Cubyl and 4-Fluorocubyl Radicals

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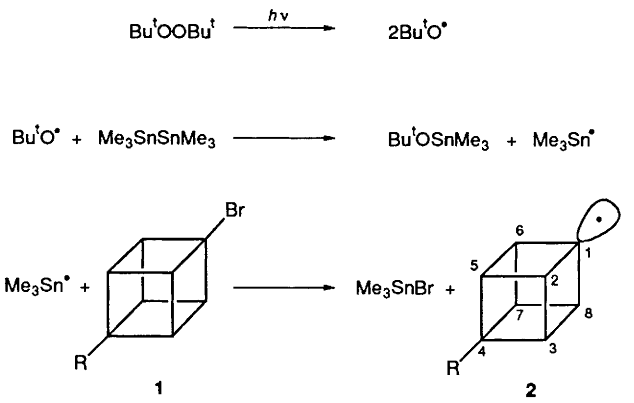
The ESR spectra of cubyl and 4-fluorocubyl radicals were observed in solution; they indicated that hyperconjugation was slight, but that significant spin density reaches C(3) and C(4).

The cubane molecule is a unique, highly strained structure, in which the geometry of each carbon atom is far removed from the ideal tetrahedral configuration. Several unusual effects have been postulated as a result of this novel structure. For example, hyperconjugation in the cubyl cation or radical is predicted to be minor because it can only occur *via* high-energy cubene-like structures.[1,2] It has also been suggested that substituents as far away as C(4) can have a major effect on the rates of solvolyses of cubyl trifluoromethanesulphonates.[1,3] Evidence that cubane-1,4-diyl has the singlet electronic configuration[4–6] also indicates that substantial long-range through-bond interactions operate.

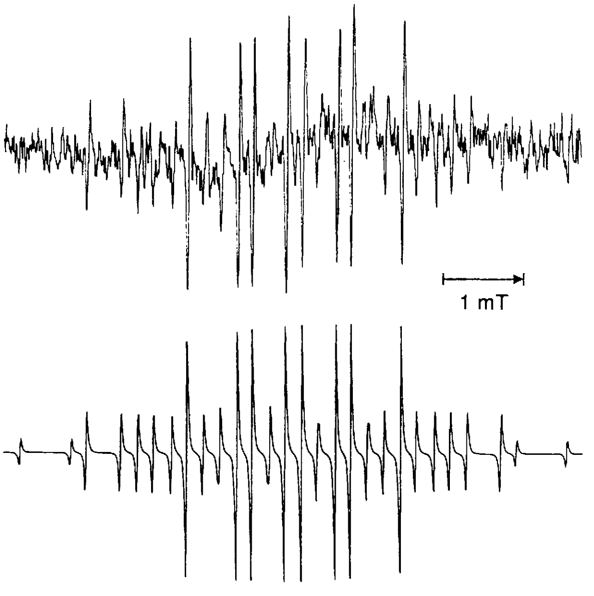
It is obviously desirable to have direct spectroscopic evidence for these effects, but attempts to observe the cubyl cation by low temperature NMR spectroscopy in various superionising media were unsuccessful.[1,3] The cubane radical cation $C_8H_8{}^{\cdot +}$ has been observed by ESR spectroscopy,[7] but the symmetry of this species rules it out as a probe of the effects described above. ESR spectroscopy is a particularly useful technique for studying substituent effects because it reveals the distribution of unpaired spin and hence the nature of the frontier orbital. Our objective, therefore, was to observe cubyl radicals **2** using this technique. Radicals **2** will be strongly pyramidal with high s-character and are expected to be highly reactive. They are known to be intermediates in several reactions,[8–13] and thus it seemed that spectroscopic detection might be possible.

In view of the success of hydride reductions of bromocubanes[9–12] we sought first to observe cubyl radicals by generating them in the cavity of the ESR spectrometer by reaction of photochemically produced trimethyltin or triethylsilyl radicals with cubyl bromides (Scheme 1).



a; R = H, b; R = F

Scheme 1



Scheme 2

Bromocubane **1a** was prepared as described previously[11] and 4-fluorobromocubane **1b** was made by fluoro-deiodination of methyl-4-iodocubanecarboxylate, followed by decarboxylative bromination of the 4-fluorocubanecarboxylic acid, using the Barton method. No ESR signals attributable to **2a** were obtained in the temperature range 170 to 240 K, in cyclopropane or t-butylbenzene, with the ditin initiator system. However, when triethylsilane was used instead, the spectrum shown in Fig. 1 was observed. This spectrum analysed for two different quartet and a doublet hyperfine splitting (HFS); the values in Table 1 led to the simulated spectrum in the lower figure and hence we attributed it to radical **2a**. The spectrum was detectable for only a few minutes and could not be observed above *ca.* 190 K. The 4-fluorocubyl radical **2b** was observed, accompanied by a second unidentified radical, under similar conditions at low temperatures; the HFS values are in Table 1.

It was shown recently that t-butyoxyl radicals will directly substitute the cubane skeleton by cleavage of the carbon–hydrogen bonds.[13] When a mixture of cubane[14] and di-t-butyl peroxide in cyclopropane was photolysed in the ESR cavity at 150 K the *same* spectrum as above was obtained accompanied by that of cyclopropyl radicals (Scheme 2). This confirms that the species under observation is radical **2a**. In this system cubyl was detectable up to 220 K. Cubane was sparingly soluble in cyclopropane at these temperatures; thus, the fact that cubyl and cyclopropyl radicals were observed in comparable concentrations indicates that the bridgehead hydrogens of cubane are actually abstracted more easily than the hydrogens of cyclopropane. Attempts to quantify the ease of hydrogen abstraction from cubane were frustrated by the poor, short-lived spectra in other solvent systems. Our results establish, however, that the bridgehead hydrogens in cubane are quite reactive to homolytic cleavage, probably of the same order as primary hydrogens in alkanes; this agrees with a previous study of the polyiodination of cubane using t-butyl hypoiodite.[13]

Table 1 ESR parameters of cubyl and 4-fluorocubyl radicals in solution at 160 K[a]

2, R	*g*-factor	Nuclei	Exptl. HFS/mT[b]	INDO[c] HFS/mT	AM1[d] ρ(H, 1s)
H	2.0028	2-, 6-, 8-H	0.82	0.73	0.0015
		3-, 5-, 7-H	1.24	0.85	0.0030
		4-H	0.63	0.91	0.0040
F	2.0028	2-, 6-, 8-H	0.62	0.61	
		3-, 5-, 7-H	1.08	0.70	
		4-F	2.91	4.95	

[a] In cyclopropane solution. [b] Tentative assignments; see text. [c] Geometries from MINDO/3 calculations; $<S^2>$ = 0.7581 and 0.7527 for R = H, F respectively. [d] Hydrogen 1s spin densities from AM1 calculations, UHF version

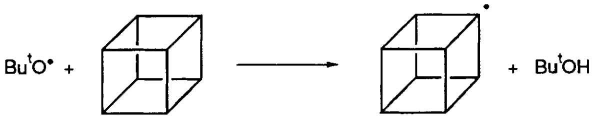
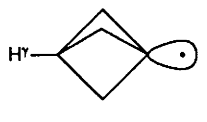


Fig. 1 9.3 GHz ESR spectrum of cubyl radicals, **2a**, in cyclopropane solution at 150 K: upper spectrum, experimental; lower spectrum, computer simulation



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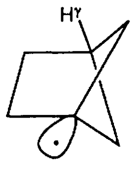

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We tentatively assign the smaller quartet HFS to Hβ (*i.e.* 2-, 6-, 8-H) and the larger to Hγ (*i.e.* 3-, 5-, 7-H) because semi-empirical SCF MO calculations of both INDO and AM1 types supported this (Table 1) and because this correlates with the ^{13}C NMR data which show a larger $^3J_{CC}$ than $^2J_{CC}$ in both cubane[^{13}C]carboxylic acid and [^{13}C]methylcubane.[15] In any case the Hβ HFS is exceptionally small for a radical in which the dihedral angle between the semi-occupied orbital at C(1) and the β-hydrogens is formally zero. This confirms that hyperconjugative delocalisation of spin is quite small in cubyl radicals. The Hγ HFS values of **2a** and **2b** are exceptionally large in comparison with alkyl radicals in general, or with bicyclo[2.2.2]octan-1-yl or norbornan-1-yl radicals in particular. However, they are smaller than the huge Hγ HFS of the highly strained bicyclo[1.1.1]pentan-1-yl **3** (*i.e.* 6.96 mT)[16] or bicyclo[2.1.1]hexan-1-yl **4**.[17]

In the cubyl radical the distance from C(1) to C(3) is calculated to be *ca.* 2.16 Å by the MINDO/3 method. This is significantly longer than the corresponding distance of *ca.* 1.75 Å in **3**. Thus, the through-space (TS) effect will be less in cubyl. Through-bond (TB) and TS effects will reinforce one another for γ-hydrogens[16,18] but in **2** the orientation of the orbitals diverges from the ideal all-*trans* (W-plan) obtaining in **3**. Thus, both TS and TB effects are expected to be less in cubyl and this explains the fact that *a*(Hγ) is smaller than in **3**. However, the fact that *a*(Hγ) in **2** is still much larger than 'normal' suggests that both TS and TB effects are still significant.

The 4-H HFS is one of the largest ever recorded for a δ-hydrogen; the same applies for the 4-F HFS in **2b**. The magnitudes of these splittings show rather clearly that the frontier orbitals of cubyl transmit spin density effectively throughout the whole skeleton. Thus, remote substituents at C(4) can substantially modify the electron density distribution in **2** and this will lead to significant substituent effects on the reactivity. The TS distance from C(1) to C(4) in **2** is calculated to be *ca.* 2.65 Å by the MINDO/3 method. Through-space overlap of orbitals on these two carbons will, therefore, be negligible and the large 4-H HFS is evidence of a substantial TB effect.

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