ESR OF FLUORENYL AND INDENYL: TWO NEUTRAL NON-ALTERNANT RADICALS

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ESR spectra have been obtained for the fluorenyl and indenyl radicals, and their isotropic proton hfcc have been compared with the predictions of semi-empirical MO calculations.

There have been several attempts to observe the ESR spectrum of fluorenyl(I) but the unsubstituted radical has apparently eluded detection [1]. Gas phase electron diffraction has been reported for indenyl(II) [2], but we are again unaware of any ESR spectrum. We have now obtained solution ESR spectra for both these neutral non-alternant radicals. Fluorenyl was generated by the reaction [3] of triethylsilyl radicals with fluorenyl bromide; indenyl was obtained by abstracting a hydrogen atom from indene with a *t*-butoxy radical. The isotropic proton hyperfine coupling constants for both I and II, checked by computer simulation, are given in table 1. Theoretical estimates calculated from π electron spin densities and the McConnell relationship, are also included for comparison. The UHF spin densities were taken from the work of Fjeldstad and Jensen [4] who attempted to optimise molecular geometries. The McLachlan results are for a regular geometry.

Both sets of calculations are in reasonable agreement with experiment and enable us to assign the hyperfine splittings for indenyl with some confidence. The values of a_3 and a_5 for fluorenyl are too close for the calculations to distinguish between them with any degree of certainty; similar reservations apply to a_4 and a_6 .

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Experimental and theoretical proton hyperfine coupling constants for fluorenyi and indenyi

	Position	Exptl.	Calculated ^{a)}		
			A	В	
	1	13.9	-12.3	-13.6	
\sim $\stackrel{6}{\sim}$	3	3.98	-2.77	-4.0	· · · · · · · ·
	4	0.91	0.47	1.82	•
	5	3.76	-2.97	-3.5	
<u>i</u> <u>i</u>	6	0.64	0.07	1.7	
	1	2.18	2.91	2.6	
$= \int_{a} \int_$	2	11.9	-10.21	-11.72	
¥ 2	4	2.18	-2.23	-1.05	
	5	1.47	-1.33	-0.57	and a second second Second second

a) A, calculated from McLachlan spin densities. B, calculated from UHF spin densities [4], Q = -25 G.

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It is of interest to compare the planar fluorenyl system with the isoelectronic diphenylmethyl radical which can adopt non-planar conformations. The coupling constants of diphenylmethyl are $a_{\rm H}^{\alpha} = 14.7$, $a_{\rm H}^{0} = 3.7$, $a_{\rm H}^{m} = 1.5$ and $a_{\rm H}^{p} = 4.2$ G [5]. The ratio of the α hydrogen splittings for diphenylmethyl and fluorenyl is 1.058 indicating slightly more electron delocalisation in fluorenyl but this is consistent with Hückel calculations on the planar structures which predict a spin density ratio of 1.087 for the α -position; McLachlan calculations predict 1.167. This suggests that any twisting of the aromatic rings in diphenylmethyl, which would tend to reduce electron delocalisation and increase $a_{\rm H}^{\alpha}$, is quite small.

References .

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