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THE E.S.R. SPECTRUM OF THE TETRA(1-ADAMANTYL)CYCLOBUTADIENE RADICAL CATION

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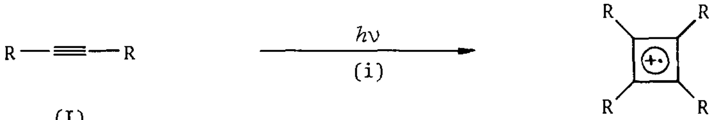
Abstract A revised interpretation is proposed for the ^{1}H and ^{13}C hyperfine coupling in the e.s.r. spectrum of the tetra-1-adamantylcyclobutadiene radical cation, and assumes that free rotation occurs about the 1-adamantyl bond.

For e.s.r. spectroscopic studies, tetra-t-alkylcyclobutadiene radical cations (II) can be generated by photolysing a solution of the corresponding di-t-alkylalkyne (I) and aluminium chloride in dichloromethane,[1,2] or of the alkyne alone in trifluoroacetic acid.[3]

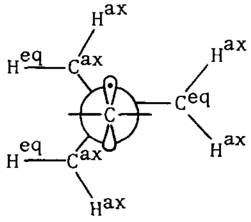


(I) (II) (1)

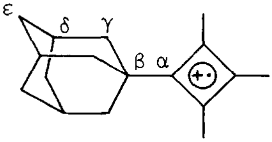
(i) = $AlCl_3/CH_2Cl_2$ or CF_3CO_2H

Broxterman, Hogeveen and Kingma have prepared the tetra-1-adamantylcyclobutadiene radical cation (II; R = 1-Ad) by the former of these two methods,[2] and have simulated the spectrum in terms of the hyperfine couplings a(16H) 0.288 G, a(8H) 0.144 G, $a(8\,^{13}C)$ 3.456 G, and a(ca. 3.6 ^{13}C) 10.9 G.

To assign these coupling constants, they made the interesting suggestion that rotation about the 1-adamantyl-ring bond is slow on the e.s.r. time scale so that the γ-hydrogen and the γ-carbon atoms are separated into sets which are pseudo-axial or equatorial with respect to the axis of the singly occupied p-orbital as shown in (III), and show large or small (or zero in the case of $C\gamma^{eq}$) coupling constants respectively. The value of $a(^{13}C)$ 10.9 G was assumed to be associated with the four Cα atoms; the labelling of atoms is shown in (IV).



(III)



(IV)

We also have been interested in the e.s.r. spectra of 1-adamantylcyclobutadiene radical cations,[4] and have used selective and complete deuterium labelling, and ENDOR spectroscopy, to determine the hyperfine coupling constants. In the case of the perdeuterio tetra-1-adamantylcyclobutadiene radical cation, the ^{13}C hyperfine coupling can be analysed in unprecedented detail. Our results confirm the values of the ^{1}H and ^{13}C hyperfine coupling constants reported in reference 2, but we propose an alternative assignment of these data.

By ENDOR and TRIPLE spectroscopy we obtained for (II; R = 1-Ad), the hyperfine coupling constants +0.28 G, and -0.14 G, in agreement with reference 2.

Introduction of deuterium at the three tertiary (δ) positions of each adamantyl group removes this larger coupling constant from the e.s.r. spectrum, and ENDOR spectroscopy then yields $a(^{1}H)$ 0.14 G, $a(^{2}H\gamma)$ 0.043 G [$\equiv a(^{1}H\gamma)$ 0.28 G]. We conclude that the spectrum should be analysed in terms of $a(24H\gamma)$ -0.14 G, $a(12H\delta)$ +0.28 G, and that the adamantyl groups are freely rotating.[5] A similar relative magnitude and sign of $a(H\gamma)$ and $a(H\delta)$ has been observed previously in other 1-adamantyl-substituted radicals.[6]

In highly symmetrical radicals with many carbon atoms, such as II (R = 1-Ad), the ^{13}C satellites constitute an important feature of the e.s.r. spectrum. If in a molecule there are n equivalent carbon atoms of one type, q of another, and r remaining carbon atoms, then the probability P of m of those n, and p of those q carbon atoms having ^{13}C nuclei (natural abundance 1.108%) is given by equation (2), where ${}_{n}C_{m} = n!/m!(n-m)!$.

$$P = (0.01108^{m} \times 0.98892^{n-m} \times {}_{n}C_{m}) \times (0.01108^{p} \times 0.98892^{q-p} \times {}_{p}C_{q}) \times 0.98892^{r} \qquad (2)$$

Thus in a $\cdot CH_3$ radical, the ^{13}C satellites constitute only 1.108% of the total spectral intensity, but in the tetra-1-adamantylcyclobutadiene radical cation, $C_{44}H_{60}^{+\bullet}$, 38.75% of the total intensity will in principle lie in the ^{13}C satellites,[7] and the high symmetry of the molecule causes this intensity to be concentrated into a few lines. Of course, satellites due to weak coupling to the more distant carbon atoms may be contained within the complex envelope of lines due to ^{1}H coupling,[8] but selective or complete deuteration of the adamantyl groups reduces the width of this envelope, so that the satellites (which are themselves made correspondingly sharper) may be revealed. Indeed, the probability of the radical (II, R = 1-Ad) containing two ^{13}C atoms is large enough (7.27%) for ^{13}C satellites of ^{13}C satellites to be observed, we believe for the first time.

The spectrum of $C_{44}{}^{2}H_{60}^{+\bullet}$ is shown in the Figure. The principal features are the central band with unresolved deuterium coupling, A, with large inner satellites B [$a(^{13}C)$ 3.08 G], and small outer satellites C, [$a(^{13}C)$ 10.76 G] each flanked by sub-satellites B' and C' characterised by the same coupling constant as B and signifying the presence of two ^{13}C atoms.

In $(CH_3CH_2)_4C_4^{+\bullet}$, the three ^{13}C hyperfine coupling constants (h.f.c.c.) are 3.72, 4.33, and 5.00 G, and the g factor is 2.0029.[1,9] As the bulk of the alkyl group is increased, the g factor drops (to 2.0022 in $Bu^{t}{}_{4}C_{4}^{+\bullet}$ and 2.00212 in $1\text{-}Ad_{4}C_{4}^{+\bullet}$), and ^{13}C satellites with an increased coupling constant can be observed if they are not obscured by the central manifold due to ^{1}H coupling.[1,3,8] These changes probably reflect the increasing distortion of the ring from planarity by the large substituents, so that some s character is introduced into the orbital containing the unpaired electron.[2,10] We therefore assume that the signals C should be ascribed to hyperfine coupling to one ^{13}C atom in the cyclobutadiene ring, i.e. $a(^{13}C\alpha)$ = 10.76 G.

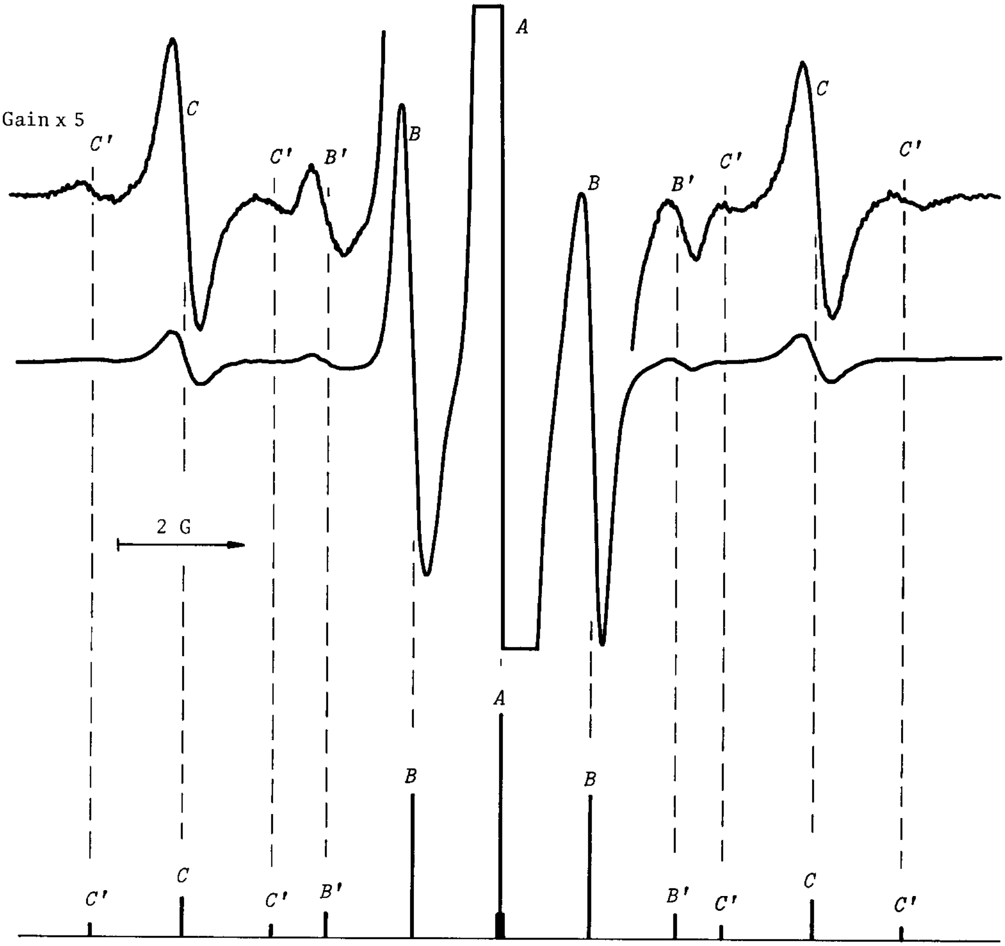


Figure. E.s.r. spectrum of the radical cation $d_{60}(1\text{-Ad}_4C_4)^{+\cdot}$ showing ^{13}C satellites. Top: observed spectrum in CH_2Cl_2 at -68 °C. Bottom: stick analysis of ^{13}C satellites.

Table. Calculated and observed relative signal intensities.

H.f.c.c. of ^{13}C atoms/C [a]					Calculated relative intensities			
α	β	γ or δ or ε			*C/C'*	*B'/C'*	*B/C*	*A/B*
10.76	3	3	3	0	7.24	3.38	7.00	6.56
10.76	0	3	3	0	8.75	2.87	6.00	7.64
10.76	3	3	0	0	14.16	1.88	4.00	11.53
10.76	0	3	0	0	19.64	1.38	3.00	15.46
					observed relative intensities			
					12.9	1.6	3.6 ± 0.2	13.0 ± 2.2

[a] 0 Signifies that the ^{13}C coupling is too small to be resolved from the central signal. 3 Signifies that there may be more than one unresolved signal, each with $a(^{13}C)$ = *ca.* 3 G.

The Table gives the relative intensities of the various signals in the spectrum calculated by equation (2), on the basis of various assumptions for the origin of the signals *B*. The intensities are compared with the experimental values obtained by measurement of the areas of the signals by numerical double integration.

Within the limited accuracy of the measurement of the areas of the signals, the experimental results correlate best with the model where $a(^{13}C\beta) = a(^{13}C$, one of γ or δ or $\varepsilon)$ = *ca.* 3 G, and $a(^{13}C$, two of γ or δ or $\varepsilon)$ = *ca.* 0 G, and in the light of the results for $(CH_3CH_2)_4C_4^{+\bullet}$, the most probable complete analysis of the spectrum appears to be $a(24H\gamma)$ = -0.14 G, $a(12H\delta)$ = +0.28 G, $a(^{13}C\alpha)$ = 10.76 G, $a(^{13}C\beta) = a(^{13}C\gamma)$ = *ca.* 3.0 G, and $a(^{13}C\delta)$ and $a(^{13}C\varepsilon) < 1.5$ G. Experiments with ^{13}C labelled compounds, and perhaps semi-empirical M.O. calculations, could be used to confirm this analysis.

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7. A similar principle of course governs the relative abundance of the M, M+1, and M+2 ions in mass spectrometry. For example, the mass spectrum of perdeuteriodi-1-adamantylethyne showed relative abundances of $M^{+\bullet}:(M+1)^{+\bullet}:(M+2)^{+\bullet} = 100.0:24.5:2.1$, whereas, by equation (2), the values are calculated to be 100.0:24.6:2.9.
8. These unrevealed strong satellites must be taken into account if satisfactory simulations of the spectra are to be obtained.
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