Steric Effects in Substituted Cyclobutadiene Radical Cations

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Steric effects on the magnitude of the hyperfine coupling constants, $a(H_\beta)$, in the e.s.r. spectra of the *cis*- and *trans*-isomers of $Et_2Bu^t{}_2C_4{}^{\cdot+}$ have been analysed by molecular mechanics calculations.

Hogeveen's route to the tetra-alkylcyclobutadiene radical cations, equation (1), has made accessible a new and very simple family of annulenes which can be studied by e.s.r. spectroscopy.[1]

We have extended this to the preparation of *cis*- and *trans*-isomers† with mixed alkyl groups [equations (2) and (3)], and have interpreted the spectra of *cis*- and *trans*-$Me_2Bu^t{}_2C_4{}^{\cdot+}$

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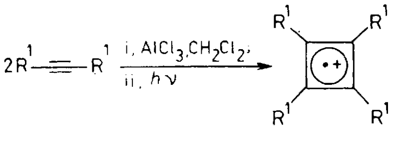
† See footnote in ref. 2 for the use of *cis* and *trans* in this context.

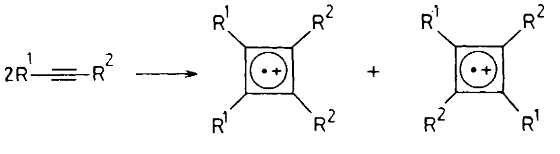
Table 1. Values of $a(H_\beta)$ in $(RCH_2)_4C_4^{\cdot+}$.[a]

RCH_2	HCH_2	$MeCH_2$	$EtCH_2$	$BuCH_2$	Pr^iCH_2
$a(H_\beta)$/G	8.70	7.99	7.15	7.10[b]	6.5

[a] In CH_2Cl_2 at 173 K. The counterion is unidentified, but may be assumed to be constant. [b] At 191 K; ref. 1(b).



(1)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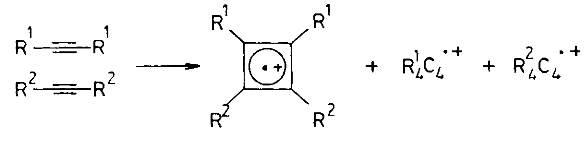

(3)

in terms of the differential electronic effect of the two substituents.[2] In the *trans*-derivative, this can break the degeneracy of the molecular orbitals, and affect the hyperfine coupling constant $a(H_\beta)$ by modulating the electronic term, $\rho_{C\alpha}$, in the Heller–McConnell equation (4).[3] Other effects, particularly differential solvation, may also be important.

$$a(H_\beta) = \rho_{C\alpha}(A + B\cos^2\theta) \qquad (4)$$

In the absence of an over-riding steric effect, alkyl radicals are most stable in the staggered conformation (I),[4] whereas alkyl cations are believed to be most stable in the eclipsed conformation (II),[5] and it is important to determine what conformation will be preferred by an alkyl group RCH_2 in a cyclobutadiene radical cation. We report here the e.s.r. spectra of a series of radical cations, $(RCH_2)_4C_4^{\cdot+}$, in which the effect of the steric term, $\cos^2\theta$, can be identified, and we analyse this steric effect in the isomers of $Et_2Bu^t_2C_4^{\cdot+}$ by molecular mechanics calculations.

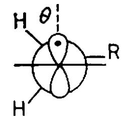
Table 1 shows the values of $a(H_\beta)$ in a series of radical cations $(RCH_2)_4C_4^{\cdot+}$, in which $\rho_{C\alpha}$ for all ring atoms is constant at 0.25. The values of $a(H_\beta)$ are seen to fall as the bulk of R increases, suggesting that the trend is set by a steric effect, the value of θ in equation (4) increasing as the larger alkyl groups R are forced out of the plane of the ring.‡ The value of a(Me) in $Me_4C_4^{\cdot+}$ suggests that, in equation (4), if A is taken to be *ca.* 1 G, B = *ca.* 68 G.

In the radicals $Et_2Bu^t_2C_4^{\cdot+}$, the electronic effect which was identified for the radicals $Me_2Bu^t_2C_4^{\cdot+}$ will be overlain by any steric effect of the type noted for the simple radicals in Table 1. Values for the hyperfine coupling constants for the *cis*- and *trans*-isomers of $Et_2Bu^t_2C_4^{\cdot+}$, prepared from $EtBu^tC_2$, or Et_2C_2 and $Bu^t_2C_2$, as appropriate, by equations (2) and (3), are given in Table 2.

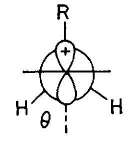
It will be seen, first, that $a(H_\beta)$ in both isomers of $Et_2Bu^t_2C_4^{\cdot+}$ is much lower than in $Me_4C_4^{\cdot+}$, $Et_4C_4^{\cdot+}$, or $Me_2Bu^t_2C_4^{\cdot+}$, although the electronic effect involving the Et and Bu^t substituents would be expected to be less than that involving the Me and Bu^t substituents; and, second, that $a(CH_\beta)$ in *trans*-$Et_2Bu^t_2C_4^{\cdot+}$ is less than that in the *cis*-isomer, opposite to the sequence shown in the isomers of $Me_2Bu^t_2C_4^{\cdot+}$.

Table 2. Hyperfine coupling constants (G) in the radicals $Me_2Bu^t_2C_4^{\cdot+}$ and $Et_2Bu^t_2C_4^{\cdot+}$ at 205 K.

	$Me_2Bu^t_2C_4^{\cdot+}$		$Et_2Bu^t_2C_4^{\cdot+}$	
	a(Me)	$a(Bu^t)$	$a(CH_2)$	$a(Bu^t)$
cis	8.00	0.24	4.45	0.20
trans	9.00	0.20	4.31	0.20



(I)



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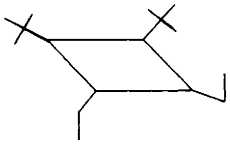
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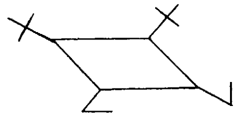
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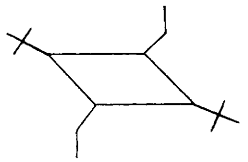
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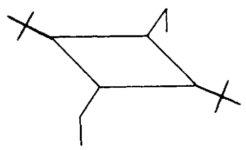
(VI)

On both these counts, the analysis of the spectra in terms of the electronic effect of the substituents would be unsatisfactory, and a dominant steric effect is suggested. We have therefore used molecular mechanics (MM2; QCPE 395) calculations to examine the steric constraints imposed on the ethyl groups in the isomers of $Et_2Bu^t_2C_4^{\cdot+}$.

The cyclobutadiene unit was assumed to be a rigid square of side 1.45 Å. The attached carbon atoms were constrained to lie within the plane of the ring, and appropriate parameters were assumed for stretching, bending, and torsion of the connecting (C_α–C_β) bonds; details will be given in a forthcoming full paper.

The molecular mechanics analysis predicts that *cis*-$Et_2Bu^t_2C_4^{\cdot+}$ has minimum energy in the conformation (III), with the two C_β–C_γ bonds of the ethyl groups orthogonal to the plane of the ring, and (IV) in which one C_β–C_γ bond is orthogonal and one coplanar; (III) is 0.7 kcal mol^{-1} more stable than (IV), with an intervening barrier of *ca.* 1.5 kcal mol^{-1}.

The low value of $a(CH_2)$ may then be seen to result from the molecule existing principally in the conformation (III), although the contribution of (IV) serves to reduce the average angle θ below the maximum of 60°.

The *trans*-isomer is calculated to have minimum energy in the conformations (V) and (VI), *both* with two orthogonal C_β–C_γ bonds, (V) being 1.7 kcal mol^{-1} more stable than (VI)

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‡ As would be expected, this effect is more pronounced in the peralkylbenzene radical cations: $Me_6C_6^{\cdot+}$, $a(H_\beta)$ 6.51 G (at 20 °C); $(MeCH_2)_6C_6^{\cdot+}$, $a(H_\beta)$ 2.63 G (at −16 °C) (ref. 6).

and separated from it by a barrier of about 6 kcal mol^{-1}. The lower value of $a(H_\beta)$ can therefore be rationalised.

This appears to be the first time that molecular mechanics calculations have been used to interpret the structures of radicals. It promises to be a useful technique in a field where the spectroscopic parameters, particularly the hyperfine coupling constants, are so directly related to molecular conformation.

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