Mirror Inversion of the Low-symmetry Ground-state Structures of the Methylcyclohexane and 1,1-Dimethylcyclohexane Radical Cations

An Electron Paramagnetic Resonance Study

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The dynamics of the methylcyclohexane and 1,1-dimethylcyclohexane radical cations in a solid perfluoromethylcyclohexane matrix at low temperature have been studied by electron paramagnetic resonance (EPR) spectroscopy. The reversible variations of the experimental EPR linewidth, observed for both cations in the temperature region 4–173 K, have been reproduced through simulations employing a dynamical model for the molecular motion. It was assumed that an interconversion between two energetically equivalent mirror images of the molecular framework occurred. The related activation energy has been determined to be 0.2 and 0.3 kcal mol^{-1} for the methylcyclohexane and 1,1-dimethycyclohexane radical cations, respectively.

The electronic and geometric structures of cyclic alkane radical cations have attracted much attention lately.[1,2] Both EPR and theoretical studies have revealed comprehensive information about these chemically important species. The radical cations can be produced by ionising radiation and stabilised in halocarbon matrices at low temperature. In addition to structural studies of these species a few investigations focusing on the dynamics have been reported.[3–7] Several neutral cyclic alkanes of high symmetry have a degenerate ground state and are thus subject to distortions upon ionisation due to the Jahn–Teller (J–T) theorem.[8] Toriyama *et al.* proposed that the cyclohexane (cC_6H_{12}) radical cation takes a ^2A_g electronic ground state (C_{2h} symmetry) in halocarbon matrices at low temperature (4.2 K) following from a J–T distortion of the D_{3d} chair structure.[7] The ^2A_g state is characterised by an elongation of the two C—C bonds parallel to the σ_h plane. A non-equivalent dynamical process, described as a pseudo-rotation in the J–T potential with three minima, was suggested to explain the variation of the EPR lineshape as a function of temperature.[7] An alternative rigid ground-state structure of $cC_6H_{12}^+$ was suggested by Lunell *et al.* from the results of *ab initio* calculations.[9] They proposed a further distortion of the cation structure from C_{2h} to C_s giving a $^2A''$ electronic ground state.

The degeneracy of the highest occupied molecular orbital (HOMO) in cC_6H_{12} can be removed by alkyl group substitution on certain positions in the cyclohexane ring. The radical cations of alkyl-substituted cyclohexanes have been studied systematically by EPR.[10–13] It was concluded that alkyl group substitution on one ring carbon resulted in cations having an electronic ground state resembling the ^2A_g state of $cC_6H_{12}^+$ but distorted.[12] In the case of methyl- or 1,1-dimethylcyclohexane cations a feature of the distorted ^2A_g state is the elongation of the two particular C—C bonds in the ring structure. One of them is adjacent to the substituted alkyl group and appears to contain a large fraction of the unpaired electron [fig. 1(*a*)].[12] Thus, hyperconjugation (or the '*trans*' effect) explains the origin of the hyperfine (hf) coupling constants due to certain methyl hydrogens being coaxial with such an elongated bond. The EPR spectra attributed to the methylcyclohexane radical cation ($Me\text{-}cC_6H_{11}^+$) exhibited a linewidth alternation between 4 and 140 K, due to a dynamical averaging process. An exchange between two energetically equivalent mirror structures was proposed to take place at higher temperature causing an averaging of certain hf coupling constants.[13] In analogy with the ground-state structure suggested for $Me\text{-}cC_6H_{11}^+$, the 1,1-dimethylcyclohexane cation ($1,1\text{-}Me_2\text{-}cC_6H_{10}^+$) was also proposed to have a ^2A_g distorted structure [fig. 1(*b*)].[13] A similar temperature-dependent EPR linewidth alternation as observed for $Me\text{-}cC_6H_{11}^+$ was also observed for this cation.

This study concerns a detailed analysis of the experimental data in the temperature region 4–173 K, for $Me\text{-}cC_6H_{11}^+$, $Me\text{-}d_3\text{-}cC_6H_{11}^+$ and $1,1\text{-}Me_2\text{-}cC_6H_{10}^+$. The linewidth alternation observed for $Me\text{-}d_3\text{-}cC_6H_{11}^+$ and $1,1\text{-}Me_2\text{-}cC_6H_{10}^+$ could be reproduced through simulations of the experimental spectra by invoking a dynamical process. The dynamical features can be explained in relation to the distorted ^2A_g structures proposed by us in an earlier report.[13] The analysis of the dynamical motion in this report gives further support for these structures. Furthermore, the activation energies related to the dynamical processes are evaluated and compared with those reported for other cyclic organic radical cations.

Experimental

The solutes, $Me\text{-}cC_6H_{11}$ (Tokyo Kagaku Seiki Co.) and $1,1\text{-}Me_2\text{-}cC_6H_{10}$ (Tokyo Kagaku Seiki Co.) and the matrix, $CF_3\text{-}cC_6F_{11}$ (Fluka and Tokyo Kasei Co.) were obtained commercially and used without further purification. The synthesis of $Me\text{-}d_3\text{-}cC_6H_{11}$ has been described elsewhere.[10] Small amounts (<1 mol %) of the solutes were mixed with the matrix ($CF_3\text{-}cC_6F_{11}$) on a vacuum line using standard

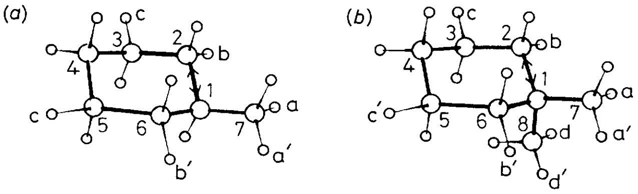


Fig. 1. (*a*) Schematical structure of $Me\text{-}cC_6H_{11}^+$ showing the distorted ^2A_g ground state. (*b*) Schematical structure of $1,1\text{-}Me_2\text{-}cC_6H_{10}^+$ showing the distorted ^2A_g ground state.

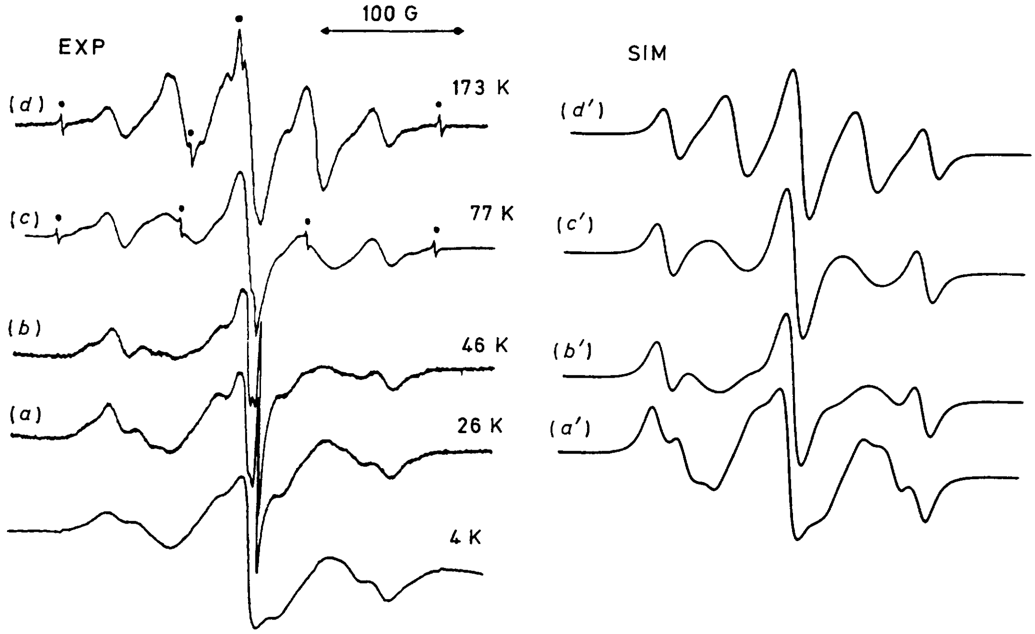


Fig. 2. Experimental EPR spectra attributed to Me-d$_3$-cC$_6$H$_{11}^{+}$ in CF$_3$-cC$_6$F$_{11}$ in the region 4–173 K (left column). The right-hand column shows simulated EPR spectra using the model described in the text and hf parameters given in table 1. The rate constants employed, k/s^{-1} are: (*a*′) 9.5 × 10^6, (*b*′) 2.7 × 10^7, (*c*′) 8.0 × 10^7, (*d*′) 2.4 × 10^8. The linewidth was taken to be 8.0 G. The dots denote signals from a standard sample containing Mn^{2+} ions.

techniques. The radical cations were generated at 4.2 K or 77 K by X- or γ-ray irradiation. The temperature was regulated using an Oxford E9 helium-flow cryostat. Irradiation at 4.2 K was performed employing a double quartz Dewar, the inner part of which was cooled with liquid helium and the outer with liquid nitrogen. All EPR measurements were carried out on a Bruker ER 200 D spectrometer. Simulations of the experimental EPR spectra were performed on a VAX 780 computer utilising a program for calculating exchange-broadened isotropic EPR spectra developed by J. Heinzer.[14] The program uses the equation of motion for the density matrix within the Liouville formalism.

Results and Discussion

Experimental Results

The EPR spectrum of Me-d$_3$-cC$_6$H$_{11}^{+}$ in CF$_3$-cC$_6$F$_{11}$ observed at 4.2 K (fig. 2) consists of an approximate 1 : 2 : 1

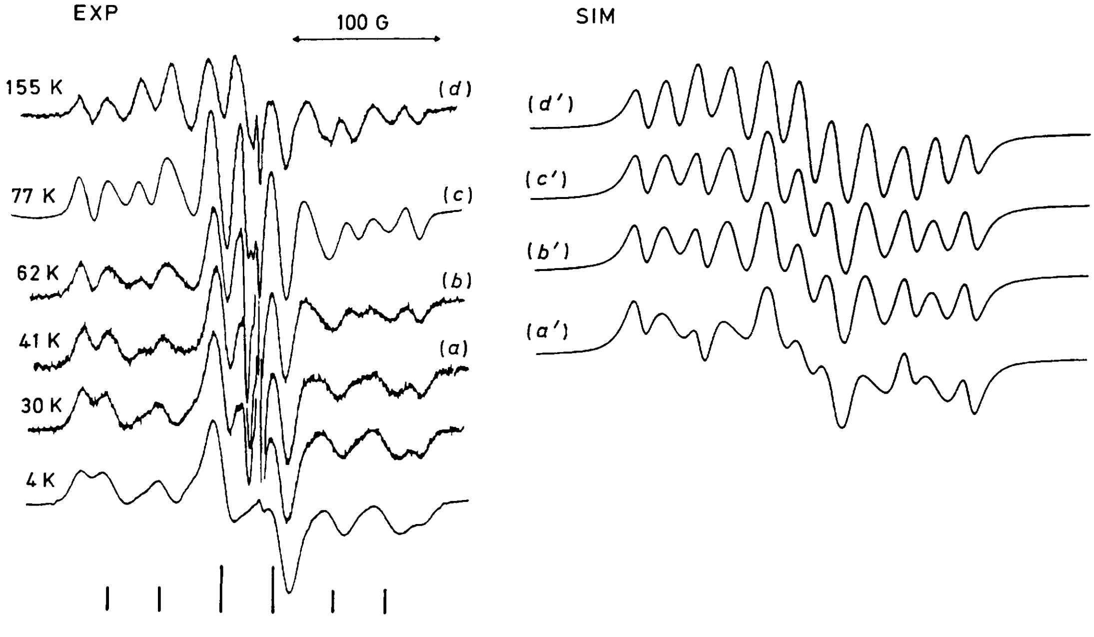


Fig. 3. Experimental EPR spectra of Me-cC$_6$H$_{11}^{+}$ in CF$_3$-cC$_6$H$_{11}$ in the region 4–155 K (left column). The right-hand column shows simulated spectra employing the model described in the text and hf parameters given in table 1. The rate constants employed, k/s^{-1} are: (*a*′) 2.4 × 10^7, (*b*′) 6.4 × 10^7, (*c*′) 7.6 × 10^7, (*d*′) 1.6 × 10^8. The linewidth was taken to be 8.0 G.

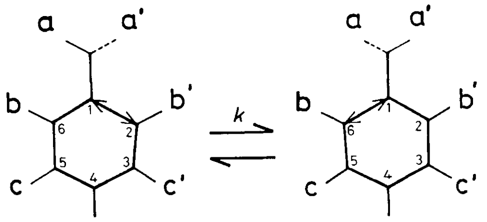
triplet with a splitting of *ca.* 74 G (2H). This spectrum is attributed to two equatorial hydrogens within the ring structure, each being in a *trans* position with respect to the elongated bonds of the distorted ^2A_g structure.[13] From the simulations of the dynamical process, the corresponding hf coupling constants were determined more accurately: a(1H) = 70 G and a(1H) = 78 G, as will be shown in the next section. Although slightly different, the latter values are consistent with the triplet spectrum due to the broad experimental linewidth. Assigning the two hydrogens slightly non-equivalent hf coupling constants is in agreement with semiempirical MO (MNDO/INDO) calculations which predicted different values for the two hydrogens.[12] The spectrum observed at 4.2 K changed reversibly into a quintet with nearly binomial intensity at 173 K, as shown in fig. 2. The high-temperature EPR spectrum can be analysed with the following hf parameters: a(2H) = 48.8 G and a (2H) = 42.7 G.[10,13] The total width of the spectra remains constant throughout the whole temperature interval. The central part of the spectra is slightly distorted due to a background signal from the matrix. The alternation of the linewidth in the temperature region 4–173 K indicates the presence of a dynamical process. The 4.2 K spectrum of Me-cC$_6$H$_{11}^+$ can be qualitatively explained as a triplet of doublets, as shown by the stick plot in fig. 3. It changes reversibly into an eleven-line spectrum at 155 K. This spectrum can be simulated with the following hf parameters: a(2H) = 48.8 G, a(2H) = 42.7 G and a(2H) = 20.1 G.[10,13] Note that the width of the spectra remains constant throughout the studied temperature interval also with the protonated methyl (Me) group.

An EPR spectrum attributed to 1,1-Me$_2$-cC$_6$H$_{10}^+$ observed at 4.2 K, is shown in fig. 4. This spectrum was analysed with the following hf coupling constants: a(2H) = 61 G and a(2H) = 29 G. A reversible change of the EPR linewidth, starting at *ca.* 30 K, was observed when the temperature was varied, as depicted in fig. 4. The thirteen-line spectrum present at 77 K can be reproduced by simulations employing a dynamical model similar to the cases above. Details are given in the next section. Some EPR spectra are distorted in the central part by a matrix background signal of relatively high amplitude.

Simulations

We have discussed the electronic structure of Me-cC$_6$H$_{11}^+$ and analogous cations in detail in previous reports.[12,13] Me-cC$_6$H$_{11}^+$ was proposed to have a distorted ^2A_g electronic ground state with one elongated C—C bond adjacent to the methyl-substituted carbon atom [fig. 1(*a*)]. This structure can be thought to originate from the ^2A_g state of the cyclohexane ring.[7] The two equatorial hydrogens at the C$_2$ and C$_5$ positions (see labelling below), give large hf coupling constants. Furthermore, if a methyl hydrogen is in a *trans* position relative to the elongated C$_1$—C$_6$ bond it also exhibits a relatively large hf coupling constant (34 G). The purpose of the present study is to verify that the proposed structure governs the dynamics. In the previous study of Me-cC$_6$H$_{11}^+$, a dynamical model was suggested, in which an interchange between two energetically equivalent distorted ^2A_g states occurred.[13]

Owing to the simpler form of the spectra belonging to Me-d$_3$-cC$_6$H$_{11}^+$ (fig. 2), we have chosen these data to be representative for the dynamics of Me-cC$_6$H$_{11}^+$ and discuss them in some detail. The dynamical model for Me-d$_3$-cC$_6$H$_{11}^+$ can be described by a two-site jump process where an interchange takes place between two distorted structures which are mirror images of each other, as depicted below.



An interchange according to this scheme will hence average the hf coupling constants of certain labelled hydrogens and their primed analogues. The unknown hf coupling constants can be evaluated from the averaged values corresponding to the spectra of Me-d$_3$-cC$_6$H$_{11}^+$ and Me-cC$_6$H$_{11}^+$

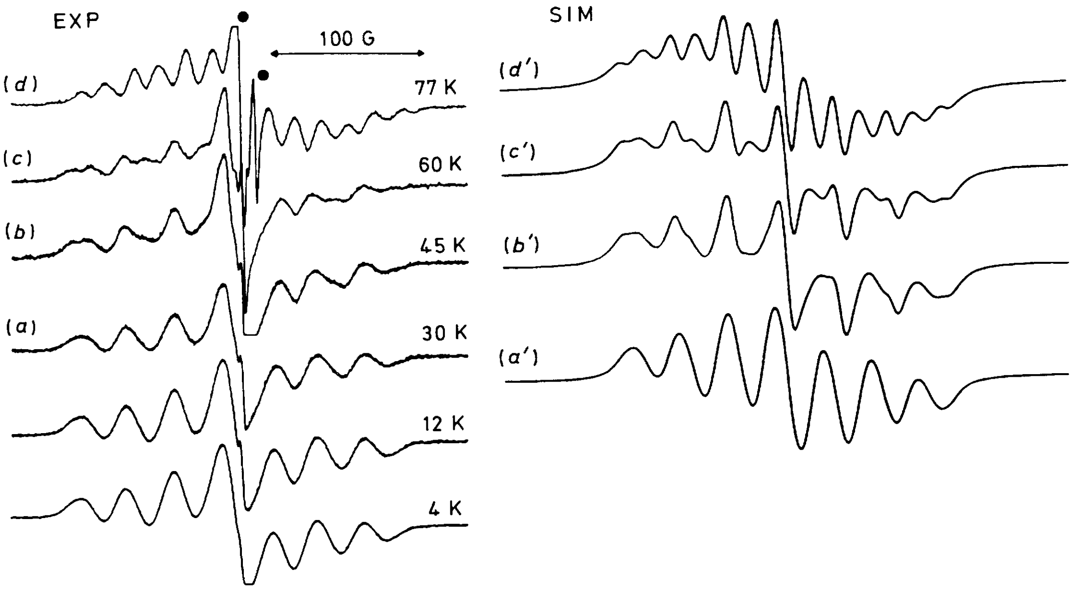


Fig. 4. Experimental EPR spectra of 1,1-Me$_2$-cC$_6$H$_{10}^+$ in CF$_3$-cC$_6$F$_{11}$ in the region 4–77 K (left-hand column). The right-hand column shows the simulated spectra employing the dynamical model described in the text and hf parameters given in table 1. The rate constants used, k/s^{-1} are: (*a'*) 2.3 × 10^6, (*b'*) 1.4 × 10^7, (*c'*) 2.2 × 10^7; (*d'*) 5.6 × 10^7. The linewidth was taken to be 10.0 G. The dots denote overlapping signals from matrix radicals and the damaged quartz sample tube.

observed at high temperaure.[10,13] Using these values the following relations are obtained: $(a + a')/2 = 20.1$ G, $(b + b')/2 = 42.7$ G, $(c + c')/2 = 48.8$ G.

We cannot be certain about the actual assignment of b(b′) and c(c′) solely from this dynamical model. The labelling of b(b′) and c(c′) might equally well be interchanged. However, MNDO/INDO calculations support the assignment made above.[12] The values of the two largest hf coupling constants (b′ and c) were varied until the best agreement between the experimental and simulated data was obtained. All hf parameters employed in the simulations are presented in table 1. The hf coupling constants for the deuterons on the Me group (1.0 and 5.2 G) were determined from the data of Me-c$C_6H_{11}^+$, using the ratio between the magnetic moments for hydrogens and deuterons (a factor 6.52). By employing this model, the experimental and simulated spectra of Me-d_3-c$C_6H_{11}^+$ in the temperature region 26–173 K were found to be in satisfactory agreement, as shown in fig. 2. The 4.2 K spectrum of Me-d_3-c$C_6H_{11}^+$ (fig. 2) is slightly broader than the 26 K spectrum. However, the 4.2 K spectrum could be simulated if the linewidth was slightly increased and the rate constant taken to be $k \approx 6 \times 10^6$ s^{-1}. This rate does not correspond to the quasi-rigid limit, *i.e.* where the EPR linewidth is not affected by the motion ($k \approx 10^6$ s^{-1}). This fact suggests that motion is already present at 4.2 K. An Arrhenius plot as shown in fig. 5, where $\ln k$ (s^{-1}) is plotted *vs.* T^{-1}/K^{-1}, gives the activation energy related to the motion, $E_a = 0.2$ kcal mol^{-1}.

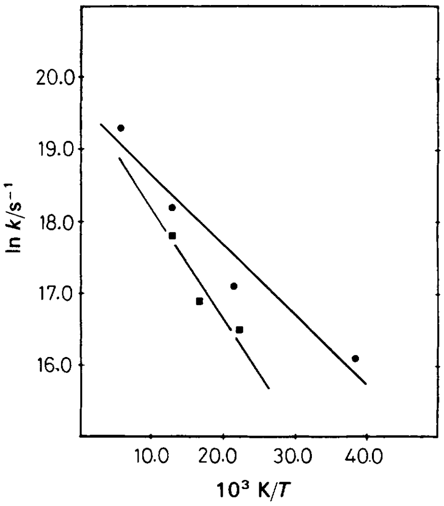
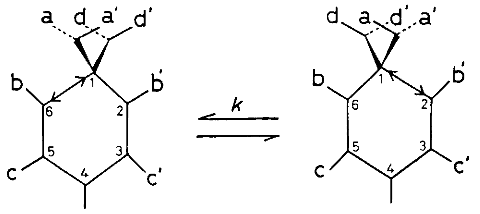


Fig. 5. Arrhenius plot. $\ln k/s^{-1}$ *vs.* 10^3 K/T for Me-d_3-c$C_6H_{11}^+$ (●) and 1,1-Me_2-c$C_6H_{10}^+$ (■). ●, $E_a = 0.2$ kcal mol^{-1}; ■, $E_a = 0.3$ kcal mol^{-1}.

Me-c$C_6H_{11}^+$ gives a more complicated hf structure as shown in fig. 3. In order to simulate these spectra we employed the same two-site model as used above (see hf coupling constants given in table 1). Using this model the experimental spectra in the temperature region 41–155 K could be simulated with qualitative agreement as shown in fig. 3. The effect of a significant contribution to the hf coupling constants from the hydrogens on the Me group seems to complicate the analysis in the low-temperature ($T < 41$ K) region. However, the rate constants corresponding to the region 41–155 K seem to be appropriate if the results from the analysis of Me-d_3-c$C_6H_{11}^+$ are considered. The simple two-site model used for Me-d_3-c$C_6H_{11}^+$ cannot account for the spectrum observed at 4.2 K for Me-c$C_6H_{11}^+$.

In attempts to explain the 4.2 K spectrum, two other models were also investigated through simulations. The first model allowed a rotation of the Me group described as a separate motion decoupled from the site jumping between the two distorted ^2A_g states, using a six-site model with two different rate constants. However, the agreement between the experimental and simulated EPR spectra was not improved when the Me group was allowed to rotate independently of the site jumping. Therefore, it is suggested that the Me group appears to be quasi-rigid on the EPR timescale. Another dynamical model studied included a nearby state of C_s symmetry with slightly higher energy, which might act as an intermediate state.[13] This model was described by a three-site jump model with two different rate constants. Although this model does not reproduce the spectrum observed at 4.2 K, the spectra in the temperature region 41–155 K could be reproduced with acceptable agreement. Thus, the existence of a state of C_s symmetry cannot completely be ruled out. However, there is no direct experimental evidence supporting a population of such a state.

As shown in fig. 4, the dynamics of 1,1-Me_2-c$C_6H_{10}^+$ start to affect the EPR linewidth above *ca.* 30 K. It was assumed that a dynamical process similar to that of Me-d_3-c$C_6H_{11}^+$ and Me-c$C_6H_{11}^+$ is present also for 1,1-Me_2-c$C_6H_{10}^+$. Therefore, the following two-site model was examined.



Here the interchange takes place between two equivalent mirror images in analogy with the case of Me-c$C_6H_{11}^+$. The

Table 1. The dynamical models employed in the simulations

	hyperfine coupling constants/G					
	Me-d_3-c$C_6H_{11}^+$		Me-c$C_6H_{11}^+$		1,1-Me_2-c$C_6H_{10}^+$	
hydrogen	site 1	site 2	site 1	site 2	site 1	site 2
a	1.0[a]	5.2[a]	6.2	34	5.0	29
a′	5.2[a]	1.0[a]	34	6.2	29	5.0
b	15.4	70	15.4	70	8.0	61
b′	70	15.4	70	15.4	61	8.0
c	78	19.6	78	19.6	61	8.0
c′	19.6	78	19.6	78	8.0	61
d	—	—	—	—	5.0	29
d′	—	—	—	—	29	5.0

[a] Nuclear spin; $I = 1$.

electronic structure of 1,1-Me_2-$cC_6H_{10}^+$ has been described in an earlier study and it resembles the structure proposed for Me-$cC_6H_{11}^+$ [fig. 1(*b*)].[12] Only the large hf coupling constants *a*(b′ and c) = 69 G and *a*(a′ and d′) = 29 G, are known from experiment. The sum of the hf couplings observed at 77 K [fig. 4(*d*)], $\Sigma a_i = 206$ G, differs from the sum observed at 4.2 K, $\Sigma a_i = 2 \times (61 + 29) = 180$ G, indicating that some of the hf couplings are buried in the linewidth which is broader at 4.2 K (*ca.* 23 G). The difference, 206 − 180 = 26 G, was assigned to the hydrogens b and c′ in the ring, and a and d on the methyl group, being pairwise equivalent, and was treated as a parameter in the simulations. The two sets of hf couplings (table 1) were varied until the best agreement with the experimental results was obtained, as shown in fig. 4. Owing to the superposition of matrix signals in the central part of the experimental spectra, the outer wings of the simulated ones appear to be more intense. Note that the Me groups were not allowed to rotate in the simulations. Plotting ln k/s^{-1} *vs.* 10^3 K/*T* as shown in fig. 5, gives an activation energy $E_a = 0.3$ kcal mol^{-1}.

Discussion

The dynamics of radical cations and neutral radicals of organic cyclic molecules stabilised in halocarbon matrices have been investigated by several groups (table 2). The reported activation energies can be divided into two groups: cations and neutral radicals with twisted ring structures having activation energies of the order 1.2–2.8 kcal mol^{-1} such as *e.g.* THF^+, $cC_5H_9^{\cdot}$ *etc.*, and the J–T active species such as $cC_3H_6^+$ and $cC_6H_{12}^+$ having considerably lower energy barriers, of the order 0.05–0.68 kcal mol^{-1}. Note that the activation energies evaluated for Me-d_3-$cC_6H_{11}^+$ and 1,1-Me_2-$cC_6H_{10}^+$, 0.2 and 0.3 kcal mol^{-1}, respectively, are close to the values, 0.17 and 0.24 kcal mol^{-1}, reported for the non-equivalent site jumping of $cC_6H_{12}^+$.[2] This suggests that $cC_6H_{12}^+$, Me-$cC_6H_{11}^+$ and Me_2-1,1-$cC_6H_{10}^+$ have similar exchange mechanisms. Hence, alkyl substitution by a methyl group in the cyclohexane ring does not increase the activation energy considerably. The dynamical processes for $cC_6H_{12}^+$ and Me-$cC_6H_{11}^+$ both involve movement of elongated carbon bonds which can be considered as rather small structural changes compared with those for five-membered rings where inversion of the ring usually occurs. This might explain why the activation energies of the radical cations of cyclopropane, cyclohexane and Me-substituted cyclohexanes are much lower (table 2). As described in the earlier section, Me-d_3-$cC_6H_{11}^+$ exhibits motional averaging at 4.2 K. It seems appropriate to attribute this motion to a population of vibrational states due to a thermal activation. Thus, the shallow energy barrier between the two energetically equivalent mirror structures makes the interchange process possible.

The fact that the activation energy evaluated for 1,1-Me_2-$cC_6H_{10}^+$, 0.3 kcal mol^{-1}, is close to the value 0.2 kcal mol^{-1}, for the motion of Me-d_3-$cC_6H_{11}^+$, supports the conclusion that both radical cations have similar electronic structures. Here we emphasise the small structural changes required for an interconversion of the molecular framework between the two mirror images. Both Me-$cC_6H_{11}^+$ and 1,1-Me_2-$cC_6H_{10}^+$ have the Me groups in a rigid conformation in CF_3-cC_6F_{11}. This conclusion was supported by trial simulations allowing a rotation of the Me group for Me-$cC_6H_{11}^+$. Hence, the σ-delocalised SOMO stabilises a hydrogen on the Me group to be coaxial relative the elongated $C_1—C_2$ bond in the ring. Werst *et al.* have recently studied Me-$cC_6H_{11}^+$ at 190 K in n-hexane solution by using the time-resolved fluorescence magnetic resonance method (FDMR).[16] They observed the following hf parameters: *a*(4H) = 48 ± 1 G and *a*(3H) = 13 ± 1 G, which corresponds to an averaged structure of the ring according to our two-site model and a rotating Me group. These averaged hf coupling constants are consistent with ours evaluated for the rigid structure of Me-$cC_6H_{11}^+$ in the CF_3-cC_6F_{11} matrix. Several alkyl-substituted cyclohexane radical cations have been studied comprehensively and none exhibited dynamical motion as observed for Me-$cC_6H_{11}^+$ and Me_2-1,1-$cC_6H_{10}^+$.[11–13] This can be explained by the geometrical structures of these cations having a higher energy barrier for interchanging between different conformations. In the discussion of the magnitude of the activation energies we must keep in mind that the rate constants sometimes depend on the matrix used.[2]

In conclusion, both Me-$cC_6H_{11}^+$ and 1,1-Me_2-$cC_6H_{10}^+$ are proposed to exhibit thermally activated dynamics characterised by an interchange between two energetically equivalent mirror images. The analysis of the alternation of the experimental EPR linewidth due to the dynamics supports the previous assignment of structures for Me-$cC_6H_{11}^+$ and 1,1-Me_2-$cC_6H_{10}^+$.[12,13] The activation energy for the exchange process was determined to be 0.2 and 0.3 kcal mol^{-1} for Me-$cC_6H_{11}^+$ and 1,1-Me_2-$cC_6H_{10}^+$, respectively. These values are close to those observed for $cC_6H_{12}^+$, suggesting a similar dynamical process and electronic ground state.

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Table 2. Dynamical motion and activation energies for some cyclic radical cations and neutral radicals stabilised in halocarbon matrices

radical	matrix	*T*/K	model	E_a/kcal mol^{-1}	ref.
c-$C_3H_6^+$	CF_3CCl_3	4–102	three-site	0.68	2
	$CF_2ClCFCl_2$	4–102	three-site	0.54	
	$CFCl_3$	4–102	three-site	0.05	
	SF_6	4–102	three-site	0.034	
c-$C_5H_{10}^+$	CF_3CCl_3	4–110	ten-site	1.2[b]	4
			two rates	3.6[c]	
c-$C_6H_{12}^+$	$CFCl_3$	18–37	two-site	0.17	2
		30–140	three-site	0.24	
c-$C_5H_9^{\cdot}$	$CF_2ClCFCl_2$	100–135	two-site	2.8	15
THF^+	$CFCl_3$	77–155	two-site	1.65	3
$C_4H_8NH^+$	$CFCl_3$	75–93	two-site	1.6	17
	CF_2ClCF_2Cl	74–111	two-site	2.0	
$C_4H_8N^{\cdot}$	$CF_2ClCFCl_2$	123–141	two-site	1.9	17
	CF_2ClCF_2Cl	111–130	two-site	1.3	
Me-d_3-cC_6^+	CF_3-cC_6F_{11}	4–173	two-site	0.2	[a]
1,1-Me_2-cC_6^+	CF_3-cC_6F_{11}	4–77	two-site	0.3	[a]

[a] This study. [b] Inversion of the ring. [c] Pseudorotation.

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