The Electron Spin Resonance Spectra of the [4]Annulene (Cyclobutadiene) Radical Cations, $R_4C_4^{+\cdot}$

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A series of simple (R = R') and mixed (R ≠ R') cyclobutadiene radical cations, $R_2R'_2C_4^{+\cdot}$, have been prepared by photolysis of the alkynes, RC≡CR' or of mixtures of the alkynes RC≡CR and R'C≡CR', in dichloromethane in the presence of aluminium chloride, and the e.s.r. spectra have been recorded.

The magnitude of the ^{13}C hyperfine coupling in $Et_4C_4^{+\cdot}$ confirms that it is a π-radical, with no evidence for out-of-plane or in-plane (Jahn–Teller) distortion.

The values of $a(H_\beta)$ for the radicals $(RCH_2)_4C_4^{+\cdot}$ and $(RCH_2)_2R'_2C_4^{+\cdot}$ indicate that, as the bulk of the alkyl substituents increases, the group R is pushed out of the plane of the ring. Some unusual temperature effects on $a(H_\beta)$ are ascribed to interaction of the radical cation with the solvent or with the counterion. As the bulk of the alkyl groups increases, the *g*-value decreases from 2.0030 to about 2.0022.

cis- and *trans*-Isomers of the radicals $Me_2Bu^t_2C_4^{+\cdot}$, $Et_2Bu^t_2C_4^{+\cdot}$, $Bu^i_2Bu^t_2C_4^{+\cdot}$, and probably $Me_2Et_2C_4^{+\cdot}$ have been identified, and the spectra of *cis*- and *trans*-$Me_2Bu^t_2C^{+\cdot}$ are analysed in terms of breaking of the degeneracy of the molecular orbitals of the cyclobutadiene system by differential electron release by the alkyl groups (Bu^t > Me).

The development of π-electron theory has been greatly helped by the study by e.s.r. spectroscopy of annulene radicals.[1] E.s.r. investigations of the cyclo-octatetraene ([8]annulene) radical anions, the cycloheptadienyl ([7]annulene) radicals, and, particularly, the benzene ([6]annulene] radical anions and cations are of long standing, but, until recently, little was known about the smaller-ring radical systems.

In the past few years, we[2] and Sakurai[3] have developed methods for studying the e.s.r. spectra of cyclopentadienyl ([5]annulene) radicals. As these are odd-numbered annulenes they are uncharged; complications arising from solvation or from the presence of a counterion can be ignored, and the spectra can be interpreted to provide evidence of the effect of substituents on the π-electron distribution. We have discussed such effects in terms of the breaking of the degeneracy of the molecular orbitals, and others[4] have used the alternative model of the differential effect of the substituents on the stability of the pseudo-Jahn–Teller isomers.

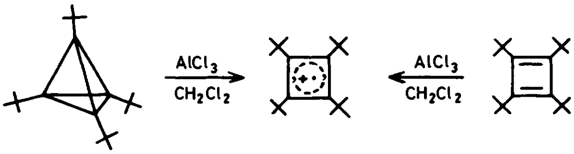
Less has been published on the cyclopropenyl ([3]annulene) radicals, but it is now clear that these are not π-radicals but σ-radicals (as are the cyclopropyl radicals), which cannot be treated by π-electron theory.[5]

This leaves the cyclobutadiene ([4]annulene) radical ions as the final group of these small annulenes which remains to be studied. If they can be confirmed to be π-radicals like the [5]annulenes rather than σ-radicals like the [3]annulenes their study should make a significant contribution to π-electron theory.

The e.s.r. spectra of only two tetra-alkylcyclobutadiene radical cations had been reported when this work was carried out. Bock, Roth, and Maier demonstrated that tetra-t-butyltetrahedrane or tetra-t-butylcyclobutadiene, when treated with aluminium chloride in dichloromethane, showed the spectrum of the persistent tetra-t-butylcyclobutadiene radical cation (1), a(36H) 0.27 G.[6]

No other tetrahedranes and few other cyclobutadienes[7] are known, however, and these routes would be difficult to generalise.

An alternative preparation of much more promising potential has recently been demonstrated by Broxterman, Hogeveen, and Kok. Dimethylacetylene (and $CD_3C{\equiv}CCD_3$) was treated with aluminium trichloride in dichloromethane to give the σ-complex of tetramethylcyclobutadiene (2),[8] and this, on u.v. irradiation at −89 °C in an e.s.r. spectrometer cavity, showed the spectrum of the tetramethylcyclobutadiene radical cation (3), a(12H) 8.75 G,[9] g 2.0030 [equation (ii)]. This route is analogous to that which we have used for the [5]annulenes, involving irradiation of σ-bonded metallic derivatives such as $C_5H_5SnBu_3$.[2a,e]



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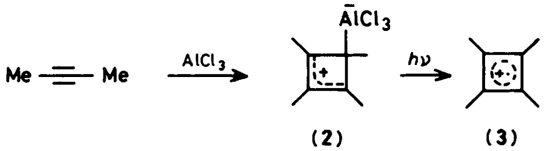


(ii)

(2) (3)

Broxterman and Hogeveen[10] have also recently reported the e.s.r. spectra of the radicals $R_4C_4^{+\cdot}$ (R = Et, Pr, and pentyl). Their results are compared with ours later in this paper.

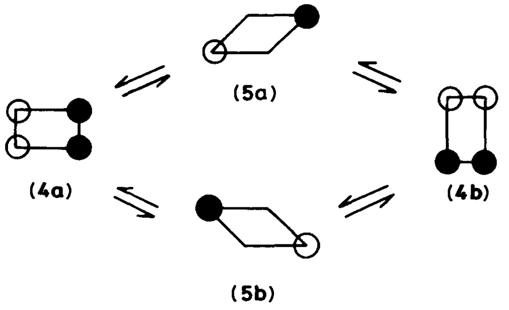
The potential surface for the cyclobutadiene radical cation was studied by Borden, Davidson, and Feller,[11] by *ab initio* calculations. They concluded that Jahn–Teller distortion gave two equivalent rectangular structures (4) of minimum energy, connected by two transition states of rhombohedral geometry (5), π-interactions between nearest neighbouring atoms being more important than between atoms diagonally across the ring, as illustrated in equation (iii).

Ring puckering was not thought to be significant in stabilizing the parent $C_4H_4^{+\cdot}$,[11] or $Me_4C_4^{+\cdot}$, though it might be important with bigger alkyl groups, as tetra-t-butylcyclobutadiene has been shown to be non-planar by *X*-ray diffraction.[12]

We report here a study of the systematics of the e.s.r. spectra of the tetra-alkylcyclobutadiene radical cations, $R_4C_4^{+\cdot}$ and $R_2R'_2C^{+\cdot}$.

Discussion

The radicals were generated in dichloromethane as solvent by Hogeveen's method [equation (ii)]. The hyperfine coupling



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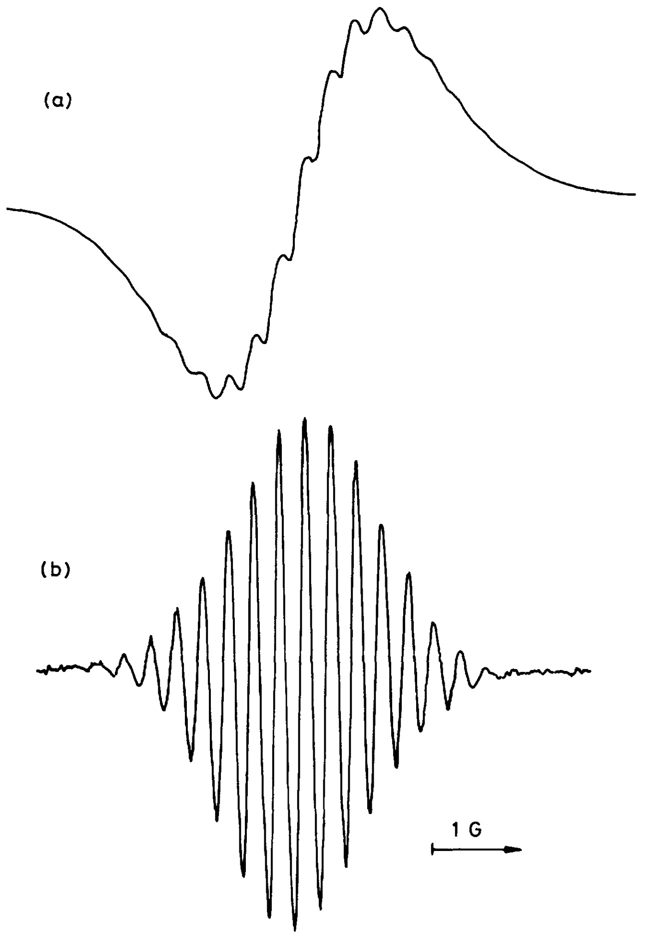

Figure 1. Comparison of (a) first derivative, and (b) third derivative, of the spectrum of *cis*-$Bu^t_2Pe^t_2C_4^{+\cdot}$ in CH_2Cl_2 at −38 °C

constants and *g* values observed are listed in Table 1. Third derivative display of the spectra was used when necessary to enhance the resolution; the improvement which this can confer is illustrated for the radical $Bu^t_2Pe^t_2C_4^{+\cdot}$ (Pe = pentyl) in Figure 1.

Broxterman, Hogeveen, and Kok reported that the spectrum of the radical $Me_4C_4^{+\cdot}$ decayed to give a much more complicated spectrum.[9] We have confirmed this, but have not observed this effect with any of the other radicals described here.

It will be noted that the *g*-factor of $Me_4C_4^{+\cdot}$ has the high value of 2.0030, but there is a consistent trend to lower values as the bulk of the alkyl group is increased, and this is equally apparent in the species with unmixed alkyl groups (*e.g.* $Bu^t_4C_4^{+\cdot}$, *g* 2.0023) and with mixed alkyl groups (*e.g.* $Bu^t_2Pe^t_2C_4^{+\cdot}$, *g* 2.0022).

Table 1. E.s.r. spectra of tetra-alkylcyclobutadiene radicals in CH_2Cl_2

	T/K	*a*/G	*g*
$Me_4C_4^{+\cdot}$	173	8.70 (12 H) 4.04 (^{13}C)	2.0030
	253	8.63	
$Et_4C_4^{+\cdot}$	173	7.99 (8 H) 3.72, 4.33, 5.00 (^{13}C) [a]	2.0029
	253	7.72	
$Pr_4C_4^{+\cdot}$	173	7.15 (8 H)	2.0029
	253	7.01	
$Pr^i_4C_4^{+\cdot}$	173	2.76 (4 H) 0.28 (24 H)	2.0027
	253	2.74 0.28	
$Bu^i_4C_4^{+\cdot}$	173	6.5 (8 H) [c]	2.0027
	253	6.5	
$Bu^t_4C_4^{+\cdot}$	200	0.27 (36 H)	2.0023
	242	0.27	
cis-$Me_2Et_2C_4^{+\cdot}$ [b]	182	8.40 (6 H) 9.37 (4 H)	—
trans-$Me_2Et_2C_4^{+\cdot}$ [b]	182	9.15 (6 H) 9.00 (4 H)	—
$Me_2Pr_2C_4^{+\cdot}$	193	8.38 (6 H) 7.62 (4 H)	2.0029
$(CD_3)_2Pr_2C_4^{+\cdot}$	188	1.34 (6 D) 7.71 (4 H)	—
$Me_2Pr^i_2C_4^{+\cdot}$	173	8.94 (6 H) 6.30 (2 H)	—
	258	9.08 5.88	
cis-$Me_2Bu^t_2C_4^{+\cdot}$ [d]	193	8.00 (6 H) 0.24 (18 H) 4.0 (^{13}C)	2.0028
	243	8.03 0.24	
trans-$Me_2Bu^t_2C_4^{+\cdot}$ [d]	193	9.00 (6 H) 4.0 (^{13}C)	2.0028
	243	9.17 (6 H) 0.20 (18 H)	
$Et_2Pr_2C_4^{+\cdot}$	193	8.12 (4 H, Et) 6.92 (4 H, Pr)	2.0028
	253	7.79 6.89	
$(CH_3CD_2)_2Pr_2C_4^{+\cdot}$	193	1.17 (4 D) 6.95 (4 H)	2.0026
	253	1.14 6.91	
$Et_2Bu_2C_4^{+\cdot}$	173	8.44 (4 H, Et) 6.95 (4 H, Bu)	2.0028
	253	8.00 6.93	
$Et_2Pr^i_2C_4^{+\cdot}$	183	7.16 (4 H) 4.61 (2 H)	—
	204	6.93 4.59	
$Et_2Bu^t_2C_4^{+\cdot}$ [b]	183	4.00 (4 H) not resolved	2.0028
	220	4.48 (4 H) 0.22 (18 H)	
$Pr^i_2Bu^s_2C_4^{+\cdot}$	183	2.05 (2 H) 1.95 (2 H) [e]	2.0027
	253	2.30 2.10	
cis-$Bu^i_2Bu^t_2C_4^{+\cdot}$ [f]	173	4.55 (4 H) [c]	
	273	4.87	2.0027
trans-$Bu^i_2Bu^t_2C_4^{+\cdot}$ [f]	173	5.50 (4 H) [c]	2.0027
	273	5.77	
$Bu^t_2Pe^t_2C_4^{+\cdot}$ [g]	254	0.29 ($\geqslant$ 18 H)	2.0022

[a] Assignment uncertain, see text; see Figure 2. [b] *cis*/*trans* assignment uncertain. [c] With alternating linewidth effect. [d] See Figure 3. [e] The larger hyperfine coupling probably relates to the isopropyl group. [f] See Figure 4. [g] First and third derivative spectra are illustrated in Figure 1.

σ or π Configurations: a($^{13}C_\alpha$) *and* a($^{13}C_\beta$).—The qualitative π-character of a cyclic radical may be discussed in terms of the angle subtended at the radical centre within the ring. In the methyl radical, the sp^2 hybridised carbon forms three equivalent bonds at 120°, with the singly occupied *p*-orbital directed along the principal D_{3h} axis. Such an atom can form part of a benzene ring, with no angle strain, or of a cyclopentadienyl ring with little angle strain (12° at each carbon atom).

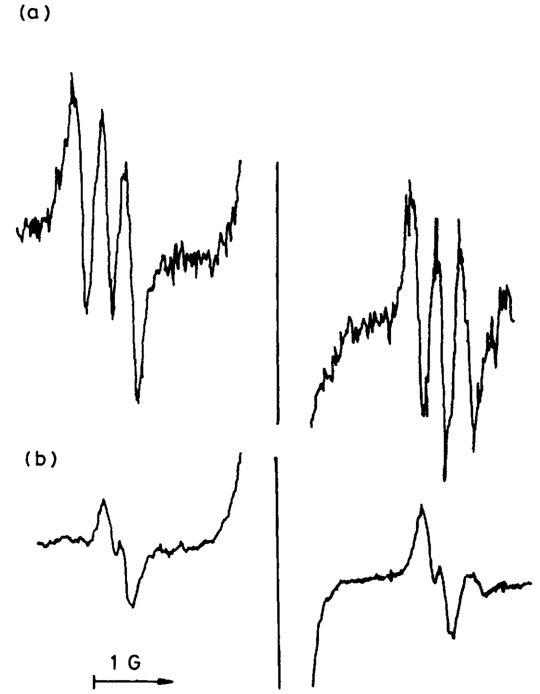

Figure 2. Central line and ^{13}C satellites of the spectrum of $\mathrm{Et_4C_4{}^{+\cdot}}$ in $\mathrm{CH_2Cl_2}$ at (a) −36 °C and (b) −81 °C

If the size of the ring is reduced, the decreasing size of the included angle is accommodated by an increase in the *p*-character of the C–C bonds within the ring at the radical centre. In an otherwise saturated ring this may be accompanied by distortion towards sp^3 hybridisation and local C_{3v} symmetry, giving the radical some σ-character. This may be seen to be the basis of the σ-configuration of the cyclopropyl radical (∠CCC 60°). The cyclobutyl radical (∠CCC 80°) shows a 'normal' value of $a(1\mathrm{H}_\alpha)$ of about 21 G,[13] and is accepted as a π-radical, but the 2-norbornyl radical (∠CCC 104°) is thought to have some σ-character with the C–H bond bent in the *endo*-direction by about 30°.[14]

In an annulene, distortion from planarity would disrupt the cyclic electron delocalisation, and to a limited degree an increase in the *p*-character of the carbon–carbon bonds in the ring is compensated for by an increase in the *s* character of the exocyclic bonds, so that the radical retains its planar π-configuration. This is possible in the cyclopentadienyl radical (∠CCC 108°) which is shown to be planar by evidence [2a] such as the value of $a(^{13}\mathrm{C}_\alpha)$ (see below) and the success of predictions based on π-electron theory which assumes planarity (*e.g.* the e.s.r. spectra of the radicals $\mathrm{Me}_n\mathrm{H}_{5-n}\mathrm{C}_5{}^{\cdot}$[2a]). The distortion in the cyclopropenyl radicals (∠CCC 60°), however, is apparently too large to be accommodated in this way; these are localised σ-radicals as described above.[5]

It is therefore an interesting and important question whether the 90° angle of the ring in the cyclobutadiene radical cations can be accommodated with retention of planarity at carbon by transfer of *s* character into the exocyclic bonds, or whether out-of-plane distortion will result.

Evidence for the structure comes most directly from the values of $a(^{13}\mathrm{C}_\alpha)$ of the annulene ring atoms, which will be low if the unpaired electron is in a *p*-orbital with the carbon atom in a model plane, but will increase if the electron is in an orbital with some *s*-character with non-vanishing electron density at the nucleus.

Our spectrum of the radical $\mathrm{Me_4C_4{}^{+\cdot}}$ showed satellites, $a(^{13}\mathrm{C})$ 4.04 G. This might reasonably be ascribed to either the C_α (ring) or the C_β (methyl) carbon atoms, and the fact that *both* are involved is indicated by the spectrum of $\mathrm{Et_4C_4{}^{+\cdot}}$ (Figure 2), in which three pairs of satellites can be resolved, $a(^{13}\mathrm{C})$ 3.72, 4.33, and 5.00 G, the outer set of lines being broader than the others, particularly at low temperatures. Isotopic labelling would be required before these hyperfine coupling constants could be assigned amongst the α, β, and γ carbon atoms,*,† but the assignment is not necessary to establish that these are π-radicals.

Table 2. Values of $a(^{13}\mathrm{C}_\alpha)$ observed for the peralkylated annulenes, $(\mathrm{RC})_n{}^{\cdot}$, and calculated for the analogues $(\mathrm{HC})_n{}^{\cdot}$

$a(^{13}\mathrm{C}_\alpha)$/G	$\mathrm{Bu^t{}_3}$-$\mathrm{C_3}^{\cdot}$ [a]	$\mathrm{Me_4C_4{}^{+\cdot}}$	$\mathrm{Me_5C_5{}^{\cdot}}$	$\mathrm{Me_6C_6{}^{+\cdot}}$
Obs. for $(\mathrm{RC})_n{}^{\cdot}$	30.0	4.0 [b]	2.68 [c]	2.4 or *ca.* 1 [d]
Calc. for $(\mathrm{CH})_n{}^{\cdot}$ (KF) [15]	2.60	1.95	1.6	1.30
Calc. for $(\mathrm{CH})_n{}^{\cdot}$ (YKK) [16]	4.41	3.83	2.0	1.58

[a] Recognised to be a σ-radical.[5] [b] This work. [c] Ref. 2*f*. [d] Ref. 19. The assignment to C_α or C_β is uncertain.

Values of $a(^{13}\mathrm{C}_\alpha)$ in annulenes, $(\mathrm{CH})_n{}^{\cdot}$ can be calculated by the Karplus–Fraenkel [16] (KF) or Yonezawa–Kawamura–Kato [17] (YKK) equation; the latter is better for annulenes which are subject to Jahn–Teller distortion or to angle strain. Neither equation has been parametrised for alkylated annulenes, but the interaction parameters for ·C–H and ·C–$\mathrm{CH_3}$ sigma bonds appear to be similar, as the observed values of $a(\mathrm{C}_\alpha)$ vary little with α-methylation [*e.g.* $\mathrm{CH_3}^{\cdot}$ and $\mathrm{MeCH_2}^{\cdot}$, $a(^{13}\mathrm{C}_\alpha)$ 38.4 and 39.07 G, respectively; $\mathrm{C_5H_5}^{\cdot}$ and $\mathrm{Me_5C_5}^{\cdot}$, $a(^{13}\mathrm{C}_\alpha)$ 2.60 and 2.68 G, respectively]. Values for $a(^{13}\mathrm{C}_\alpha)$ observed for the peralkylated annulenes, and calculated for the annulenes $(\mathrm{CH})_n{}^{\cdot}$, are given in Table 2. Despite the limitations noted above, the observed value of $a(^{13}\mathrm{C}_\alpha)$ establishes that the cyclobutadienyl radical cations represent a planar delocalised π-electron system, with no significant puckering, in accord with calculation.[6,10]

The observed value of $a(^{13}\mathrm{C}_\beta)$ for $\mathrm{Me_4C_4{}^{+\cdot}}$ is in agreement with this model. The π-radical $\mathrm{Me_5C_5}^{\cdot}$, with $\rho\mathrm{C}_\alpha$ 0.2, shows $a(^{13}\mathrm{C}_\beta)$ 3.35 G,[2f] and if allowance is made for the higher value of $\rho\mathrm{C}_\alpha$ 0.25, and of the 'excess charge effect',[18] a value of $a(^{13}\mathrm{C}_\beta)$ of about 4.6 G would be expected for $\mathrm{Me_4C_4{}^{+\cdot}}$, near the observed value of about 4.0 G.

The Value of $a(\mathrm{H}_\beta)$.—The hyperfine coupling constants, $a(\mathrm{H}_\beta)$, for the three known permethylated annulene radicals, $\mathrm{Me}_n\mathrm{C}_n{}^{\cdot}$, are $\mathrm{Me_4C_4{}^{+\cdot}}$ 8.7, $\mathrm{Me_5C_5}^{\cdot}$ 6.37, $\mathrm{Me_6C_6{}^{+\cdot}}$ 6.53 G.[2b,9,19] If these values are normalised for unit spin density on C_α by the equation $Q_{\mathrm{Me}} = a_n$, we obtain for $\mathrm{Me_4C_4{}^{+\cdot}}$ 34.8, $\mathrm{Me_5C_5}^{\cdot}$ 31.85, and $\mathrm{Me_6C_6{}^{+\cdot}}$ 39.18 G. This coupling is mainly hyperconjugative in origin, and, as the methyl groups are electron-releasing,[2a,c] the principal interaction must be between the singly occupied π-orbital of the ring, and the occupied σ, rather than the unoccupied σ*, orbital of the C–H bonds. Two factors may then be seen to contribute to this variation in *Q* values. First, in the radical cations, the 2*p*π orbital will contract because of the nuclear charge,[18] and participate in hyperconjugation more effectively. Second, the singly occupied MO in $\mathrm{Me_6C_6{}^{+\cdot}}$ is of lower energy (α + β), than that in $\mathrm{Me_4C_4{}^{+\cdot}}$ (α) and may interact more effectively with the C–H σ-orbital.

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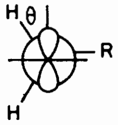
* The atoms are labelled as follows: $\mathrm{\overline{CCCC}_{\alpha}{}^{\cdot}{-}C_{\beta}(H_{\beta}){-}C_{\gamma}(H_{\gamma})}$.

† Values of $a(\mathrm{C}_\beta)$ and $a(\mathrm{C}_\gamma)$ are usually similar in π-radicals, *e.g.* $(\mathrm{Me_3C})_3\mathrm{C}^{\cdot}$, $a(^{13}\mathrm{C}_\beta)$ 10.71, $a(^{13}\mathrm{C}_\gamma)$ 10.99 G.[15]

Table 3. Values of $a(H_\beta)$/G in corresponding sets of β-methylated radicals (T/K in parentheses)

β-Me$_0$	$H_2\dot{C}CH_3$ 26.87	$Me_2\dot{C}CH_3$ 22.74	$(CH_3)_4C_4^{+\cdot}$ 8.70 [a]	$(CH_3)_6C_6^{+\cdot}$ 6.53 [b]
β-Me$_1$	$H_2\dot{C}{-}CH_2Me$ 31.12 (143)	$Me_2\dot{C}CH_2Me$ 18.68 (159)	$(MeCH_2)_4C_4^{+\cdot}$ 7.99 (173) [a]	$(MeCH_2)_6C_6^{+\cdot}$ 2.63 (253) [b]
β-Me$_2$	$H_2\dot{C}CHMe_2$ 35.1 (128)	$Me_2\dot{C}CHMe_2$ 10.77 (298)	$(Me_2CH)_4C_4^{+\cdot}$ 2.76 (173) [a]	

[a] This work. [b] Ref. 19. Other values are taken from Landolt-Börnstein, 1977, *9b*.



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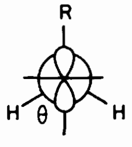

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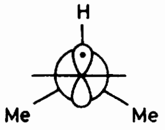

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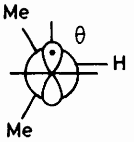


(9)

Hyperfine coupling to β-hydrogen is governed by equation (iv). The constants A and B have values of about 1 and 54 G,

$$a(H_\beta) = (A + B\cos^2\theta)\rho C_\alpha \qquad \text{(iv)}$$

and θ is the torsion angle between the axis of the p-orbital and the C_β–H bond. In n-alkyl radicals, $a(H_\beta)$ is greater than 27 G, and has a positive temperature coefficient, implying that at low temperature the radicals tend to assume the conformation (6).[20]

Relatively little is known about the conformations of alkyl cations, but *ab initio* calculations [21] suggest that the propyl cation is most stable in the eclipsed geometry (7) and that, in the isobutyl cation, the two methyl groups subtend an angle of 30° with the axis of the vacant p-orbital, placing the C_β–H bond in the nodal plane; in both species, the barrier to rotation is calculated to be about 10 kJ mol^{-1}. The conformational preferences in the corresponding radicals and cations are therefore opposed, and it is interesting to see what behaviour will be followed by the radical cations.

As the values of Q_H depend on the environment of C_α as discussed above, values of $a(H_\beta)$ for β-methylated radicals at the lowest temperatures for which values are available are compared in columns in Table 3 with $a(H_\beta)$ for the corresponding α-methylated radicals. An increase in $a(H_\beta)$ with β-methylation should indicate a preference for the conformation (6; X = Me) and a decrease should point to the conformation (7).

The high value and negative temperature coefficient of the propyl radical indicate the conformation (6), whereas the opposite characteristics in the t-pentyl radical and the hexaethylbenzene radical cation show that these are most stable in the conformation (7), with the methyl groups lying out of the nodal plane of the radical.

By this criterion, the $(MeCH_2)_4C_4^{+\cdot}$ radical cation appears to have a slight preference for the eclipsed conformation (7) and the decreasing values of $a(H_\beta)$ for the radicals $(EtCH_2)_4C_4^{+\cdot}$ and $(Pr^iCH_2)_4C_4^{+\cdot}$ (Table 1) show an increasing tendency for the radicals to adopt this conformation. If A in equation (iv) is neglected, B is taken, from the $Me_4C_4^{+\cdot}$ radical, to be 69.2 G, and ρC_α is taken to be 0.25, the values of $a(H_\beta)$ in the radicals $R_4C_4^{+\cdot}$ imply that the average value of θ increases with R in the sequence Me 45°, Et 48°, Pr 51°, Bu^t 52°, whereas a rigidly eclipsed structure (7) would have θ 60°.

The alkyltetramethylcyclopentadienyl radicals $C_5Me_4R^\cdot$, (R = Et, Pr, and Bu) similarly are most stable in the eclipsed conformation (7),[2d] but the ethylcyclopentadienyl radical, $C_5H_4Et^\cdot$, in which steric hindrance is smaller, prefers the conformation (6).[2a]

In the acyclic radicals, two β-methyl substituents confer in the primary radical the conformation (8) (see Table 3) but the tertiary radical $Me_2\dot{C}CHMe_2$ is more stable in the conformation (9), presumably because of steric hindrance between the α- and the β-methyl substituents.

The low value of $a(H_\beta)$ for the radical ion $C_4(CHMe_2)_4^{+\cdot}$ then clearly indicates the conformation (9), and, by equation (iv), the average torsion angle θ is calculated to be 66.5°.

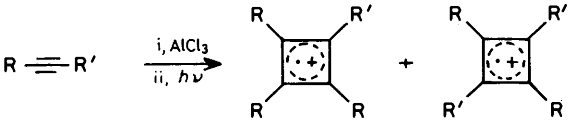
For the isopropylcyclopentadienyl radical, $a(H_\beta)$ = 12.4 G at −70 °C, but $da/dT = -6.25$ mG K^{-1}, suggesting that the most stable conformation is (8).[2a]

The puzzling feature, in this otherwise consistent picture, is the anomalous temperature dependence of $a(H_\beta)$. As the temperature is raised, the freedom of rotation about the C_α–C_β bond will increase and the value of $a(H_\beta)$ should approach that of the unsubstituted α-methyl radical; this is the behaviour which is commonly observed in acyclic alkyl radicals, and also in the alkyltetramethylcyclopentadienyl radicals. In contrast, instead of showing an expected pronounced positive temperature coefficient, the low values of $a(H_\beta)$ for the radicals $R_4C_4^{+\cdot}$ (R = Et, Pr, Bu^t, or Pr^i), if anything, *decrease* slightly as the temperature is raised, away from the value of $a(H_\beta)$ for $Me_4C_4^{+\cdot}$, which itself shows a very small negative temperature coefficient. This same phenomenon was noted by Broxterman and Hogeveen.[10]

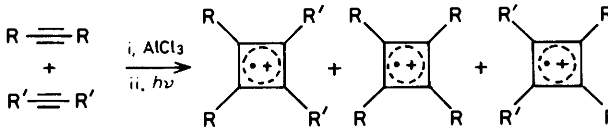
This unfamiliar behaviour may be related to the fact that we are dealing here with charged radicals, which will be susceptible to strong temperature-dependent interactions with the solvent and with the (unidentified) counterion, whereas the familiar picture of hyperfine coupling to β-hydrogens is based on studies of neutral radicals where these effects are not important.

Radicals with Mixed Alkyl Groups, $R_2R'_2C_4^{+\cdot}$.—The reaction of a mixed alkyne might be expected to lead to the formation of both the *cis*- and *trans*-isomers of the cyclobutadienyl radical cation [(10) and (11) respectively, equation (v)], and the reaction of a mixture of two alkynes should give only the *cis*-isomer, together with the two simple radical cations [equation (vi)].

Of the twelve mixed alkynes, RC≡CR′, from which we obtained spectra, only four (MeC≡CEt, MeC≡CBu^t, EtC≡CBu^t, and Bu^{t}C≡CBu^t) showed clearly the formation of two



(10) (11) (v)



(10) (vi)

Table 4. Dependence of $a(H_\beta)$/G of R, on R', in $R_2R'_2C_4^{+\bullet}$

R	R' =	Me	Et	Pr	Pr^i	Bu^t
Me		8.7	9.0 [a]	8.4	8.9	
Et		9.0 [a]	8.0	8.1	7.2	4.0
Pr^i		6.3	4.6		2.76	

[a] Or 9.37; see text.

radicals. The others (see Table 1) which we discuss first, gave spectra usually with rather broad lines (ΔH_{pp} *ca.* 0.6 G), which might be caused by unresolved γ coupling and/or by the presence of two isomers with closely similar coupling constants. The radical $Et_2Pr_2C_4^{+\bullet}$ was prepared by both routes, (v) and (vi), and, to confirm the analysis of the spectrum, from the deuterium-labelled alkyne $(CH_3CD_2)PrC_2$.

Values at −100 °C of $a(H_\beta)$ for the group R as R' is varied in $R_2R'_2C_4^{+\bullet}$, are collected in Table 4. Whereas *a*(Me) remains constant at 8.7—9.0 G as R' is varied, there is a consistent trend in $a(H_\beta)$ in Et or Pr^i towards lower values as the bulk of R' increases. This reinforces the conclusion reached for the radicals $R_4C_4^{+\bullet}$, that increasing steric congestion by the substituents forces the C_β–C_γ bond out of the plane of the ring towards the limiting conformations (7) and (8); the special behaviour of $Bu^i_2Bu^t_2C_4^{+\bullet}$ is discussed below. At higher temperatures, $a(H_\beta)$ might be expected to increase towards the value of *a*(Me) (*ca.* 9.0 G) as freedom of rotation about the C_α–C_β bond increases, but no such general effect is apparent: complications due to the interactions of the radical cation with the solvent and counterion may now be compounded by splitting of the degeneracy of the molecular orbitals, which is discussed below.

The evidence for the formation of *cis*- and *trans*-isomers was best for the radicals $Me_2Bu^t_2C_4^{+\bullet}$ and $Bu^i_2Bu^t_2C_4^{+\bullet}$. Figure 3(a) illustrates the spectrum obtained from MeC≡CBu^t [equation (v); R = Me, R' = Bu^t] and two species can be distinguished, *A* with *a*(Me) 8.00, *a*(Bu^t) 0.24 G; and *B* with *a*(Me) 9.00 G, *a*(Bu^t) 0.20 G.

Figure 3(c) shows the spectrum obtained from a mixture of MeC≡CMe and Bu^{t}C≡CBu^t [equation (vi); R = Me, R' = Bu^t], and the lines *A* from the previous spectrum together with those (*C*) for $Me_4C_4^{+\bullet}$, and (*D*) for $Bu^t_4C_4^{+\bullet}$ can be distinguished. Lines *A* therefore relate to the *cis*-isomer (10), and *B* to the *trans*-isomer (11) (R = Me, R' = Bu^t).

The situation is similar for the radicals $Bu^i_2Bu^t_2C_4^{+\bullet}$, though the hyperfine coupling by the t-butyl groups was not resolved at first derivative. Figure 4(a) shows the spectrum obtained at −50 °C with Bu^{i}Bu^{t}C$_2$ and Figure 4(c) the result of the same experiment with a mixture of $Bu^i_2C_2$ and $Bu^t_2C_2$; it is clear that the lines *E* relate to *cis*-$Bu^i_2Bu^t_2C_4^{+\bullet}$, *F* to *trans*-$Bu^i_2Bu^t_2C_4^{+\bullet}$, and *G* to $Bu^t_4C_4^{+\bullet}$.

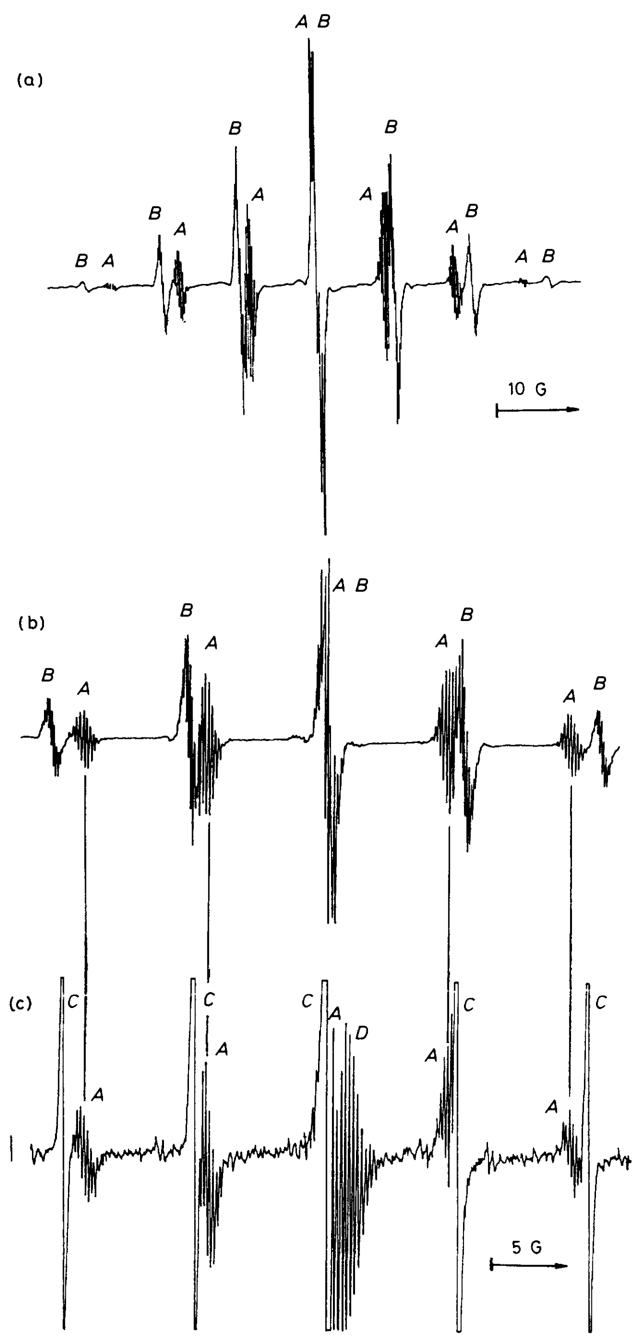


Figure 3. E.s.r. spectra obtained from (a) and (b) MeBu^{t}C$_2$, and (c) Me_2C_2 + $Bu^t_2C_2$, at −50 °C; assignment of the signals as follows: *A*, *cis*-$Me_2Bu^t_2C_4^{+\bullet}$; *B*, *trans*-$Me_2Bu^t_2C_4^{+\bullet}$; *C*, $Me_4C_4^{+\bullet}$, and *D*, $Bu^t_4C_4^{+\bullet}$; note the obvious differences in the *g*-factors shown in (c)

As the temperature was reduced, the value of $a(4H_\beta)$ for both *cis*- and *trans*-$Bu^i_2Bu^t_2C_4^{+\bullet}$ decreased, as would be expected, but both spectra showed a strong alternating linewidth effect [see Figure 4(b) and (c)] so that at −100 °C the lines with M_I ±1 cannot be observed. A similar, though less pronounced effect is present in the spectrum of $Bu^t_4C_4^{+\bullet}$. It appears that with a sufficiently bulky substituent adjacent to the isobutyl group, there is restriction of rotation about the

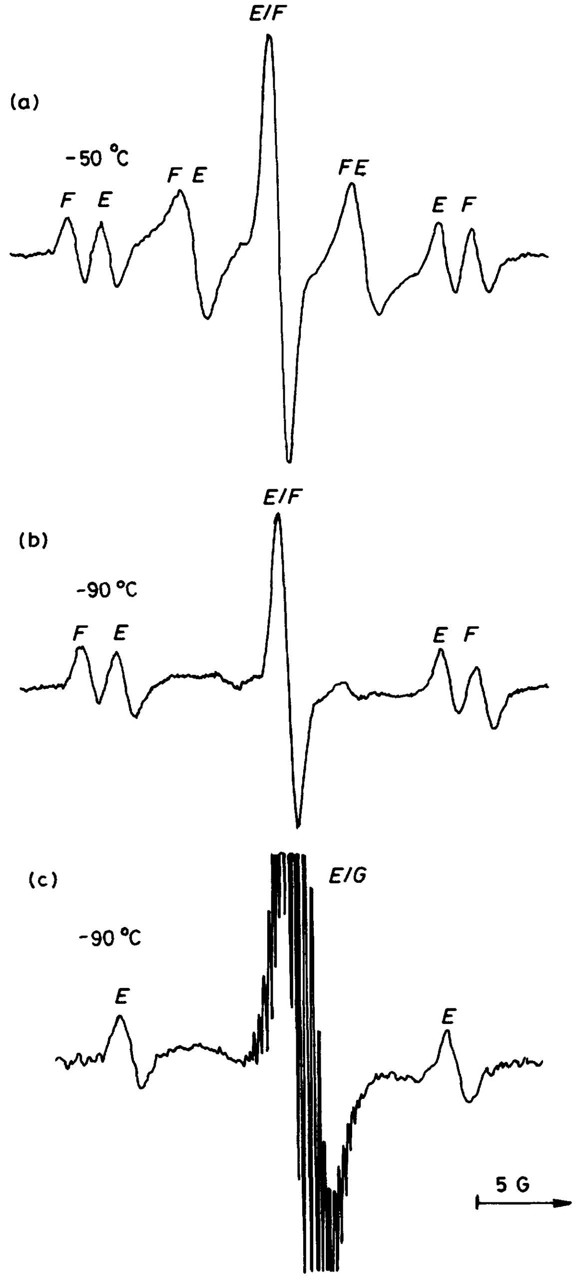
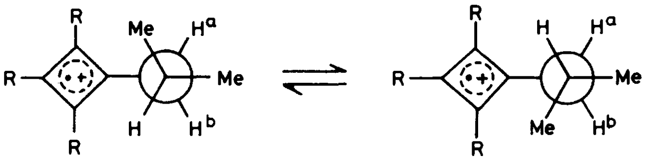


Figure 4. E.s.r. spectra obtained from (a) $\mathrm{Bu^iBu^tC_2}$ at −50 °C, and (b) at −90 °C, and (c) from $\mathrm{Bu^i_2C_2}$ + $\mathrm{Bu^t_2C_2}$ at −90 °C (in the ratio 1 : 4 to minimise the formation of $\mathrm{Bu^t_4C_4^{+\cdot}}$); assignment of the signals is as follows: *E*, *cis*-$\mathrm{Bu^i_2Bu^t_2C_4^{+\cdot}}$; *F*, *trans*-$\mathrm{Bu^i_2Bu^t_2C_4^{+\cdot}}$; and *G*, $\mathrm{Bu^t_4C_4^{+\cdot}}$

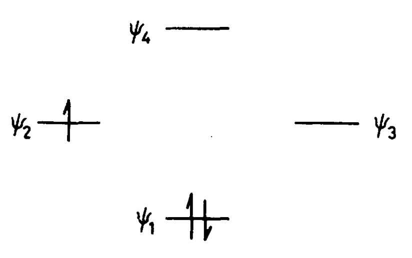
$\mathrm{C_\beta{-}C_\gamma}$ bond, probably as shown in (12), which renders $\mathrm{H_\beta{}^a}$ and $\mathrm{H_\beta{}^b}$ non-equivalent.

Two species were also apparent in the spectrum obtained from the reaction of $\mathrm{EtBu^tC_2}$, but the two sets of signals overlapped, and the hyperfine coupling constants of the two isomers could not clearly be distinguished.

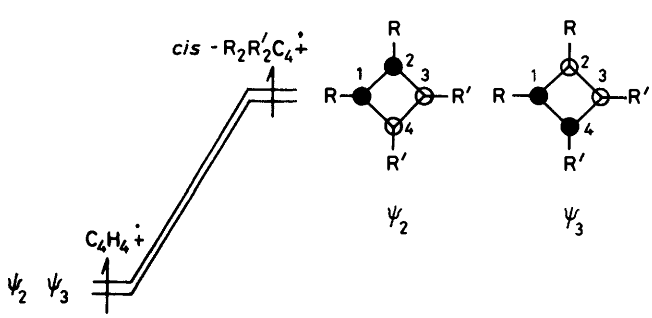
The final radical which showed the presence of isomeric species was $\mathrm{Me_2Et_2C^{+\cdot}}$, but the interpretation is less obvious. The spectrum obtained from a mixture of $\mathrm{Me_2C_2}$ and $\mathrm{Et_2C_2}$ shows lines due to $\mathrm{Me_4C_4^{+\cdot}}$ and $\mathrm{Et_4C_4^{+\cdot}}$, and the remaining spectrum of *cis*-$\mathrm{Me_2Et_2C_4^{+\cdot}}$ can be interpreted in terms of the hyperfine coupling constants *a*(6H) 8.40, *a*(4H) 9.37 G at −91 °C.



(12)



(13)



Scheme 1.

The spectrum obtained from $\mathrm{MeEtC_2}$ can be analysed in terms of two spectra with *a*(6H) 8.58, *a*(4 H) 9.18 G, and *a*(6 H) 9.15, *a*(4H) 9.00 G. We believe that this first spectrum again relates to *cis*-$\mathrm{Me_2Et_2C_4^{+\cdot}}$ in which the coupling constants have been altered slightly by changes in solvation or in counterion interaction. The second set of hyperfine coupling constants then relates to *trans*-$\mathrm{Me_2Et_2C_4^{+\cdot}}$, but the differences between the spectra are too small, and the apparent sensitivity to medium effects is apparently too large, to allow any attempt at a more detailed analysis.

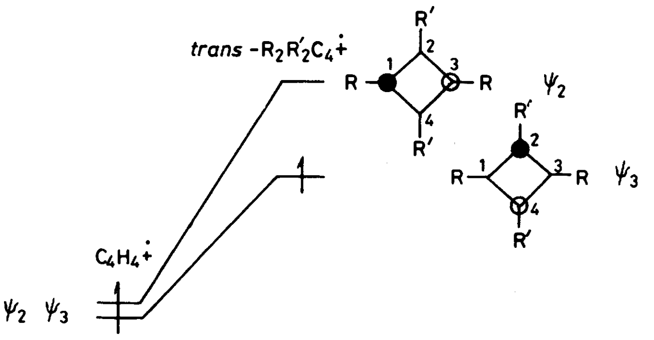
Substituent Effects on Orbital Population.—The model of the breaking of orbital degeneracy by alkyl substituents was first used to interpret the e.s.r. spectra of alkylbenzene radical ions, and has been shown to give a consistent picture of the effect of substituents in the cyclopentadienyl system.[2a,c–e,3] It is interesting to examine the results obtained here on this same model.

The arrangement of the π molecular orbitals in $\mathrm{C_4H_4^{+\cdot}}$ (or $\mathrm{R_4C_4^{+\cdot}}$) is shown in (13): ψ_2 and ψ_3 are degenerate and will be equally occupied by the unpaired electron.

In the mixed alkyl derivatives, $\mathrm{R_2R'_2C_4^{+\cdot}}$, the form of the molecular orbitals ψ_2 and ψ_3 must be chosen to be appropriate to the pattern of substitution. For the *cis*-isomer, the appropriate wave functions are given in equations (vii) and (viii). Although different alkyl substituents may repel

$$\psi_2 = 0.5(\varphi_1 + \varphi_2 - \varphi_3 - \varphi_4) \tag{vii}$$

$$\psi_3 = 0.5\,(\varphi_1 - \varphi_2 - \varphi_3 + \varphi_4) \tag{viii}$$



Scheme 2.

electrons to different degrees, their effects on ψ_2 and ψ_3 will be the same, and the energy levels will stay equal.

For the *trans*-isomer, however, the appropriate wave functions are given in equations (ix) and (x). If, say, the substituents R repel electrons more strongly than the substituents R′, ψ_3 will be destabilised more than ψ_2: the orbital degeneracy will be broken, there will be a Boltzmann distribution of the unpaired electron between ψ_2 and ψ_3, and the e.s.r. spectrum will be changed to reflect the increased occupancy of ψ_2.

$$\psi_2 = 0.71(\varphi_1 - \varphi_3) \quad \text{(ix)}$$

$$\psi_3 = 0.71(\varphi_2 - \varphi_4) \quad \text{(x)}$$

The best evidence for this effect will be given by *cis*/*trans* pairs of radicals for which the two different spectra can be clearly distinguished, and in which the hyperfine coupling constants will not be subject to conformational effects of the type illustrated in Table 4. This effectively limits the evidence to coupling involving the methyl and t-butyl groups, and our best example is provided by the spectra of the *cis*- and *trans*-isomers of $Me_2Bu^t_2C_4^{+\cdot}$ (Figure 3).

One weakness of this model is immediately apparent in that it does not explain why a(Me) in *cis*-$Me_2Bu^t_2C_4^{+\cdot}$ (8.00 G) should be less than in $Me_4C_4^{+\cdot}$ (8.65 G). Possible complications which it ignores are configuration interaction which could lead to splitting of the ψ_2 and ψ_3 energy levels in the *cis*-derivative, irrespective of any substituent effect, molecular distortion as a result of steric interaction by the bulky t-butyl groups, and differential steric hindrance to solvation.

We have shown already that, in the *trans*-isomer, a(Me) is greater and $a(Bu^t)$ is less than in the *cis*-isomer. On the model of differential orbital population, this implies that, in Scheme 2, R = Bu^t and R′ = Me, that is that the Bu^t group is more electron-releasing than the methyl group, so that ψ_2 is more destabilised than ψ_3.

An estimate of the relative population of ψ_2 and ψ_3 by the unpaired electron can be obtained from the hyperfine coupling constants calculated on the Hückel–McLachlan–McConnell model.[1] The McLachlan calculation, taking $\lambda = 0.75$,[2c] gives the spin densities +0.547 and −0.062 for diagonally opposed pairs of atoms in ψ_2 and ψ_3, and if Q_{Me} is taken, from the *cis*-isomer, to be 32 G, the McConnell equation predicts the hyperfine coupling constants a(Me) in ψ_3 (R′ = Me) to be 17.50 G, and a(Me) in ψ_2 (R′ = Me) to be 1.50 G. This suggests that the relative population of ψ_2 and ψ_3 at 183 K is 0.425 : 0.575, implying an energy separation of about 0.46 kJ mol^{-1}. A similar calculation based on the hyperfine coupling constant of the Bu^t group gives the same qualitative conclusion, but is less accurate because $a(Bu^t)$ is relatively small.

Some comparison can be made between this result and those obtained from other alkyl-substituted annulenes. From a study of the e.s.r. spectra of the radicals $RC_5H_4^{\cdot}$, Sakurai[3a] concluded that electron release decreased in the order Me > Et > Pr^i > Bu^t, and, from the spectra of the radicals $RC_5Me_4^{\cdot}$, we concluded that the sequence was (relative interaction energies in kJ mol^{-1}) Me(0) > Et(1.79) ~ Pr(1.84) ~ Bu^t (1.99). There appear to be no similar data for the [6]annulene radical ions.

This apparent inversion of the order of electron release by methyl and t-butyl substituents in the [4]annulenes (Me < Bu^t) and the [5]annulenes (Me > Bu^t) may be real, but equally it might reflect a perturbation by interaction of the radical cation with the solvent and the counterion[22] which would be absent or negligible in the neutral radicals.

Conclusion.—We conclude that the cyclobutadiene radical cations are π-radicals which are essentially planar (at least when the substituents are primary alkyl groups); the e.s.r. spectra under our experimental conditions provide no evidence for Jahn–Teller distortion. The conformation of the alkyl substituents is closer to that expected for cations than for radicals, but this appears to be the result of steric crowding round the ring.

When the alkyl groups in $R_2R'_2C_4^{+\cdot}$ are sufficiently different (*e.g.* Me and Bu^t, or Bu^i and Bu^t), the isomeric *cis*- and *trans*-radicals give rise to different spectra, and analysis of these on the model of the differential population of non-degenerate molecular orbitals suggests that the order of electron release is Bu^t > Me. The interpretation may, however, be complicated by strong interactions between the radical cation and the solvent and counteranion, and these may also be the cause of some of the unusual temperature effects on the hyperfine coupling constants.

Experimental

Dimethylethyne, diethylethyne, di-n-propylethyne, methylethylethyne, ethylpropylethyne, and ethylbutylethyne were commercial specimens supplied by Koch-Light Ltd. Isopropyl-s-butylethyne, isobutyl-t-butylethyne, and t-butyl-t-pentylethyne were provided by Professor L. Miginiac, Université de Poitiers.

Di-isopropylethyne (2,5-*Dimethylhex*-3-*yne*).—Isobutyric acid was esterified with ethanol in the presence of sulphuric acid, then converted into the acyloin,[23] which was oxidised with copper(II) acetate to give 2,5-dimethylhexane-3,4-dione,[24] b.p. 60 °C at 31 mmHg, in 24% overall yield. The dione was refluxed for 60 h with hydrazine hydrate in propan-1-ol[25] giving the 2,5-*dimethylhexane*-3,4-*dione bishydrazone*, m.p. 70—71 °C (from light petroleum) in 11% yield, $\delta(^1H)$ ($CDCl_3$) 1.08 (12 H, d, Me), 2.58 (2 H, septet, C*H*, *J* 9.6 Hz), and 5.25 (4 H, br, NH_2); $\delta(^{13}C)$ ($CDCl_3$) 18.91, 20.43 (CH_3), 32.00 (CH), and 151.33 (C=N); $\nu_{max.}$ (CCl_4) 3 460 (NH_2) and 1 590—1 640 (C=N) (Found: C, 56.1; H, 10.6; N, 32.9. $C_8H_{18}N_4$ requires C, 56.4; H, 10.6; N, 32.9%).

The bishydrazone was converted into the acetylene by a prodecure mentioned but not described in ref. 26. Yellow mercury(II) oxide (1.50 g, 6.91 mmol) was added in portions to a stirred solution of the bishydrazone (0.56 g, 3.29 mmol) in dichloromethane (1 cm^3); nitrogen was evolved and mercury separated. The mixture was stirred for 36 h, then filtered; the n.m.r. spectrum of the filtrate showed that the principal component was di-isopropylethyne, $\delta(^1H)$ (CH_2Cl_2) 1.05 (12 H, d, Me) and 2.35 (2 H, septet, CH); lit. δ(CCl_4) 1.05 and 2.40. This solution was distilled on the vacuum line directly into the e.s.r. tube and used without further purification.

Di-isobutylethyne (2,7-*Dimethyloct*-4-*yne*).—Two attempted preparations from lithium acetylide ($LiNH_2 + C_2H_2$) and isobutyl bromide in the absence or presence of hexamethylphosphoric triamide (HMPT) in the manner described for di-n-butylethyne [27] gave none of the required product. The following method, however, was successful.[28]

1,4-Dichlorobut-2-yne (0.1 mol; b.p. 65—68 °C at 12 mmHg) was added during 1 h to isopropylmagnesium bromide (0.2 mol) in ether (40 cm^3) at −78 °C. After a further 3 h at −78 °C, the mixture was left, stirring, at room temperature overnight.

The resulting grey suspension was treated with glacial acetic acid (11 cm^3), and then poured into water. The organic layer yielded a crude product, boiling over the range 70—190 °C at 760 mmHg.

The ^{13}C n.m.r. spectrum [29] showed that the product was mainly $Bu^iC{\equiv}CBu^i$, along with traces of the impurities reported by Levine *et al.* Careful fractional distillation gave a fraction b.p. 47—58 °C at 10 mmHg, >90% pure (13% yield), which was further purified for e.s.r. studies by preparative g.l.c. (PEG 20 M; 150 °C; N_2 40 cm^3 min^{-1}).

Di-t-butylethyne (2,2,5,5-*Tetramethylhex*-3-*yne*).—(1) 3,3-Dimethylbut-1-ene was treated with bromine in chloroform at −78 °C giving 1,2-dibromo-3,3-dimethylbutane, b.p. 75 °C at 6 mmHg (83%),[30] which reacted with potassium t-butoxide in petroleum (b.p. >200 °C) in the presence of 18-crown-6 to give t-butylethyne (84% yield).[31] This was irradiated in the presence of tosyl iodide to give crude t-butylethynyl tosylate (83%, m.p. 90 °C; lit.,[32] 99—100 °C), which was then treated with t-butyl-lithium, giving di-t-butylethyne (60%), purified for e.s.r. studies by preparative g.l.c.[33]

(2) Bis(trimethylsilyl)ethyne and t-butyl chloride were mixed at −78 °C.[34] Samples were withdrawn, quenched with water, and examined by i.r. and ^1H n.m.r. spectroscopy; after 3 h, the reaction had proceeded to the stage of the formation of $Me_3CC{\equiv}CSiMe_3$.[35] After 30 min at room temperature, the reaction was complete. The solvent was removed at 30 mmHg and 0 °C, and the residue was extracted three times with pentane, giving the crude product (1.54 g, 68%). This was purified by column chromatography on neutral alumina, yielding essentially pure di-t-butylethyne (1.39 g, 61%), which was purified further for e.s.r. purposes by preparative g.l.c. (PEG 20 M; N_2, 40 cm^3 min^{-1}; 60 °C).

Methylpropylethyne (*Hex*-2-*yne*).—Pent-1-yne (Koch-Light) was treated with lithium amide in liquid ammonia, then with methyl iodide.[27] The product was hydrolysed and extracted into 1,3,5-trimethylhexane, and then distilled up to 160 °C at 1 atm. The distillate was purified by preparative g.l.c. (PEG 20 M) yielding methylpropylethyne, δ(200 MHz; $CDCl_3$) 0.97 (3 H, t, CH_2CH_3, *J* 7.43 Hz), 1.49 (2 H, sextet, CH_2CH_3), 7.78 (3 H, t, CH_3C, ^5J 2.54 Hz), and 2.10 (2 H, m, $CHCH_2$).

A similar preparation using $[^2H_3]$methyl iodide gave, after preparative g.l.c. (15% isodecyl phthalate, temperature programmed 80—150 °C, N_2 40 cm^3 min^{-1}), $CD_3C{\equiv}CPr$ (20%); δ($CDCl_3$) 0.97 (3 H, t, CH_2CH_3, *J* 7.02 Hz), 1.49 (2 H, sextet, CH_2CH_3), and 2.10 (2 H, t, CCH_2).

Methylisopropylethyne (4-*Methylpent*-2-*yne*).—Isobutyraldehyde was treated with triphenylphosphine and carbon tetrabromide [36] in dichloromethane, giving 1,1-dibromo-3-methylbut-1-ene.[37] This reacted with 2 equiv. of butyl-lithium in tetrahydrofuran at −78 °C for 1 h, and room temperature for 1 h, to give pent-1-ynyl-lithium, which was treated with methyl iodide, giving methylisopropylethyne.[38]

Methyl-t-butylethyne (4,4-*Dimethylpent*-2-*yne*).—t-Butylethyne was converted into the lithium derivative in liquid ammonia, and treated with methyl iodide giving methyl-t-butylethyne in 25% yield.[27]

Ethyl$[^2H_2]$*propylethyne*.—Pent-1-yne was lithiated with butyl-lithium in HMPT at room temperature for 45 min, then 65 °C for 45 min, and treated with $[1,1\text{-}^2H_2]$ethyl bromide [39] for 30 min at 0 °C, yielding $CH_3CD_2C{\equiv}CPr$.

Ethylisopropylethyne (5-*Methylhex*-3-*yne*).—This was prepared by the ethylation of pent-1-ynyl-lithium with ethyl iodide, as described for the methylation, and purified by preparative g.l.c. The ^1H n.m.r. spectrum agreed with that in the literature.[25b]

Ethyl-t-butylethyne (5,5-*Dimethylhex*-3-*yne*).—t-Butylethynyl-lithium was caused to react with ethyl bromide as described for the reaction with methyl iodide.

E.s.r. Experiments.—E.s.r. experiments were carried out using a Varian E109 spectrometer, fitted with a field-frequency lock, and Telmore sub-harmonic generation for displaying higher-derivative spectra.

The e.s.r. samples were prepared in two distinct ways. In each case a suspension of freshly sublimed (× 2) $AlCl_3$ in dry CH_2Cl_2 (distilled under N_2, from P_2O_5) was introduced into the sample tube using a hypodermic syringe fitted with a wide-bore needle. The commercially available alkynes were routinely used as received; those alkynes prepared as just described were purified by preparative g.l.c. (PEG 20 M; N_2, 40 cm^3 min^{-1}; column temperature 60—100 °C) prior to use.

In those experiments where a single, volatile alkyne was used, a thoroughly degassed sample of the hydrocarbon (50—100 μl) diluted with dry CH_2Cl_2 (40—100 μl) was allowed to distil on the vacuum line ($p \leqslant 0.01$ mmHg) onto a frozen, degassed sample (*ca.* 100 μl) of the $AlCl_3$ suspension contained in the e.s.r. tube. After sealing off, the tube contents were very carefully melted by hand and the tube was rapidly transferred to the pre-cooled (*ca.* −100 °C) spectrometer cavity. Judicious irradiation and/or shaking resulted in the observation of the spectra discussed.

For relatively involatile alkynes or in those experiments where mixtures of alkynes were used, the procedure was modified as follows. The $AlCl_3$ suspension was thoroughly and continuously degassed with dry nitrogen in an e.s.r. tube *via* a thin glass capillary. While a dry nitrogen atmosphere was maintained over the sample (by means of a side arm fitted to the top of the sample tube) and the capillary flow was also maintained, the tube contents were cooled to −95 to −100 °C (acetone–liquid nitrogen slush). The alkyne(s) was then introduced by briefly interrupting the capilliary gas flow and then restarting it to ensure thorough mixing. The tube was then sealed with a PTFE–glass screw seal (J. Young, Acton, England) and then transferred, without warming, to the pre-cooled cavity.

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