

ELECTRON SPIN RESONANCE SPECTRA FOR ADAMANTYL RADICALS IN THE SOLID STATE:
¹³C HYPERFINE COUPLING CONSTANTS.

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Recently, well resolved liquid-phase e.s.r. spectra for bridgehead adamantyl and bicyclo[2,2,2]octyl radicals have been presented¹ which establish their pyramidal character. Indeed, the proton hyperfine parameters agree remarkably well with those calculated by the INDO M.O. method, and differ markedly from those expected for planar radicals. In view of the controversy regarding the shapes of normal alkyl radicals² and the considerable weight placed upon the use of ¹³C coupling constants to establish "non-planarity", it is of interest to measure the ¹³C coupling constants for such bridgehead radicals.

Some years ago we attempted to obtain the 1-adamantyl radical by exposing adamantane and 1-bromoadamantane to ⁶⁰Co γ-rays at 77 K, but failed to obtain convincing evidence for its formation. The hydrocarbon gave an e.s.r. spectrum which was, in our view, characteristic of normal, planar radicals formed by loss of hydrogen from CH₂ groups, whilst the bromide gave a broad, flat-topped singlet, having only slight indication of structure and a width between points of maximum slope, ΔH_{ms} , of 35 ± 1 G. The latter, whilst probably being a property of the required radical, which we had expected to be formed by dissociative electron capture, could not be clearly identified.

However, when a liquid-phase spectrum became available,¹ we were able, with the aid of a Du Pont Curve Resolver, to estimate a value of 34 G for ΔH_{ms} for such radicals with broad component lines, which strongly suggested that the major species formed from the bromide was indeed the 1-adamantyl radical. This species should have ¹³C hyperfine tensor components sufficiently large to be clear of the wings of the central line, and we now

report that at high gain, broad parallel features are indeed clearly resolved. Definite inflections were also found on the rapidly rising wings in the expected perpendicular region, and $A_{\perp} (^{13}\text{C})$ was obtained therefrom, again using the Curve Resolver. Features for $\text{Br}_2^{\cdot -}$ radicals were also detected at about the same level of intensity.

It has been our experience that alkyl halides in perdeuterated methanol, CD_3OD , often give well resolved alkyl radical spectra, free of other species. In this case, after bleaching the trapped electrons with visible light, the same broad central line was obtained, and both parallel and perpendicular satellites of about the correct width and intensities were found at high gain. These were not formed from the pure solvent in the absence of the bromide. In this case, as expected, $\text{Br}_2^{\cdot -}$ ions were not formed.

Other solvents gave similar results (Table). In several cases, definite structure appeared in the parallel features which fitted well with a reconstruction based upon the liquid-phase data. These satellite lines were better resolved than the central line because of the invariable presence of other absorptions in the central spectral region.

An approximate estimate of the intensities expected for these parallel and perpendicular features relative to the central component agreed reasonably well with the experimental values. We conclude that these features are due to 1-adamantyl radicals containing bridgehead ^{13}C in natural abundance.

These results give $A_{\text{iso}} \approx 136.7$ G and $2B \approx 43.3$ G. These values, divided by the calculated atomic values,³ give ca. 12% $2s$ character and 66% $2p$ character for the orbital of the unpaired electron on carbon. This gives a $2p:2s$ ratio of 5.5 and a total spin-density of 78%, which seems reasonable for this radical. Although the experimental error for A_{\perp} is large, these results can certainly be taken as good confirmation of the previous conclusions¹ and show that relatively slight relaxation towards planarity has occurred, in marked contrast with comparable results for normal alkyl radicals, which are almost certainly planar or nearly so.³

It should be mentioned that Filby and Gunther⁴ have also recently reported the detection of 1-adamantyl radicals in adamantane irradiated at room temperature. However, their spectra are quite different from those of Krusic et al.¹ and the derived proton coupling constants in no way agree with our expectation for a non-planar radical such as 1-adamantyl, nor with the values calculated by Krusic et al.¹ It therefore seems probable that these results⁴ pertain to some more stable break-down product.

References

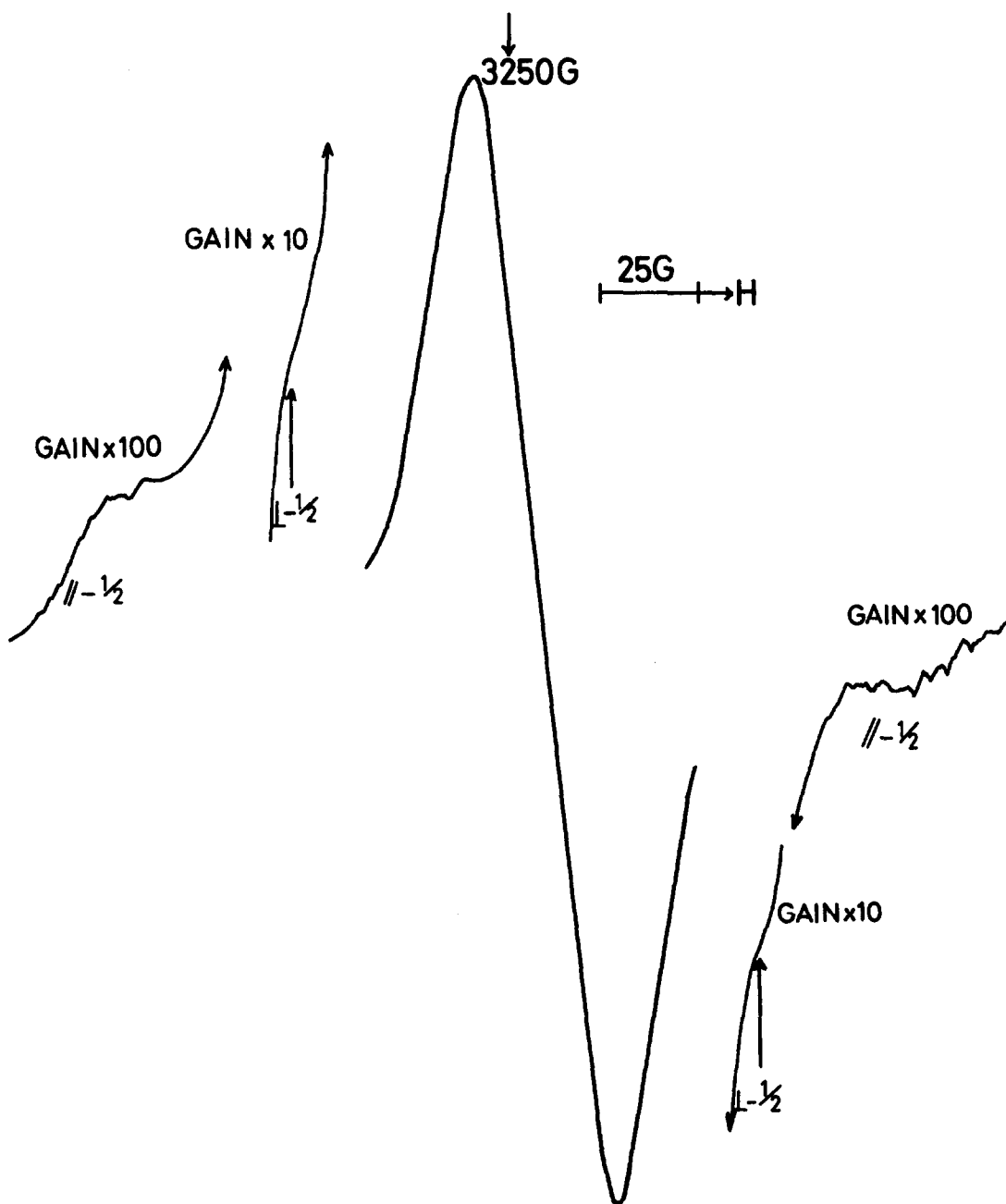
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Table

Carbon-13 Hyperfine Tensor Compounds Assigned to
1-Adamantyl Radicals in Various Media at 77 K

Medium	¹³ C Hyperfine Compounds (G)		Comments
	I(± 5)	II(± 5)	
CD ₃ OD ^a	115	180	Broad structureless components
CD ₃ CN	hidden	ca.182	Very weak, but signs of extra structure
CS ₂	hidden	180	Signs of proton structure
1-Bromoadamantane	ca.110	179	Definite extra structure in features.

^a After bleaching with visible light.



First derivative e.s.r. spectrum for γ -irradiated bromadamantane showing satellite lines at very high gain. The parallel features are reasonably well resolved, but the perpendicular features appear only as inflections on the rising part of the central line.