The Electron Spin Resonance Spectra of 1-Adamantylcyclobutadiene Radical Cations

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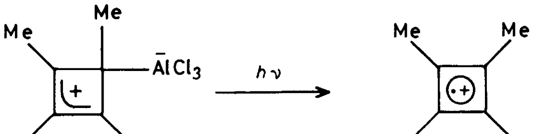
By photolysing solutions of the appropriate alkynes and aluminium chloride in dichloromethane, the following cyclobutadiene radical cations have been generated, and their e.s.r. spectra recorded: $\text{1-Ad}_4\text{C}_4^{+\cdot}$, $([3,5,8\text{-}^2\text{H}_3]\text{-1-Ad})_4\text{C}_4^{+\cdot}$, $([^2\text{H}_{15}]\text{-1-Ad})_4\text{C}_4^{+\cdot}$, *cis*- and *trans*-$\text{Me}_2\text{-1-Ad}_2\text{C}_4^{+\cdot}$, and *cis*-$\text{Et}_2\text{-1-Ad}_2\text{C}_4^{+\cdot}$ (1-Ad = 1-adamantyl). It is concluded that in $\text{1-Ad}_4\text{C}_4^{+\cdot}$, the bulky adamantyl groups cause the central ring to distort from planar, but that there is no restriction of rotation about the adamantyl–ring bond, and that proton hyperfine coupling to the δ-CH group is larger than to the γ-CH_2 groups. In the e.s.r. spectra of the deuteriated compounds, a variety of ^{13}C satellites can be distinguished, and they have been assigned using probability theory. The interpretation of the spectra is supported by UMINDO/3-INDO calculations. In *cis*-$\text{Me}_2\text{-1-Ad}_2\text{C}_4^{+\cdot}$, *a*(Me) is lower, and in *trans*-$\text{Me}_2\text{-1-Ad}_2\text{C}_4^{+\cdot}$ it is higher, than in $\text{Me}_4\text{C}_4^{+\cdot}$. The various steric and electronic effects, and solvent and counterion interactions, which may contribute to this ordering, are discussed.

The cyclobutadienes, as [4]annulenes, constitute a very important family of compounds, which have been intensively studied in recent years.[1] Unless the cyclobutadienes are sterically stabilised they are difficult to observe directly, and hence the ease with which the corresponding radical cations can be generated and studied by e.s.r. spectroscopy is attracting a lot of attention.[2–12]

Bock *et al.* showed that treatment of tetra-t-butylcyclobutadiene or tetra-t-butyltetrahedrane with aluminium chloride in dichloromethane gave the tetra-t-butylcyclobutadiene radical cation. Broxterman *et al.* published the first example of a much more general method [equation (1)],[4] and we simplifed the procedure further by establising the route shown in equation (2).[9]



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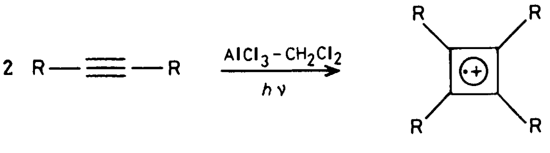

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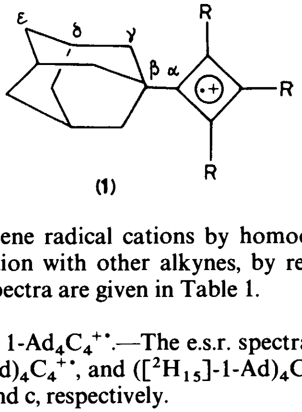
By reactions (1) and (2), a large number of cyclobutadiene radical cations have now been prepared and studied by e.s.r. spectroscopy, so that they are already the largest family of structurally related radical cations for which such spectroscopic systematics are available.[2–12]

We report here a study of some 1-adamantyl-substituted cyclobutadiene radical cations (1) prepared by reaction (2) [1-Ad = 1-adamantyl (2)]. Points of particular interest are the analysis of the ^{1}H and ^{13}C hyperfine coupling, and the steric and electronic effects of the 1-adamantyl groups on the cyclobutadiene ring system.

The alkynes 1-Ad-C≡C-1-Ad, $([3,5,8\text{-}^2\text{H}_3]\text{-1-Ad})\text{C}{\equiv}\text{C}([3,5,8\text{-}^2\text{H}_3]\text{-1-Ad})$, $([^2\text{H}_{15}]\text{-1-Ad})\text{C}{\equiv}\text{C}([^2\text{H}_{15}]\text{-1-Ad})$, MeC≡C-1-Ad, and EtC≡C-1-Ad were prepared and converted into cyclobutadiene radical cations by homodimerization, or by codimerization with other alkynes, by reaction (2). Details of the e.s.r. spectra are given in Table 1.



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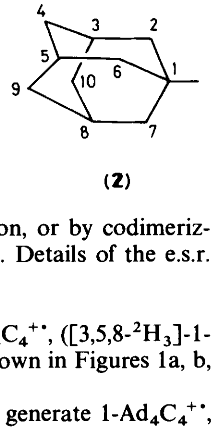

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$\text{1-Ad}_4\text{C}_4^{+\cdot}$.—The e.s.r. spectra of $\text{1-Ad}_4\text{C}_4^{+\cdot}$, $([3,5,8\text{-}^2\text{H}_3]\text{-1-Ad})_4\text{C}_4^{+\cdot}$, and $([^2\text{H}_{15}]\text{-1-Ad})_4\text{C}_4^{+\cdot}$ are shown in Figures 1a, b, and c, respectively.

Broxterman *et al.* used reaction (2) to generate $\text{1-Ad}_4\text{C}_4^{+\cdot}$, and obtained a good simulation of the spectrum using the hyperfine coupling constants *a*(16H) 0.288, *a*(8H) 0.144, *a*(^{13}C in 8C) 3.456, *a*(^{13}C in ?C) 10.9 G. They suggested that the non-equivalence of the coupling hydrogen atoms and carbon atoms might result from restriction of rotation about the 1-adamantyl bond, which would separate the γ-C and γ-H atoms into pseudoaxial and pseudoequatorial sets, as shown in (3).

Our ENDOR and TRIPLE spectra confirmed and gave signs to the proton hyperfine coupling constants of +0.28 and −0.14 G,[12] but the spectrum of $([3,5,8\text{-}^2\text{H}_3]\text{-1-Ad})_4\text{C}_4^{+\cdot}$ (Figure 1b), from which the larger hyperfine coupling is absent, shows that the value of +0.28 G should be ascribed to the 12 H_δ atoms. We conclude that there is no restriction of rotation about the 1-adamantyl bond † on the e.s.r. time scale, and that the proton hyperfine coupling should be analysed as *a*(12H_δ) +0.28, *a*(24H_γ) −0.14 G. This assignment is supported by semi-empirical MO calculations, as described below.

The presence of one pair of ^{13}C satellites is obvious in the spectrum of $\text{1-Ad}_4\text{C}_4^{+\cdot}$ (Figure 1a). As the temperature is reduced, these lines broaden, and the splitting due to proton

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† A similar conclusion has been reached from dynamic n.m.r. experiments on 1-adamantyl and t-butyl compounds, supported by molecular mechanics calculations. Though the 1-adamantyl group is larger and more difficult to deform than the t-butyl group, is also presents a smoother surface and will normally have a lower barrier to rotation about the 1-adamantyl–carbon bond.[13]

Table 1. E.s.r. parameters for 1-adamantyl-substituted cyclobutadiene radical cations and related species

	Hyperfine coupling constants/G				
		$1\text{-}Ad_4C_4^{+\bullet}$			
T/K	$a(24H_\gamma)$	$a(12H_\delta)$	$a(^{13}C_\alpha)$	$a(^{13}C_{\beta,\gamma})$	g
200	−0.14	+0.28	1.76	3.07	2.002 13
255	−0.14	+0.28	11.00	3.04	2.002 12
		cis-$Me_2\text{-}1\text{-}Ad_2C_4^{+\bullet a}$			
	$a(12H_\gamma)$	$a(6H_\delta)$	a(Me)		
208	0.24	0.47	7.96		2.0027
245	0.24	0.45	7.96		2.0028
258	0.25	0.44	7.93		2.0027
		trans-$Me_2\text{-}1\text{-}Ad_2C_4^{+\bullet}$			
	$a(12H_\gamma)$	$a(6H_\delta)$	a(Me)		
208	0.25	0.40	9.43		
215	0.25	0.39	9.43		2.0027
245	0.24	0.39	9.51		2.0028
258	0.23	0.39	9.50		2.0028
		cis-$Et_2\text{-}1\text{-}Ad_2C_4^{+\bullet}$			
	$a(12H_\gamma)$	$a(6H_\delta)$	$a(CH_2)$		
188	0.25	0.49	3.98		2.0028
208	0.25	0.47	4.14		2.0027
233	0.25	0.45	4.33		2.0027
253	0.25	0.43	4.45		2.0027
		$Me_4C_4^{+\bullet}$			
			a(Me)		
253			8.63		2.0030
		$Et_4C_4^{+\bullet}$			
			$a(CH_2)$		
233			7.69		2.0029

[a] Broxterman[8] reports a(Me) 7.96, $a(H_\gamma)$ 0.23 G at 188 K

hyperfine coupling is first lost, and the satellites themselves may then become difficult to detect. Thus at 180 K, the equivalent satellites were not detected in the spectrum of $Bu^t_4C_4^{+\bullet}$[2] although at higher temperatures they are obvious and their proton hyperfine structure can be resolved.

Hogeveen *et al.*[7,8] detected in the spectrum of $1\text{-}Ad_4C_4^{+\bullet}$ a second inner pair of ^{13}C satellites concealed within the wings of the envelope due to proton coupling. This second pair is revealed in the δ-deuteriated compound (Figure 1b), and yet further ^{13}C satellites can be detected in the spectrum of the perdeuterio compound as the envelope due to ^1H coupling, and its satellites, become narrower (Figure 1c, inset).

In a highly symmetrical radical such as $1\text{-}Ad_4C_4^{+\bullet}$, where long-range coupling may occur to a number of equivalent ^{13}C atoms, the ^{13}C satellites may provide a substantial fraction of the total spectral intensity, making it possible to analyse the ^{13}C hyperfine coupling in unusual detail.[12,*]

The ^{13}C satellites showed in Figure 1c consist of two primary doublets BB (a 3.0 G) and CC (a 10.76 G), relating to molecules containing one ^{13}C atom of either of two types. Each of these lines has as its own attendant sub-satellites the doublets B′B′ and C′C′ with the same separation as the lines BB (3.0 G), and arising from molecules containing one ^{13}C atom of either of the first two types, and a second one of the type which is responsible for the strongest satellites BB.

The assignment of these ^{13}C hyperfine coupling constants is assisted by calculation of the relative intensities which would be predicted by probability theory on the basis of various possible assignments.†

If in a molecule there are n equivalent carbon atoms of one set, q of another, and r remaining carbon atoms, 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 (3), where ${}_xC_y = x!/y!(x-y)!$

$$p = (0.01108^m \times 0.98892^{n-m} \times {}_nC_m) \times (0.01108^p \times 0.98892^{q-p} \times {}_pC_q) \times 0.98892^r \quad (3)$$

In $1\text{-}Ad_4C_4^{+\bullet}$, with freely rotating 1-adamantyl groups, the possible sets are $4C_\alpha$, $4C_\beta$, $12C_\gamma$, $12C_\delta$, and $12C_\varepsilon$.

The results of such calculations are given in our preliminary note.[12] The observed relative intensities are C/C′ 12.9, B′/C′ 1.6, B/C 3.6 ± 0.2, and A/B 13.0 ± 2.2, and these correlate best with the intensities calculated on the basis of the assignment a(^{13}C in a set of 4C) 10.76 G, a(^{13}C in a set of 4C) 3.0 G, and a(^{13}C in a set of 12C) 3.0 G, which should show the relative intensities C/C′ 14.16, B′/C′ 1.88, B/C 4.00, and A/B 11.53. Accurate measurement of the areas of the satellites is rendered difficult because of the differential line broadening as mentioned above.

Further assignment can be based on analogies with simpler tetra-alkylcyclobutadiene radical cations. In $(\overset{\gamma}{C}H_3\overset{\beta}{C}H_2)_4\overset{\alpha}{C}_4^{+\bullet}$ (g 2.0029), the values for the three ^{13}C hyperfine coupling constants are 3.72, 4.33, and 5.00 G.[5,11] As the bulk of the alkyl groups is increased, the g value drops and the magnitude of one of the ^{13}C hyperfine coupling constants increases to a (present) limit of 2.0022 and *ca.* 10 G in $Bu_4C_4^{+\bullet}$, and g 2.00212 (independent of temperature) and *ca.* 11 G in $1\text{-}Ad_4C_4^{+\bullet}$. We believe that this trend represents distortion of the central C_4 ring from planar towards the structure shown in (**4**), by steric repulsion between the bulky ligands, which puts more s-character into the orbital containing the unpaired electron, and that the constant $a(^{13}C)$ 10.76 G should be assigned at ^{13}C in the four (α) cyclobutadiene ring atoms. Distortion of this type occurs in tetra-t-butyl-cyclobutadiene where *X*-ray crystallography shows that the angle ø in (**4**) is 169.9°.[14]

In view of the spectrum of $Et_4C_4^{+\bullet}$ it would be reasonable to assign the second hyperfine coupling constant of 3.0 G to the ^{13}C atoms occurring in the 4β and 12γ positions, although of course the introduction of some s-character at C_α weakens the analogy.‡

To probe further this assignment, semiempirical MO calculations were carried out on the 1-adamantylmethyl radical (**5**) as the methyl centre was distorted from planarity. The extent of deformation is defined by θ, which is the perpendicular angle between the extension of the C_β–C_α bond and the plane containing the atoms of the $C_\alpha H_2$ group.

Calculations were carried out on the conformer (**6**) where the C_β–C_γ bond eclipses the $2p$ orbital when the deformation angle θ = 0, and on the staggered conformer (**7**). The optimised geometry was derived from UMINDO/3 calculations, and this was then used in INDO calculations to provide the hyperfine coupling constants. For (**6**), the CH_2 plane was tilted both down (positive values of θ) and up (negative values of θ).

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* A similar analysis has been given of the satellites in the spectra if the radical ions of dithieno[3,4-*b*; 3′,4′-*e*]paradithiin-1,3,5,7-tetraone (F. Gerson, W. Wyber, and F. Kluge, *J. Magn. Reson.*, 1977, **26**, 271).

† The intensities of ^{29}Si satellites have been calculated in a similar way (W. Kaim and H. Bock, *J. Organomet. Chem.*, 1979, **164**, 281).

‡ In the spectrum of $(CH_3CH_2)_4C_4^{+\bullet}$, only the pair of satellites with a 5.00 G shows considerable broadening at low temperature. By analogy with our analysis of the spectra of $1\text{-}Ad_4C_4^{+\bullet}$ and $Bu^t_4C_4^{+\bullet}$, we believe that this pair of satellites should be ascribed to the $^{13}C_\alpha$ atoms.

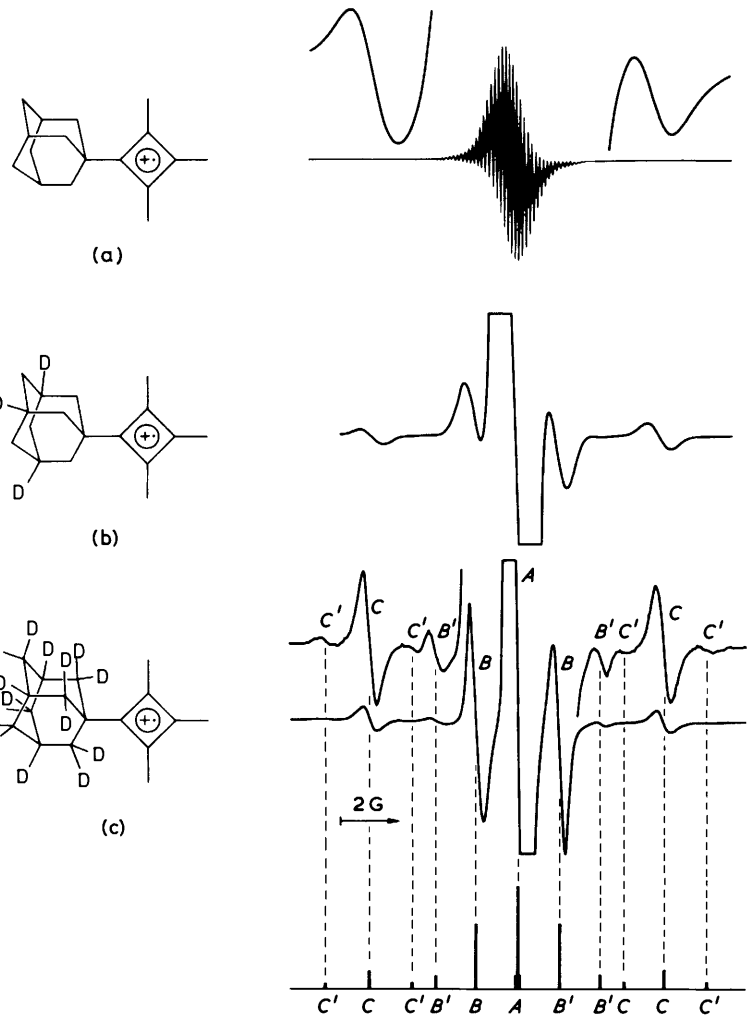
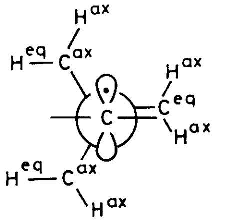


Figure 1. E.s.r. spectra of tetra-1-adamantylcyclobutadiene radical cations in CH_2Cl_2. a, $1\text{-}Ad_4C_4^{+\bullet}$ at 196 K; b, $([3,5,8\text{-}^2H_3]\text{-}1\text{-}Ad)_4C_4^{+\bullet}$ at 223 K; c $([^2H_{15}]\text{-}1\text{-}Ad)_4C_4^{+\bullet}$ at 205 K; d, stick spectrum analysis of the ^{13}C satellites



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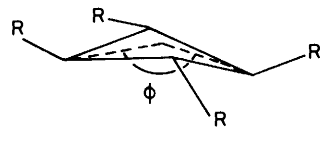

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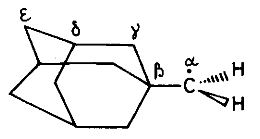

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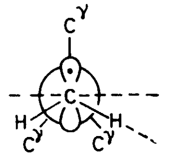

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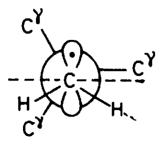


(7)

Table 2. Hyperfine coupling constants (G) calculated for the 1-adamantylmethyl radical (**5**), as the tilt angle (θ) is varied

θ (°)	0	7	14	21
$^{13}C_\alpha$	40.90	43.39	50.07	60.31
$^{13}C_\beta$	−9.70	−10.44	−9.99	−9.37
$^{13}C_\gamma$	8.85	10.15	9.89	9.50
$^{1}H_\gamma$	−1.14	−1.43	−1.39	−1.33
$^{13}C_\delta$	0.05	0.13	0.14	0.14
$^{1}H_\delta$	1.38	1.76	1.72	1.67

To simulate rotation about the C_α–C_β bond the outputs of the calculations for each set of atoms were averaged over each atom in the set and each conformer of that tilt angle, giving the appropriate weighting to the two isomeric forms of (**6**) and to the two enantiomeric forms of (**7**) (θ positive or negative).

The results are given in Table 2.

Bearing in mind that $1\text{-}Ad_4C_4^{+\bullet}$ has a quarter of an electron at each C_α atom, our assignment of the hyperfine coupling constants $a(C_\alpha)$ 10.76, $a(C_\beta)$ 3.07, $a(C_\gamma)$ 3.07, $a(24H_\gamma)$ −0.14, $a(12H_\delta)$ +0.28 G would be equivalent for the 1-adamantylmethyl radical to $a(C_\alpha)$ 43.0, $a(C_\beta)$ 12.3, $a(C_\gamma)$ 12.3, $a(24H_\delta)$ − 0.56, $a(12H_\delta)$ + 1.12 G. These values correlate best with those calculated for a tilt angle of *ca.* 7°. It will be noted that the

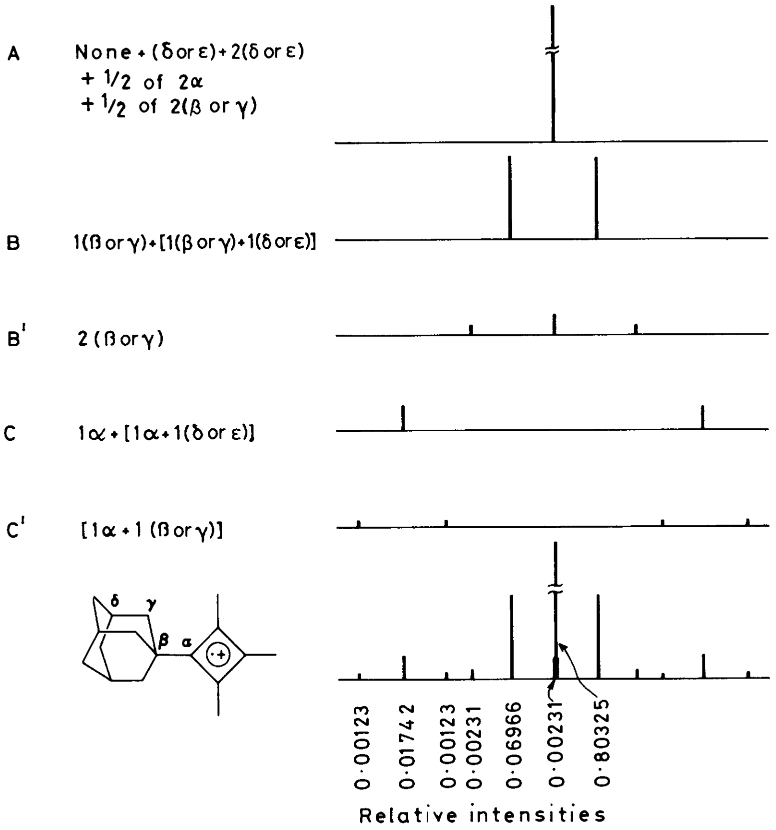
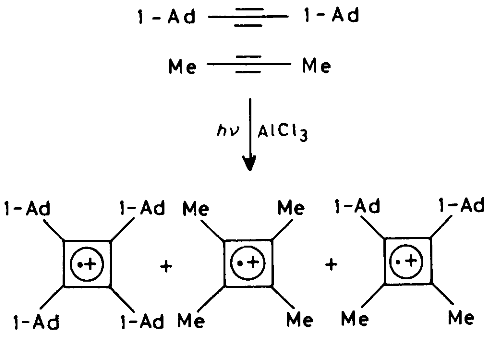


Figure 2. ^{13}C Isotopomeric contributions to the e.s.r. spectrum of 1-Ad$_4$C$_4^{+\bullet}$. The location of the ^{13}C isotopes giving rise to the individual spectra A–C′ are as follows: A, None + 1(δ + ε) + 2(δ + ε) + ½ of 2α + ½ of 2(β + γ); B, 1(β + γ) + [1(β + γ) + 1(δ + ε)]; B′, 2(β + γ); C, 1α + [(1α + 1(δ + ε)]; C′, 1α + 1(β + γ). For example, spectrum C is that arising from a mixture of three different isotopomers, namely that with one ^{13}C atom in the α-position, and the two with one ^{13}C atom in the α-position and a second one in either the δ-position or the ε-position



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calculations reproduce the predicted dependence of $a(^{13}C_\alpha)$ on θ, the similarity of the absolute values of $a(^{13}C_\beta)$ and $a(^{13}C_\gamma)$, and the relative signs and (less accurately) the relative magnitudes of $a(H_\gamma)$ and $a(H_\delta)$.

The contributions which each of the ^{13}C isotopomers makes to the overall satellite spectrum as calculated by equation (3) is illustrated in Figure 2. The signals which are shown contribute 0.98694 of the total spectral intensity.

Me$_2$-1-Ad$_2$C$_4^{+\bullet}$ *and* Et$_2$-1-Ad$_2$C$_4^{+\bullet}$.—If a mixture of di-1-adamantylethyne and but-2-yne is treated with aluminium chloride in dichloromethane, the three possible cyclobutadiene radical cations shown in equation (4) can be formed.

Figure 3 shows the central region of the e.s.r. spectrum which is obtained with a 1:2 ratio of Me$_2$C$_2$ to 1-Ad$_2$C$_2$ at −61 °C. It shows the presence principally of the *cis*-codimer (8) with some distortion of the central multiplet by signals from 1-Ad$_4$C$_4^{+\bullet}$, and also of distinguishable lines from the spectrum of the radical Me$_4$C$_4^{+\bullet}$, a 8.7 G, as marked. The spectral parameters for (8) are given in Table 1.

Under similar conditions, 1-adamantylpropyne generated the spectrum shown in Figure 4, consisting of the superimposed spectra of the *cis*-codimer (8) and the *trans*-codimer (9); data for the radical (9) are included in Table 1.

From a similar reaction with aluminium bromide, Broxterman obtained[8] only a weak spectrum, which could not be interpreted with confidence, but which appeared to consist of *cis*- and *trans*-Me$_2$-1-Ad$_2$C$_4^{+\bullet}$, together with a third spectrum, a(6H) 13.8, a(2H) 2.4 G, which persisted at high temperature. We saw no trace of this unidentified spectrum.

Similar experiments were carried out to generate cyclobutadiene radical cations with mixed ethyl and 1-adamantyl groups. Co-reaction of hex-3-yne and di-1-adamantylethyne gave the spectrum shown in Figure 5, from which the parameters for *cis*-Et$_2$-1-Ad$_2$C$_4^{+\bullet}$ could be abstracted (see Table 1), but dimerisation of 1-adamantylbutyne gave a spectrum in which overlap between the spectra of *cis*- and *trans*-Et$_2$-1-Ad$_2$C$_4^{+\bullet}$, even in the wings, defeated a convincing analysis.

Steric and Electronic Effects.—If, as discussed above, the g value can be used as a criterion of planarity of the ring, *cis*- and *trans*-Me$_2$-1-Ad$_2$C$_4^{+\bullet}$, and *cis*-Et$_2$-1-Ad$_2$C$_4^{+\bullet}$, with g values of 2.0027—2.0028, close to those of Me$_4$C$_4^{+\bullet}$ (2.0030) and Et$_4$C$_4^{+\bullet}$ (2.0029), can probably be treated as having planar ring systems.

We have examined previously the electronic effect of substituents on such a ring system in terms of the model of the

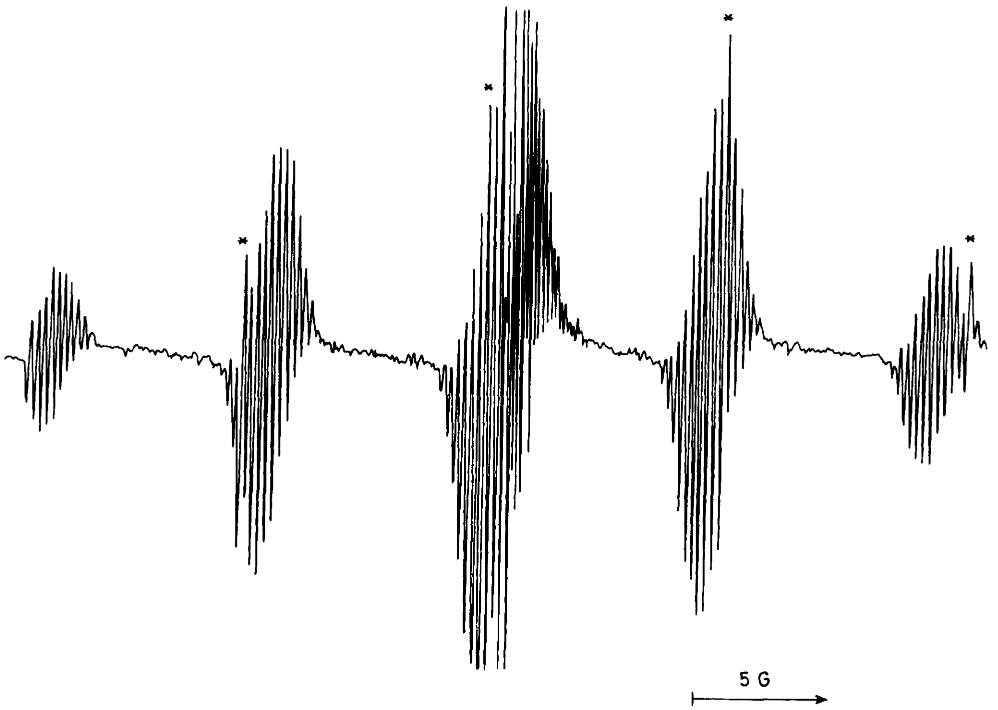


Figure 3. Central region of the e.s.r. spectrum obtained from a mixture (1:2) of Me_2C_2 and $1\text{-}Ad_2C_2$ in CH_2Cl_2 containing $AlCl_3$ at 212 K. The principal spectrum is that of *cis*-$Me_2\text{-}1\text{-}Ad_2C_4^{+\bullet}$. The high-field side of the central multiplet is distorted by the spectrum of $1\text{-}Ad_4C_4^{+\bullet}$, and four of the singlets of the spectrum of $Me_4C_4^{+\bullet}$, marked with an asterisk, can be distinguished

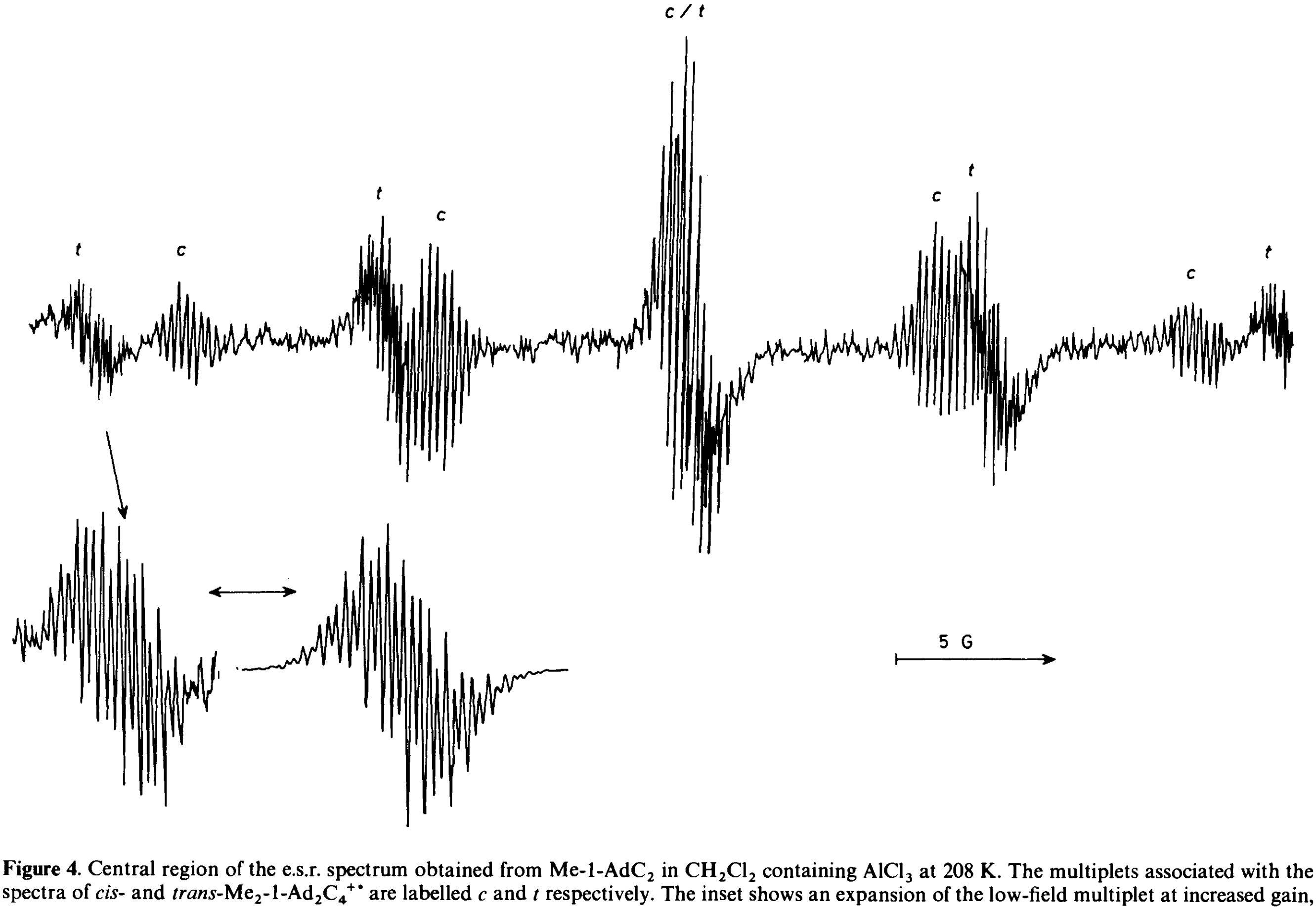


Figure 4. Central region of the e.s.r. spectrum obtained from $Me\text{-}1\text{-}AdC_2$ in CH_2Cl_2 containing $AlCl_3$ at 208 K. The multiplets associated with the spectra of *cis*- and *trans*-$Me_2\text{-}1\text{-}Ad_2C_4^{+\bullet}$ are labelled *c* and *t* respectively. The inset shows an expansion of the low-field multiplet at increased gain, together with a simulation using the hyperfine coupling constants given in Table 1

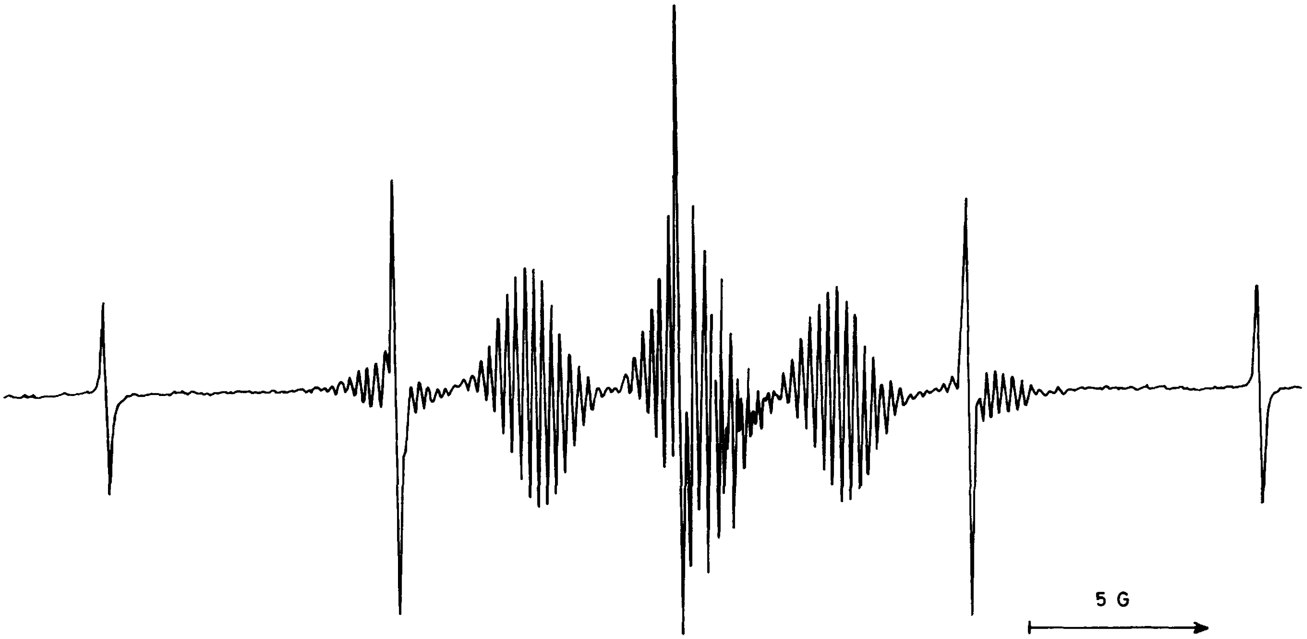
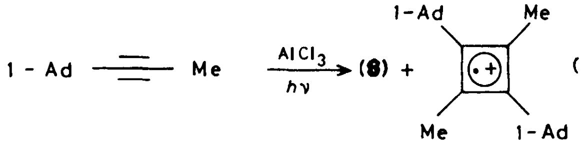


Figure 5. Central region of the e.s.r. spectrum obtained from a mixture of Et_2C_2 and $1\text{-}Ad_2C_2$ in CH_2Cl_2 containing $AlCl_3$ at 209 K. The quintet of multiplets is due to *cis*-$Et_2\text{-}1\text{-}Ad_2C_4^{+\bullet}$; the upfield side of the central multiplet is distorted by the superposition of the spectrum of $1\text{-}Ad_4C_4^{+\bullet}$, and the whole spectrum is overlain by the central quintet of singlets associated with spectrum of $Et_4C_4^{+\bullet}$



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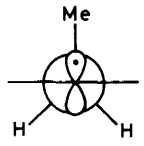

(10)

breaking of the degeneracy of the molecular orbitals. A similar model has been used extensively to interpret substituent effects in benzene radical anions and cations,[15] and cyclopentadienyl radicals.[16,17]

The situation is complicated however by potential ring distortion, and by solvent and counter-ion effects which could be ignored with the neutral cyclopentadienyl radicals,[16,17] but may be significant with the cyclobutadiene (and benzene) radical ions and we do not feel that we can profitably follow the argument further at the present time.

We have noted before[12] that in the radicals $(CH_3CH_2)_2\text{-}R_2C_4^{+\bullet}$, the value of $a(CH_2)$ decreases below that for $Et_4C_4^{+\bullet}$ (7.99 G at 173 K) as the bulk of R increases, and this was ascribed to steric repulsion of the CH_3 group into the position eclipsing the *p*-orbital as shown in (**10**). The very low value of $a(CH_2)$ which we observe in *cis*-$1\text{-}Ad_2Et_2C_4^{+\bullet}$ (3.88 G at 188 K) is obviously an extreme example of this effect, but a more detailed comparison with, for example, the values found in *cis*- and *trans*-$Et_2Bu^t{}_2C_4^{+\bullet}$ would not be justified because of possible variations in the orbital coefficients.

Experimental

Di-(1-adamantyl)ethyne.—The reaction of 1-bromoadamantane and bis(trimethylsilyl)ethyne in dichloromethane containing aluminium chloride at −78 °C for 2 h, and then at room temperature for 1 h gave bis-(1-adamantyl)ethyne in 78% yield, m.p. 150 °C.[18]

Di-([3,5,8-$^2H_3$*]-1-adamantyl)ethyne.*—Adamantane was converted into the 1,3,5-tribromo derivative by reaction with bromine in the presence of iron(III) bromide,[19] then the product was converted into the 1,3,5,8-tetrabomide by further bromination in the presence of aluminium bromide.[20] Reduction with lithium aluminium deuteride in the presence of tributyltin chloride gave 1,3,5,8-tetradeuterioadamantane.[21] This was treated with bromine giving 1-bromo-3,5,8-trideuterioadamantane, which reacted with bistrimethylsilylethyne, giving bis-(3,5,8-trideuterio-1-admantantyl)ethyne, *m/z* 301 (27%), 300 (M^+, 100), 242 (21), 221 (24), 138 (44), and 73 (32).

Di-([$^2H_{15}$*]-1-adamantyl)ethyne.*—A mixture of perdeuterioadamantane (0.694 g, 4.56 mmol) and bromine (15 cm³, 0.29 mol) was stirred at room temperature for 100 min, then poured over ice, and collected in carbon tetrachloride, washed ($NaHSO_4$ and the Na_2CO_3), and dried ($MgSO_4$). Removal of the solvent gave perdeuterio-1-bromoadamantane in 92% yield.

This was treated with bis(trimethylsilyl)ethyne in the presence of aluminium chloride, giving di-([$^2H_{15}$]-1-adamantyl)-ethyne as a waxy solid (78%) which was sublimed before use as required, *m/z* 325 (24%), 324 (M^+, 100), 258 (21), 232 (42), 150 (37), 101 (22), 86 (25), and 46 (21).

1-Adamantylmethylethyne.—Butyl-lithium (9.6 mmol) in hexane was added over a period of 20 min to a solution of 1-adamantylethyne (1.343 g, 8.39 mmol) in dry tetrahydrofuran (50 cm³) below −20 °C, and the mixture was stored at this temperature for a further 30 min. A large excess (5 cm³, 80.3 mmol) of methyl iodide was added dropwise, causing the temperature to rise rapidly from −25 to 0 °C. The mixture was allowed to warm slowly to room temperature, then heated under reflux for 20 min.

Hydrolysis and extraction with pentane gave crude 1-adamantylethylethyne, which was then sublimed at 60—70 °C at 0.3—0.8 Torr (1.24 g, 87%), δ ($CDCl_3$) 1.69—1.87 (m, 15 H) and 1.70 (s, 3 H); *m/z* 174 (*M*, 100%), 131 (22), 117 (87), 91 (47), 79 (32), 77 (25), 41 (46), and 39 (47); Broxterman [8] reports m.p. 102—103 °C (Found: C, 89.6; H, 10.4. Calc. for $C_{13}H_{18}$: C, 89.6; H, 10.4%).

1-*Adamantylethylethyne.*—1-Adamantylethyne[22] (1.629 g, 10.2 mmol) was lithiated at −20 °C as above. Hexamethylphosphorotriamide (7 cm^3) was added, followed by a large excess (5 cm^3, 62 mmol) of ethyl iodide. The mixture was allowed to warm to room temperature then stirred for 1 h, and heated under reflux for a further hour. Work-up as above gave 1-adamantylethylethyne, subliming at 40 °C and 0.8 Torr (1.42 g, 72%), δ($CDCl_3$) 1.12 (t, 3 H, CH_3), 1.78—1.89 (m, 15 H), and 2.08 (q, 2 H, CH_2CH_3); *m/z* 188 (*M*, 94%), 131 (100), 117 (30), 91 (66), 79 (39), 41 (38), and 28 (33) (Found: C, 89.0; H, 10.7. $C_{14}H_{20}$ requires C, 89.3; H, 10.7%).

E.s.r. Spectroscopy.—E.s.r. spectra were obtained using a Varian E4 or E109 spectrometer fitted with a 500 W high-pressure mercury arc, by the technique described previously.[11] For measuring the relative areas of the signals, spectra were recorded at 1 mW microwave power,[23] where differential saturation appeared to be absent.

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References

1 G. Maier, *Angew. Chem., Int. Edn. Engl.*, 1974, **13**, 425; T. Bally and S. Masamune, *Tetrahedron*, 1980, **36**, 343.
2 H. Bock, B. Roth, and G. Maier, *Angew. Chem., Int. Edn. Engl.*, 1980, **19**, 209.
3 H. Bock, B. Roth, and G. Maier, *Chem. Ber.*, 1984, **117**, 172.
4 Q. B. Broxterman, H. Hogeveen, and D. M. Kok, *Tetrahedron Lett.*, 1981, **22**, 173.
5 Q. B. Broxterman and H. Hogeveen, *Tetrahedron Lett.*, 1983, **24**, 639.
6 Q. B. Broxterman and H. Hogeveen, *J. Org. Chem.*, 1983, **48**, 1386.
7 Q. B. Broxterman, H. Hogeveen, and R. F. Kingma, *Tetrahedron Lett.*, 1984, **25**, 2043.
8 Q. B. Broxterman, Thesis, Groningen, 1985.
9 J. L. Courtneidge, A. G. Davies, and J. Lusztyk, *J. Chem. Soc., Chem. Commun.*, 1983, 893.
10 J. L. Courtneidge, A. G. Davies, and J. E. Parkin, *J. Chem. Soc., Chem. Commun.*, 1983, 1262.
11 J. L. Courtneidge, A. G. Davies, E. Lusztyk, and J. Lusztyk, *J. Chem. Soc., Perkin Trans. 2*, 1984, 155.
12 W. Chang, J. L. Courtneidge, A. G. Davies, J. C. Evans, A. G. Neville, and C. C. Rowlands, *Tetrahedron Lett.*, 1985, **26**, 4121.
13 J. E. Anderson, H. Pearson, and D. I. Rawson, *J. Am. Chem. Soc.*, 1985, **107**, 1446.
14 H. Irngartinger, N. Riegler, K. D. Malsch, K. A. Schneider, and G. Maier, *Angew. Chem., Int. Edn. Engl.*, 1980, **19**, 211; H. Irngartinger and M. Nixdorf, *ibid.*, 1983, **22**, 403.
15 F. Gerson, 'High Resolution E.S.R. Spectroscopy,' Wiley–Verlag Chemie, Weinheim, 1970.
16 M. Kira, M. Watanabe, and H. Sakurai, *J. Am. Chem. Soc.*, 1977, **99**, 7780; 1980, **102**, 5202.
17 P. J. Barker, A. G. Davies, and M. W. Tse, *J. Chem. Soc., Perkin Trans. 2*, 1980, 941; A. G. Davies, E. Lusztyk, and J. Lusztyk, *ibid.*, 1982, 729; A. G. Davies, J. P. Goddard, E. Lustztyk, and J. Lusztyk, *ibid.*, p. 737; P. J. Barker, A. G. Davies, R. Henriquez, and J.-Y. Nedelec, *ibid.*, p. 745.
18 G. Capozzi, G. Romeo, and F. Marcuzzi, *J. Chem. Soc., Chem. Commun.*, 1982, 959.
19 D. E. Sunko, S. Hiršl-Starčevic, S. K. Pollack, and W. J. Hehre, *J. Am. Chem. Soc.*, 1979, **101**, 6163.
20 H. Stetter and C. Wulff, *Chem. Ber.*, 1960, **93**, 1366.
21 J. E. Leibner and J. Jacobus, *J. Org. Chem.*, 1979, **44**, 449.
22 H. Stetter and P. Goebel, *Chem. Ber.*, 1962, **95**, 1039.
23 G. Brunton, D. Forrest, D. Griller, K. U. Ingold, and A. H. Reddoch, *J. Am. Chem. Soc.*, 1978, **100**, 3721.

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