we need to consider eqn. (4), where $2B$ is the anisotropic

$$A_{\parallel} = a + 2B \qquad (4)$$

contribution to the coupling, and to rewrite this as eqn. (5),

$$A_{\parallel} = mJ + C + 2B \qquad (5)$$

using the definition for a in eqn. (1). From eqn. (5) it is clear that the term $(C + 2B)$ is constant $[-147.6, \text{from eqn. (3)}]$. Since $2B$ is a measure of the 2p carbon spin population, it is this population that is effectively constant throughout the series. While at first surprising, a consideration of the variation in the 2s population of the parent hydrocarbons (0.08: see later section) would lead to an apparent change in $2B$ of only $ca.$ 5 G in the radicals, assuming simple hybridisation arguments, and that a similar variation occurs in the radicals. Therefore, the isotropic term is dominant and overrides this small change in $2B$ through the series.

A plot of a against $A_{\parallel}$ leads to eqn. (6) from which isotropic couplings may be estimated in cases where $A_{\parallel}$ is determined and not the full tensor. A full set of a values was calculated using eqn. (6) and is included in Table 1. It is very reassuring to see

$$a = 1.024A_{\parallel} - 51.66;\ r = 0.999 \qquad (6)$$

that the agreement is to within 1–2 G of a values as calculated from the full ^{13}C tensor components in the four cases where these were available, and so we believe this approach to be valid. If we take the full set of (calculated) a values and plot them against the $^{1}J_{\text{C-H}}$ couplings, a good correlation is obtained [eqn. (7)], which further convinces us that we have a set of

$$a = 2.53\ ^{1}J_{\text{C-H}} - 201.89;\ r = 0.991 \qquad (7)$$

reasonably self-consistent data.

Table 2 Bond angles derived for bridgehead radicals[a]

Radical	ρ_{2p}	ρ_{2s}[b]	$\rho_{p/s}$	ρ_{p+s}	θ/deg
III	0.712	0.119	5.98	0.831	113.6
VI	0.712	0.129	5.52	0.841	113.2
IV	0.712	0.136	5.24	0.848	112.9
VII	0.697	0.185	4.44	0.854	111.9
II, R=H	0.697	0.167	4.18	0.864	111.6
II, R=MeO$_2$C	0.697	0.172	4.05	0.869	111.4
II, R=Br	0.697	0.175	3.98	0.872	111.3
V	0.697	0.185	3.77	0.882	111.0
VIII	0.682	0.201	3.39	0.883	110.3

[a] Calculated using the equation derived by Coulson[18] for C_{3v} symmetry: $\theta = \cos^{-1}\{[1.5/2(\text{p/s}) + 3] - 0.5\};$ [b] for consistency, the 2s populations are all estimated from the a values obtained from eqn. (6). The experimental $A_{\parallel}$ values are used throughout.

Bond Angles.—By processing the hyperfine data in the usual way, we find that 86% of the spin is localised at the central, bridgehead atom in cubyl (**II**) and, assuming complete orbital following ($i.e.$ that the nuclear coordinates follow the interorbital angles), we obtain C–C–C angles of $111.5 \pm 1°$ for this and the 4-methoxycarbonyl derivative. In Table 2 are displayed bond angle data thus derived from the estimated 2s and 2p orbital populations (ρ_{2p}) shown. For consistency, the a values from eqn. (6) have been used, along with the measured $A_{\parallel}$ data. It is apparent that all these bridgehead radicals possess strongly pyramidal carbon centres: approaching the tetrahedral angle for the highly strained bicyclo[1.1.1]pentyl system (**VIII**) (110.3°). It also appears that the total spin density at the central atom is in the range 83–88% for all cases, in accord with our previous arguments. It is clear that, for example, bond angles of 111.5° and 110.3° cannot be accommodated within the cage structures of cubyl (**II**) and bicyclo[1.1.1]pentyl (**VIII**) radicals without introducing gross additional strain. Our results provide therefore experimental evidence that the bonds of the radicals, and probably also the corresponding hydrocarbons, are appreciably 'bent'.

Comparison with the Parent Bridgehead Hydrocarbons.—The $^{1}J_{\text{C-H}}$ coupling has been used[15] as a means for assessing the contribution of the carbon 2s orbital to the bonding in the C–H unit, by means of eqn. (8), where the scaling factor (corresponding to a 100% 2s participation) has been estimated from the coupling of 125 Hz in methane, with sp^3 hybridisation. By
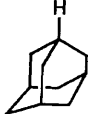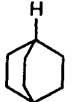
$$\rho_{2s} = {}^{1}J_{\text{C-H}}/500 \qquad (8)$$

means of eqn. (8), the 2s participation listed in Table 3 may be deduced for the parent bridgehead hydrocarbons. Comparison with the data in Table 2 for the corresponding radicals shows an essentially constant fall of 0.14 on going from the hydrocarbon to the radical, and so, while the radical centres remain pyramidal, as noted earlier, there is an appreciable structural relaxation that occurs to flatten the bridgehead 'fragment' R$^{\bullet}$ on the (hypothetical) cleavage of the R—H bond in the bridgehead hydrocarbon.

It is precisely this relaxation that gives rise to the constant (C) in correlation equations of the general type of eqn. (1), and which is therefore always negative in sign, since radicals always expand their bond angles from those in the parent hydrides, partly because of reduced steric effects but also because less s-electron density is attracted into the fourth orbital which is no longer involved in binding a fourth atom (substituent). Other views of this situation have been voiced in molecular orbital terms.[16]

The constant m in eqn. (1) may be taken as the ratio of the contributions for 100% occupancy of s-orbitals in the radical and in the parent hydride. Thus we would predict that unit

Table 3 $^1J_{C-H}$ coupling constants (Hz) measured for bridgehead alkanes,[12-14] along with derived 2s populations at carbon in the C–H bonding orbital

Alkane	$^1J_{C-H}$	ρ_{2s}[a]
	130	0.26
	134.3	0.27
	140.1	0.28
	150.5	0.30
	153.8	0.31
	157.9	0.32
	167.8	0.34

[a] Calculated using eqn. (8).

occupancy of the 2s orbital on carbon would be 500 × 2.53 = 1265 G. Reassuringly, this is fairly close to the value of 1110 G[17] with which we have estimated 2s orbital populations in Tables 1 and 2. Taking C from eqn. (7) leads to 201.89/1265 = 0.16 for the drop in 2s character which is close to that (0.14) deduced above. The essential feature, therefore, of the formation of bridgehead radicals from their corresponding hydrocarbons is that the full decrease in 2s character of 22–25% found for unconstrained hydrocarbons (*i.e.* CH$_4$ ——→ CH$_3$·) does not

occur, as a consequence of geometries which are too strained to permit this.

Experimental

In each case, the bridgehead bromide was degassed using standard freeze–pump–thaw cycles and was then sealed into a silica EPR tube. The samples were cooled to 77 K and were exposed to γ-radiation from a ^{60}Co source to a nominal dose of 1 Mrad. The EPR spectra were recorded, also at 77 K, using a Varian E9 spectrometer. In some instances, the resolution of the ^{13}C features was improved by annealing the sample above 77 K, simply by pouring the liquid-nitrogen coolant from the insert Dewar and allowing warming, and then recooling to 77 K for the final measurement.

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