Electronic Effects in Cyclobutadiene Radical Cations

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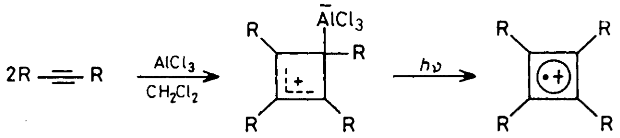
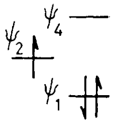
The e.s.r. spectra of the *cis*- and *trans*-radical ions† cyclo-$Me_2Bu^t{}_2C_4^{\cdot +}$, obtained from methyl-t-butylethyne, can be interpreted in terms of the breaking of the degeneracy of the molecular orbitals in the *trans*-isomer by more powerful electron release from the t-butyl groups than from the methyl groups.

The electron distribution in alkyl-substituted benzene radical anions and cations,[1] and in cyclopentadienyl radicals,[2,3] has been studied by e.s.r. spectroscopy, and interpreted in terms of the breaking of the degeneracy of the molecular orbitals. We report here the first evidence for a similar substituent effect in cyclobutadiene radical cations.

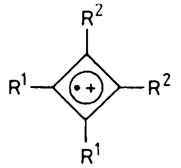
The tetra-alkylcyclobutadiene radical cations (**1**) can be prepared by photolysis of the σ complexes formed between dimerized dialkylalkynes and aluminium chloride.[4] The magnitude of the ^{13}C hyperfine coupling by the atoms of the ring[5,6] establishes that, like the cyclopentadienyl radicals,[2,3] but unlike the cyclopropenyl radicals,[7] the [4]annulenes (**1**) are π rather than σ radicals. The π-electron configuration is illustrated in (**2**).



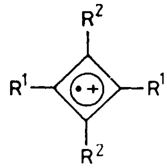
(**1**)



(2)



(3)



(4)

A mixed alkyne, $R^1C{\equiv}CR^2$, could in principle give both the *cis*- and *trans*-isomers† of $R^1{}_2R^2{}_2C_4^{\cdot +}$, (**3**) and (**4**) respectively, but a mixture of the two simple alkynes, $R^1C{\equiv}CR^1$ and $R^2C{\equiv}CR^2$, should give only the *cis*-isomer (**3**) (together with the two simple products $R^1{}_4C_4^{\cdot +}$ and $R^2{}_4C_4^{\cdot +}$).

Most mixed alkynes, when R^1 and R^2 are primary or secondary alkyl groups, give rise to spectra with rather broad lines (*ca.* 0.6 G) which may conceal the presence of two isomers, (**3**) and (**4**), with closely similar hyperfine coupling

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† *cis* and *trans* in this communication indicate the relative positions of R^1 and R^2 on the C_4 ring. *cis* = 1,2-$R^1{}_2$-3,4-$R^2{}_2$; *trans* = 1,3-$R^1{}_2$-2,4-$R^2{}_2$.

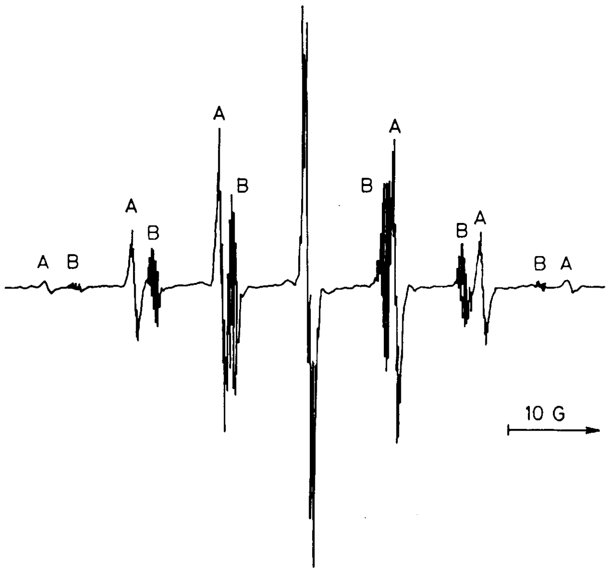
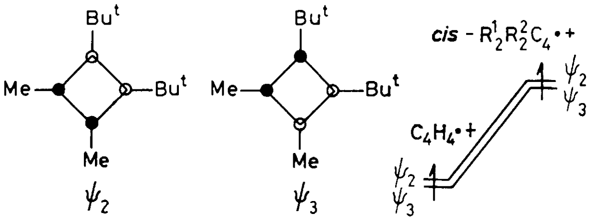


Figure 1. E.s.r. spectrum of the radical cations *trans*-$Me_2Bu^t{}_2C_4{}^{\bullet+}$ [lines (A)] and *cis*-$Me_2Bu^t{}_2C_4{}^{\bullet+}$ [lines (B)], in CH_2Cl_2 at −50 °C.

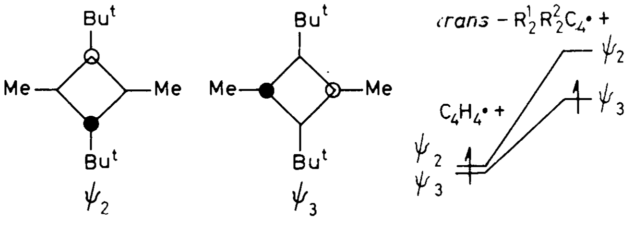


Scheme 1

constants, but methyl-t-butylethyne gives a spectrum (see Figure 1) which shows clearly the signals for two radicals, (A), a(2Me) 9.00 G and a(2Bu^t) 0.20 G, and (B), a(2Me) 8.00 G, a(2Bu^t) 0.24 G at 193 K. The reaction with a mixture of dimethylethyne and di-t-butylethyne gives a spectrum which shows signals due to the radicals $Me_4C_4{}^{\bullet+}$ [a(12H) 8.6 G],[4] and $Bu^t{}_4C_4{}^{\bullet+}$, [a(36H) 0.27 G],[8] and also the lines (B) but not the lines (A), which are present in the spectrum obtained from methyl-t-butylethyne. We conclude that the lines (B) relate to the *cis*-isomer (**3**) and the lines (A) to the *trans*-isomer (**4**) (R^1 = Me, R^2 = Bu^t).

The difference between the two spectra reflects differences in the electron spin distribution in the two isomers. If this spin distribution were to be interpreted on the model of the breaking of the degeneracy of the molecular orbitals, which was used successfully for the cyclopentadienyl radicals, the argument would be as follows. For the *cis*-derivative, the appropriate combination of atomic orbitals is shown in Scheme 1. As the coefficients are the same at each carbon atom, differential electron release by the two types of substituent will have the same effect on ψ_2 and ψ_3 as illustrated. For the *trans*-derivative, the appropriate combination of atomic orbitals is shown in Scheme 2.

If the t-butyl substituents repel electrons more strongly than the methyl substituents, the ψ_2 M.O. will be preferentially destabilised, and the unpaired electron will occupy principally the ψ_3 M.O., so that hyperfine coupling to the methyl group will be enhanced, and that to the t-butyl group will be reduced.



Scheme 2

Table 1. Wave functions and coupling constants for *cis*- and *trans*-$Me_2Bu^t{}_2C_4{}^{\bullet+}$.

cis-$Me_2Bu^t{}_2C_4{}^{\bullet+}$	a(Me)/G
$\psi_2 = 0.50(\phi_1 + \phi_2 - \phi_3 - \phi_4)$	+8.00 (obs.)
$\psi_3 = -0.50(\phi_1 - \phi_2 - \phi_3 + \phi_4)$	+8.00 (obs.)
trans-$Me_2Bu^t{}_2C_4{}^{\bullet+}$	
$\psi_2 = 0.71(\phi_1 - \phi_3)$	+17.50 (calc.)[a]
$\psi_3 = 0.71(\phi_2 - \phi_4)$	−1.50 (calc.)[a]

[a] Taking Q(Me) in the McConnell equation as +32.00 G, (from *cis*-$Me_2Bu^t{}_2C_4{}^{\bullet+}$), and λ in the McLachlan equation as 0.75 (refs. 2b and c).

Coefficients for the molecular orbitals, and the hyperfine coupling constants for the radical in the pure ψ_2 and ψ_3 configurations, calculated on the Hückel–McConnell–McLachlan model,[1–3] are shown in Table 1. The observed hyperfine coupling of 9.0 G in *trans*-$Me_2Bu^t{}_2C_4{}^{\bullet+}$ thus corresponds to a Boltzmann population of 0.425 ψ_2 and 0.575 ψ_3 at 183 K with an energy separation between ψ_2 and ψ_3 of about 0.46 kJ mol^{-1}.

The quantitative significance of this, however, is dubious. This simple model is less satisfactory than it is for the cyclopentadienyl radicals, in particular in that it does not accommodate the fact that a(Me) in $Me_4C_4{}^{\bullet+}$ is different from that in *cis*-$Me_2Bu^t{}_2C_4{}^{\bullet+}$. It is likely that other subtle factors may be involved, such as strain induced by the bulky t-butyl groups, or strong interactions between the radical cation and the solvent and/or counterion, which are not significant with the neutral cyclopentadienyl radicals.

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