Radical Cations of Cyclohexanes Alkyl-substituted on One Carbon: An ESR Study of The Jahn–Teller Distorted HOMO of Cyclohexane

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Cation radicals of cyclohexanes alkyl-substituted on one carbon have been stabilized in perfluoromethylcyclohexane and other halocarbon matrices at 4.2 K and studied by means of ESR spectroscopy. It was found that all have an electronic ground state resembling the ^2A_g state of the cyclohexane cation, one of the possible states following a Jahn–Teller distortion of the D_{3d} cyclohexane chair structure. The cations can be classified into two groups depending on the substituted alkyl group. To the first group belong the cations with a methyl group or a primary carbon (ethyl, n-propyl or isobutyl group) attached to the ring. The disubstituted cyclohexane cations of 1,1-dimethylcyclohexane and 1-methyl-1-ethylcyclohexane were also found to have a similar structure. The ESR spectra are characterized by a 1:2:1 three-line pattern with the hyperfine (hf) splitting due to two magnetically equivalent equatorial ring hydrogens. The magnitude of the splitting was found to depend on the size and number of substituents, ranging from 74 G (methylcyclohexane$^{\cdot+}$) to 55 G (isobutylcyclohexane$^{\cdot+}$). An additional doublet, 17–34 G, due to a hydrogen on the substituent could be detected in certain cases. Such hydrogens are axial with one of the elongated C–C bonds in the ring structure which contains a relatively large fraction of the unpaired electron. It follows that the substituents are located asymmetrically with respect to an a_g-like SOMO in the ring. In the second group a secondary or tertiary carbon connects the substituent to the ring, such as an isopropyl or *tert*-butyl group. The largest hf splittings are *ca.* 30 G in magnitude, due to certain hydrogens on the substituent which are axial with respect to the cyclohexyl bond. It follows that an a_g-like SOMO in the ring here is symmetrically arranged with respect to the position of the substituent. Hyperconjugation is the dominating mechanism for the spin transfer in all cations reported in this study.

Radical cations of cycloalkanes with high symmetry have attracted much attention,[1–5] since in the neutral form they usually have a degenerate highest-occupied molecular orbital (HOMO). In such cases, the cations formed by ionization can provide important experimental information on the static and dynamic Jahn–Teller effect.[6] The radical cation of cyclohexane is of particular interest.[7–10] Iwasaki and Toriyama[8,9] have proposed a ^2A_g state in C_{2h} symmetry which is consistent with the Jahn–Teller effect. The authors base their arguments on ESR data with ^1H hyperfine (hf) splittings for a rigid structure extrapolated from the dynamics of the cation above 4 K. It was assumed that the cation exhibits 'site-jumping' even at liquid helium temperature. Lunell *et al.*,[10] on the other hand, suggested an electronic ground state of lower symmetry, $^2A''$ in C_s, from the results of *ab initio* calculations. More persuasive experimental and theoretical investigations seem necessary in order to elucidate further details on the ground-state structure for the cyclohexane cation, especially since it is of such fundamental interest.

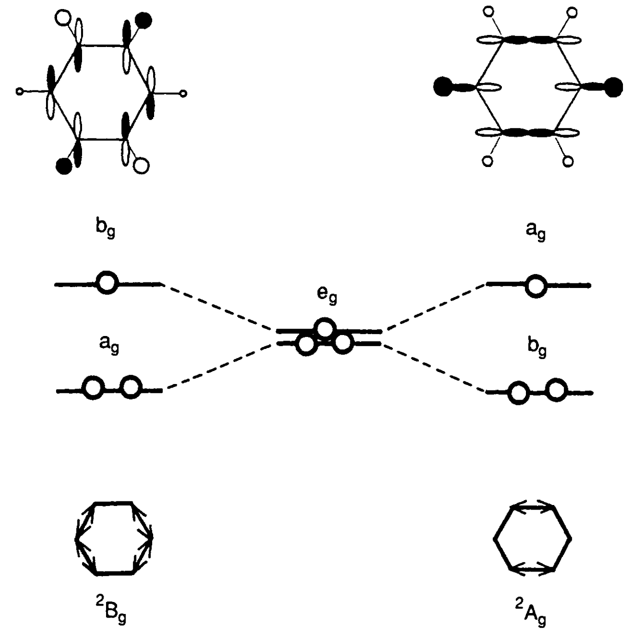
The introduction of substituents to cyclohexane is a chemically intuitive way of splitting the degenerate HOMO, and makes it possible to study electronic states similar to those predicted by the Jahn–Teller theorem.[11,12] We have recently reported ESR studies on radical cations of cyclohexanes substituted with two or three alkyl groups in a certain symmetrical or asymmetrical manner.[13] It was found that such cations can be classified into electronic ground states resembling either the ^2A_g, ^2B_g or $^2A''$ ground states possible for the cyclohexane cation itself. This classification was possible by comparing experimental ^1H hf splittings with those calculated using semiempirical MNDO and INDO MO methods. MNDO gave the optimized geometry for each state and INDO the associated hf splittings.

In this report we present the experimental results of radical cations of certain monosubstituted alkylcyclohexanes, such as methyl-, ethyl-, n-propyl-, isopropyl-, isobutyl- and *tert*-butylcyclohexane and the cations of 1,1-dimethylcyclohexane and 1-methyl-1-ethylcyclohexane. It will be shown how the SOMO in all cations originates from an a_g orbital of the Jahn–Teller distorted ring structure. The ESR line shapes for the methyl- and 1,1-dimethylcyclohexane cations were found to depend on the temperature. The latter phenomenon can be explained by a dynamic process, which brings a 'distorted' A_g structure to interchange with its own mirror image.

Ionization of Cyclohexane.—All alkylcyclohexanes presented in this study can be expected to adopt a chair conformation with the substituent in the equatorial position.[14] 1,1-Dimethylcyclohexane and 1-methyl-1-ethylcyclohexane have one of the substituents in the axial position. As an introduction to the various structures of the cations, it is instructive to give a brief summary of the ionization of the chair form of unsubstituted cyclohexane.

By the loss of one electron from the degenerate e_g orbital of cyclohexane (D_{3d}) either an ^2A_g or ^2B_g state of lower symmetry (C_{2h}) is stabilized according to the Jahn–Teller effect. The geometrical distortion is an elongation or a contraction of certain carbon–carbon bonds,[10,12,13] as depicted in the diagram.

The ESR hf pattern of the ^2A_g state is dominated by a large ^1H hf splitting due to the two equivalent equatorial hydrogens located in *trans* position with respect to the elongated bonds. The magnitude of the ^1H hf interaction has been estimated to be



ca. 100 G from *ab initio*[10] and INDO[12,13] calculations of geometries optimized with respect to the energy. The ESR signal associated with the ^2B_g state is characterized by an hf splitting of *ca.* 60 G due to a set of four equivalent equatorial hydrogens.[10,12,13]

We have not considered here the $^2A''$ state (in C_s), which was suggested by Lunell *et al.*[10]

Experimental

Perfluoromethylcyclohexane (CF_3-*c*C_6F_{11}, >95%) and other halocarbons (>99%) obtained from Tokyo Kasei were used as matrix.[11–13,15,16] Solutes of non-deuteriated compounds (>99%) were obtained from Tokyo Kagaku Seiki and used without further purification. [$^2H_3$]Methylcyclohexane ([$^2H_3$]Me*c*C_6; 95 at.%) was obtained by hydrogenation of [α,α,α-$^2H_3$]-toluene. [3,3,5,5-$^2H_4$]-Methylcyclohexane ([3,3,5,5-$^2H_4$]Me-*c*C_6; 90 at.%) was synthesized by the following procedures: base-catalysed exchange of 4-methylcyclohexanone with D_2O; reduction of [2,2,6,6-$^2H_4$]-4-methylcyclohexanone with lithium aluminium hydride; bromination of [2,6,6-$^2H_4$]-4-methylcyclohehanol and reduction of [3,3,5,5-$^2H_4$]-4-bromomethylcyclohexane. Frozen solutions containing *ca.* 1 mol% of solute, degassed by several freeze and thaw cycles, were irradiated with γ-rays at 4.2 and 77 K. This is a well-established method to generate the solute radical cations and stabilize them in the matrix.[16–19] The ESR spectra were recorded at temperatures from 4.2 K to phase transitions in the matrix (for example, *ca.* 180 K for CF_3-*c*C_6F_{11}[20]), where the cations decay out under the formation of neutral radicals. The associated reaction mechanisms and radical structures will be described elsewhere.[21]

Results and Discussion

Methylcyclohexane and Ethylcyclohexane.—Our previous work on the methylcyclohexane cation[11,12] has been considerably extended and is discussed here in more detail. ESR spectra of radical cations of protiated methylcyclohexane (Me-*c*C6) and two selectively deuteriated methylcyclohexanes, [$^2H_3$]Me-*c*C6 and [3,3,5,5-$^2H_4$]Me-*c*C6 are shown in Fig. 1. The spectrum of Me-*c*C6$^{\bullet +}$ consists of a triplet of doublets with hf splittings of *ca.* 74 G (2H) and *ca.* 34 G (1H), assuming isotropic hf splittings [the stick plot under Fig. 1(*a*)]. The doublet is suppressed in the spectrum of [$^2H_3$]Me-*c*C6$^{\bullet +}$ [Fig. 1(*c*)], and the corresponding hf interaction can be attributed to one of the methyl hydrogens; the ratio of the magnetic moments of hydrogen and deuterium is 6.5 and the deuterium splitting becomes too small to be resolved. The triplet splitting of *ca.* 74 G is attributed to two hydrogens in the ring having approximately the same unpaired electron density. The cation of the isoopically-labelled compound, [3,3,5,5-$^2H_4$]Me-*c*C6, has an ESR signal dominated by a doublet of doublets with 74 G (1H) and 34 G (1H) splittings, as shown in Fig. 1(*b*). The lines marked with an asterisk are due to an isotopic impurity. Conclusively, the splitting of 74 G is due to one of the four hydrogens as either C-3 or C-5 (see Fig. 2).

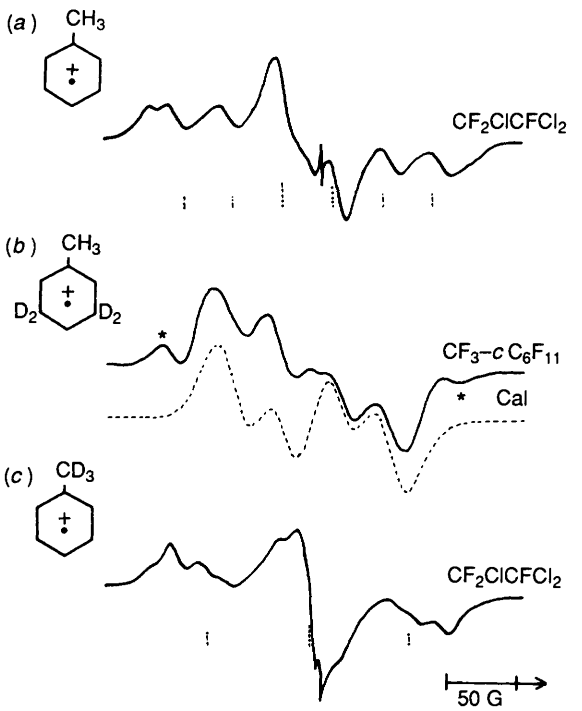
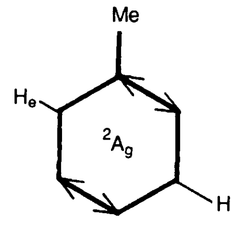


Fig. 1 The ESR spectra of (*a*) Me-*c*C6$^{\bullet +}$ in the $CFCl_2CF_2Cl$ matrix, (*b*) [3,3,5,5-$^2H_4$]Me-*c*C6 in the CF_3-*c*C_6F_{11} matrix and (*c*) [$^2H_3$]Me-*c*C6$^{\bullet +}$ in the $CFCl_2CF_2Cl$ matrix, recorded at 4 K. Essentially identical spectra were obtained using $CFCl_2CF_2Cl$ and CF_3-*c*C_6F_{11} at 4.2 K. The dashed curve in (*b*) is a simulation using the isotropic hf splittings, 74 G (1H) and 34 G (1H), and a Gaussian line width of 30 G. The stick plots (*a*) and (*c*) show the positions corresponding to the isotropic hf splittings of 74 G (2H) and 34 G (1H) for Me-*c*C6$^{\bullet +}$ and 74 G (2H) for [$^2H_3$]Me-*c*C6$^{\bullet +}$. The lines marked with asterisks in (*b*) are due to the cation of the isotopic impurity, [3,5,5-$^2H_3$]Me-*c*C6$^{\bullet +}$ (21% from GC).

A chair structure of cyclohexane having the alkyl substituent in the equatorial position is the conformation of lowest energy[14] [see Fig. 2(*a*)]. Note the numbering of the carbons and the position of certain hydrogens, H_e and H_t, which will be referred to in the discussions below. From the experimental ^1H hf splittings of the three cations with various isotope labellings and the knowledge of the unpaired electron distribution of the ^2A_g state of the cyclohexane cation, it is postulated that the cation of methylcyclohexane has an a_g-like SOMO in the ring structure being asymmetrical with respect to the position of the methyl group, as shown in the diagram below. The A_g structure of



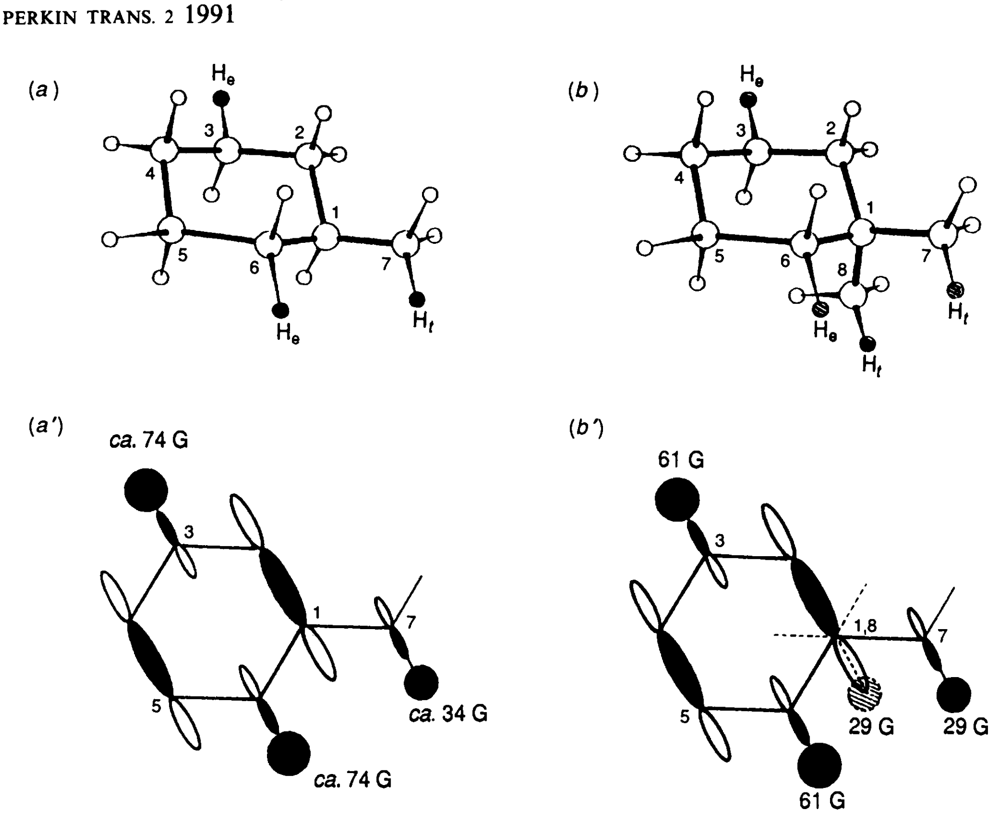


Fig. 2 The geometries of (*a*) Me-*c*C6$^{\bullet+}$ and (*b*) 1,1-Me^2-*c*C6$^{\bullet+}$ in the chair conformation. The methyl group of Me-*c*C6$^{\bullet+}$ is in an equatorial position. One hydrogen on each of the methyl groups in 1,1-Me2-*c*C6$^{\bullet+}$ is in the *trans* position with respect to the C(1)–C(2) bond. (*a'*) and (*b'*): schematics of the SOMO together with the assignment of experimental ^{1}H hf splittings of Me-*c*C6$^{\bullet+}$ and 1,1-Me$_2$-*c*C6$^{\bullet+}$, respectively.

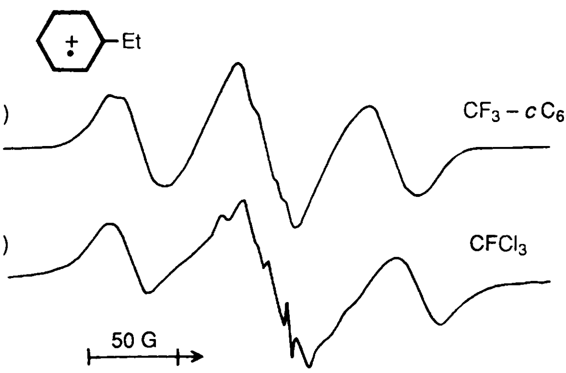


Fig. 3 The ESR spectra of Et-*c*C6$^{\bullet+}$ at 4.2 K in (*a*) CF$_3$-*c*C$_6$F$_{11}$ and (*b*) CFCl$_3$

the cyclohexane cation is predicted to have two elongated C–C bonds. A large hf interaction (*ca.* 100 G) due to the two equatorial hydrogens being *trans* with respect to these elongated bonds has been reported.[8,9,13] Having the methyl group connected as in the insert shown in the diagram, part of the spin density can be transferred *via* an hyperconjugative effect from one of the elongated bonds in the ring structure [C(1)–C(2)] into one of the methyl hydrogens, H$_t$, in Fig. 2(*a*). These two bonds are approximately coaxial and the hyperconjugation becomes efficient to direct unpaired spin density into the substituent. As a consequence, the hf interaction between the unpaired electron and the pair of equatorial hydrogens (at C-3 and C-6) in the cyclohexyl ring diminishes in magnitude. The distribution of the unpaired electron follows the *trans* effect proposed in early work by Wang and Williams on n-alkanes and branched alkanes[22] (see also refs. 23–29).

The ESR spectrum of the ethylcyclohexane (Et-*c*C6) cation at 4.2 K is shown in Fig. 3. It comprises a 1:2:1 three-line pattern having an isotropic hf splitting of 69 G (2H) in the CF$_3$-*c*C$_6$H$_{11}$ matrix. Thus, the methyl group in Et-*c*C6$^{\bullet+}$ suppresses the doublet splitting which appeared for Me-*c*C6$^{\bullet+}$. This can be explained as follows: the methyl group in Et-*c*C6$^{\bullet+}$ prefers to take a *gauche* structure with respect to the cyclohexyl group [Fig. 4(*a*)]. Now, if the a$_g$-like SOMO in the ring structure is arranged to have the elongated bonds coaxial with respect to the methylene–methyl bond of the substituent, there is no hydrogen in the substituent at the position of high spin-density as in Me-*c*C6$^{\bullet+}$ [compare Fig. 4(*a*) with Fig. 2(*a*)]. Consequently, additional hf structure due to the substituent cannot be detected. If this assumption is correct, it demonstrates that the methyl–methylene bond is more likely to attract the unpaired electron than the carbon–hydrogen bond of a methylene group. The splitting of the hf triplet was found to be the same, 69 G, using CFCl$_2$CF$_2$Cl or CF$_3$-*c*C$_6$F$_{11}$ as matrix, but slightly larger, 76 G, using CFCl$_3$ [see Fig. 3(*b*)]. The electronic structures are the same, however, there are apparently small changes in the hf splitting depending on the choice of matrix. Similar matrix effects have been reported for linear alkane cations.[19,30]

The ESR line shape of the methylcyclohexane cation exhibits a considerable temperature dependence.[12] On increasing the sample temperature above 4.2 K, the spectrum of [^{2}H$_3$]Me-*c*C6$^{\bullet+}$ [Fig. 1(*c*)] reversibly changed into a quintet of approximately binomial intensity distribution: $a_1{}^{\rm H}$ = 48.8 G (2 H) and $a_2{}^{\rm H}$ = 42.7 G (2H) at 140 K.[11] At the intermediate temperatures a line-width alternation effect was observed. The ESR spectrum of the protiated methylcyclohexane cation showed a similar temperature effect; however, the large number of lines made the spectra at intermediate temperatures more complicated. The ESR spectrum recorded at 140 K could be simulated by adding an hf triplet, $a_{3\rm H}$ = 20.1 G (2H), to the $a_1{}^{\rm H}$ and $a_2{}^{\rm H}$ splittings measured for [^{2}H$_3$]Me-*c*C6$^{\bullet+}$. This means that two hydrogens of the methyl group become magnetically equivalent at higher temperature. A reasonable model to explain the temperature dependence is an exchange between

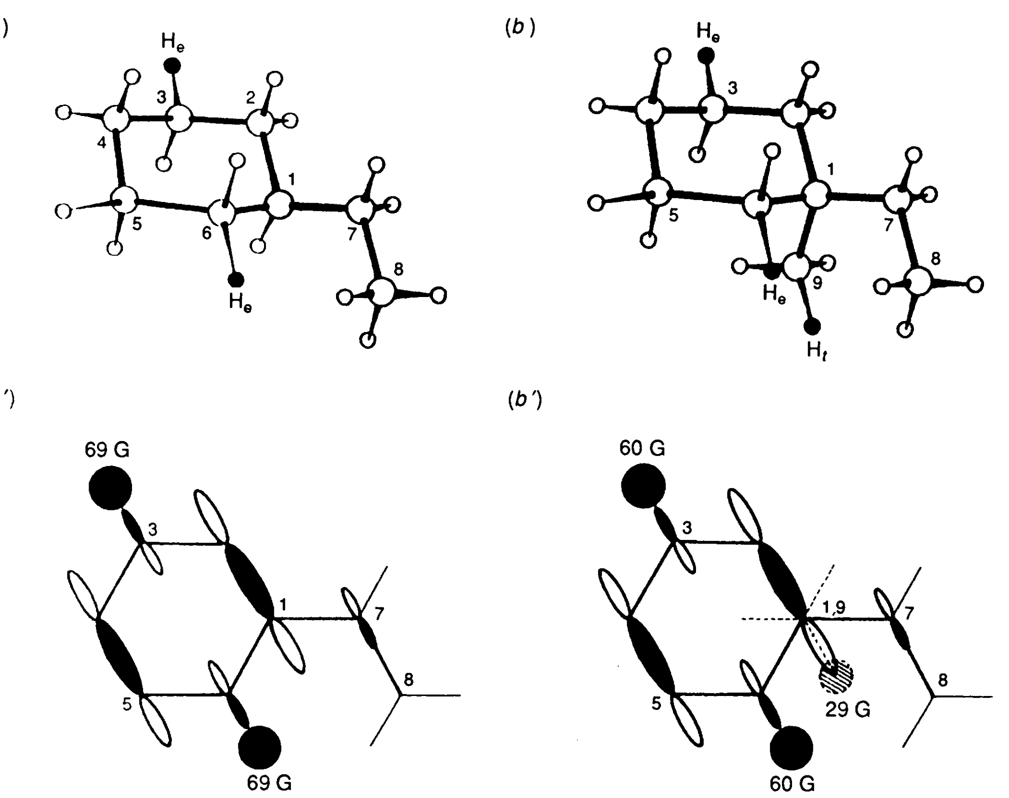
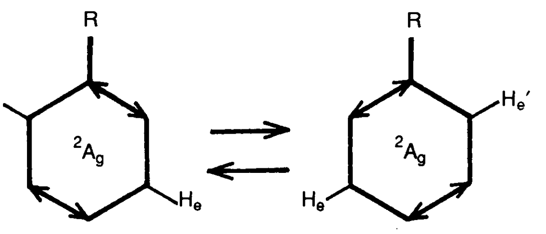


Fig. 4 The geometries of (*a*) Et-*c*C6$^{\cdot +}$ and (*b*) 1-Me-1-Et-*c*6$^{\cdot +}$ in a chair conformation, both with the ethyl group in the equatorial position. In both cases the ethyl group is *gauche* with respect to the cyclohexyl ring. One of the methyl hydrogens in 1-Me-1-Et-*c*C6$^{\cdot +}$ is coaxial with respect to the C(1)–C(2) bond. (*a′*) and (*b′*): schematics of the SOMO together with an assignment of ^{1}H hf splittings.



two different but equivalent structures, each being the mirror image of the other and having a distorted A_g structure, see the diagram. In the model depicted in the diagrams the hf splitting of two pairs of the equatorial ring hydrogens (at C-2 and C-6, and C-3 and C-5) and two of the methyl hydrogens are interchanged to be equivalent on the ESR time scale. Note the somewhat surprising fact that no methyl group rotation occurs, even at 140 K. The observed temperature dependence of the ESR line shape can thus give further evidence for the distorted A_g structure.

The temperature dependence of the ESR signal was not observed for the cation of ethylcyclohexane (Et-*c*C6$^{\cdot +}$). As was argued earlier, this cation has the methyl group in the *trans* position with respect to the elongated C(1)–C(2) bond. It makes the mirror images of an a_g-like SOMO in the ring structure non-equivalent and it seems as if the structure presented in Fig. 4(*a*) is energetically the most favourable one also at elevated temperatures. Rotation of the ethyl group is required for exchange between two such equivalent mirror structures. Such rearrangement is hindered owing to steric reasons and/or matrix cage effects.

The details of the dynamics of the methylcyclohexane cation are presently being analysed by comparing the experimental data with exchange-broadened spectra obtained from computer

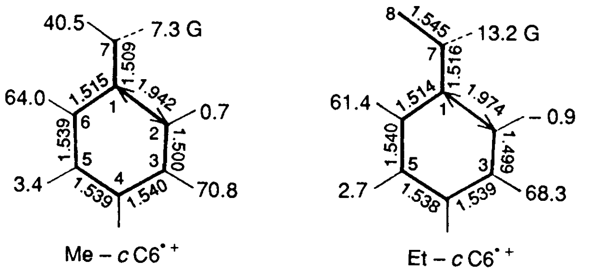


Fig. 5 Isotropic ^{1}H hf splittings/G of Me-*c*C6$^{\cdot +}$ and Et-*c*C6$^{\cdot +}$ calculated with INDO. These are due to the equatorial ring hydrogens and the hydrogens on the substituents being coaxial with ring carbon–carbon bonds, see the text for further details. The carbon–carbon bond lengths/Å calculated with MNDO geometry optimizations are also given.

simulations. Part of the results will appear elsewhere.[31] Preliminary results[32] support the exchange mechanisms presented above with the quasi-rigid methyl group up to 170 K.

MNDO/INDO Calculations of Cations of Methylcyclohexane and Ethylcyclohexane.—MO calculations give qualitative support to the structures proposed for Me-*c*C6$^{\cdot +}$ and Et-*c*C6$^{\cdot +}$. Geometry optimizations were carried out for the distorted A_g structures of Me-*c*C6$^{\cdot +}$ and Et-*c*C$^{\cdot +}$ using the MNDO semiempirical MO method.[33] For the radical cations an UHF scheme was adopted. The spin density in terms of isotropic ^{1}H hf splittings was calculated for the optimized geometries by using the INDO method.[34] The main results are summarized in Fig. 5. The C(1)–C(2) bond length was calculated to be 1.942 and 1.974 Å for Me-*c*C6$^{\cdot +}$ and Et-*c*C6$^{\cdot +}$, respectively. These

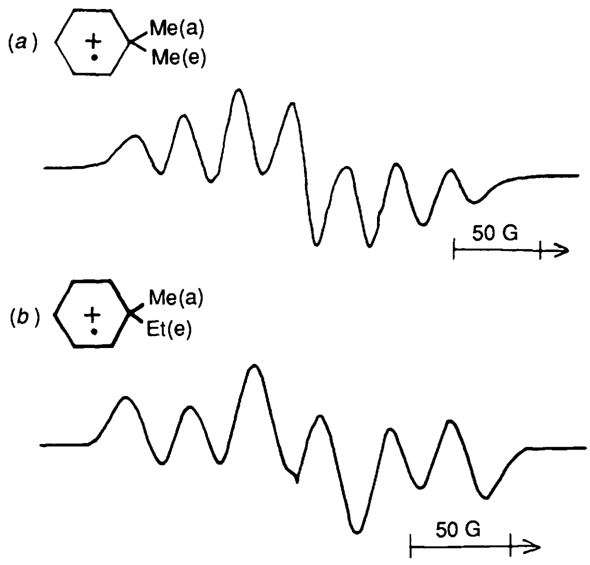


Fig. 6 The ESR spectra of (*a*) 1,1-Me_2-*c*C6$^{\cdot +}$ and (*b*) 1-Me-1-Et-*c*C6$^{\cdot +}$ in a CF_3-*c*C_6F_{11} matrix at 4.2 K

values are considerably larger than the 'standard' C–C bond, 1.54 Å.[35] The calculated hf splittings of the equatorial hydrogens at the C-3 and C-6 positions reproduce rather well the experimental values: for Me-*c*C6$^{\cdot +}$ 64.0 and 70.8 G *vs.* 74 G (experimental) and for Et-*c*C6$^{\cdot +}$ 61.4 and 68.3 G *vs.* 69 G (experimental). The hf splitting of the *trans* hydrogen [H_t in Fig. 2(*a*)] of the methyl group was calculated to be 40.5 G, in qualitative agreement with the experimental value, 34 G. All other calculated ^{1}H hf splittings were found to be considerably smaller than the experimental linewidth (*ca.* 30 G) and are not discussed here.

As mentioned in the introduction, the A_g structure of the cyclohexane cation has two elongated C–C bonds. The MNDO calculations of Me-*c*C6$^{\cdot +}$ presented above suggest that elongation occurs predominantly in one of the two bonds; the one containing the tertiary carbon, which is the carbon–carbon bond, having the highest unpaired electron density. The result is reasonable, recalling that such bonds are known to possess the largest fraction of the unpaired electrons in cations of branched alkanes.[22–24,27] However, the bond elongation as predicted by the MNDO method seems rather large and more sophisticated theoretical investigations ought to be carried out before discussing the matter in further detail.

1,1-*Dimethylcyclohexane and* 1-*Methyl*-1-*ethylcyclohexane*.—The ESR spectra of the 1,1-dimethylcyclohexane (1,1-Me_2-*c*C6) and 1-methyl-1-ethylcyclohexane (1-Me-1-Et-*c*C6) cations are shown in Figs. 6(*a*) and 6(*b*), respectively. The experimental spectra were reproduced in computer simulations by using the following isotropic hf splittings: for 1,1-Me_2-*c*C6$^{\cdot +}$ 61 G (2H) and 29 G (2H) and for 1-Me-1-Et-*c*C6$^{\cdot +}$ 60 G (2H) and 29 G (1H). Both cations are characterized by a large hf splitting, *ca.* 60 G, due to two hydrogens. Furthermore, 1,1-Me_2-*c*C6$^{\cdot +}$ has two additional ^{1}H hf splittings of 29 G, whereas 1-Me-1-Et-*c*C6$^{\cdot +}$ has only one. The ESR hf patterns can be explained by assuming a distorted A_g structure in the ring, analogous to the case of Me-*c*C6$^{\cdot +}$ and Et-*c*C6$^{\cdot +}$ discussed in an earlier section. Thus, the larger hf splittings (*ca.* 60 G) are assigned to the equatorial ring hydrogens at C-3 and C-6 and the smaller ones (29 G) to methyl hydrogens in the *trans* position to the elongated C(1)–C(2) bond in the ring [see Figs. 2(*b*′) and 4(*b*′)]. Note that the presence of an ethyl group in 1-Me-1-Et-*c*C6$^{\cdot +}$ suppresses one of the two splittings due to methyl hydrogens which can be detected for 1,1-Me_2-*c*C6$^{\cdot +}$.

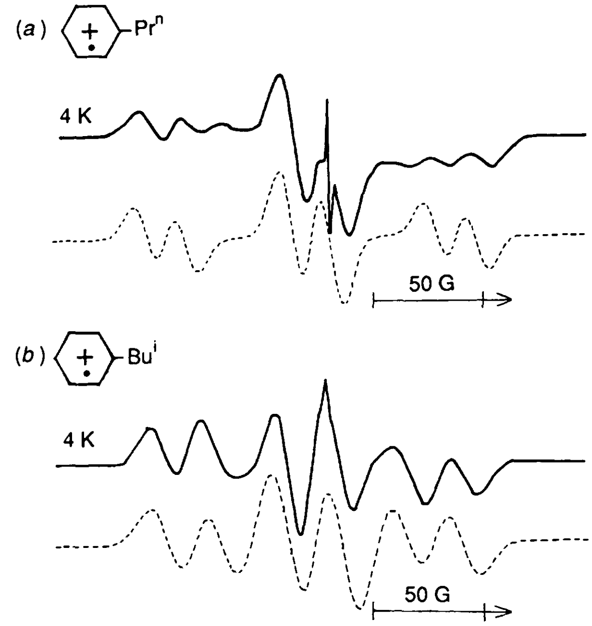


Fig. 7 The ESR spectra of (*a*) Pr^n-*c*C6$^{\cdot +}$ and (*b*) Bu^i-*c*C6$^{\cdot +}$ in a CF_3-*c*C_6F_{11} matrix, recorded at 4.2 K. The dashed curves are simulations using the following ESR parameters: for Pr^n*c*C6$^{\cdot +}$ 67 G (2H), 17 G (1H), linewidth 12 G, and for Bu^i-*c*C6$^+$ 55 G (2H), 24 G (1H) and linewidth 16 G.

The ^{1}H hf splittings of the cations discussed above are close to those found for the *cis* and *trans* isomer cations of 1,2-dimethylcyclohexane.[13] These cations were found to have an a_g-like SOMO in the cyclohexane ring structure with one of the elongated bonds lying between the ring carbons (C-1 and C-2) bearing the methyl substituents. Large hf splittings were detected for the equatorial hydrogens on C-3 and C-6, 59 G (2H), and two hydrogens on the substituents in the *trans* position to the C(1)–C(2) bond, 33 G (2H) (one on each methyl). Thus, the electronic structures and related mechanism for spin localization on ring hydrogens as well as on the methyl substituents of these cations are mutually consistent with the cations presented so far in this study.

A temperature dependence of the ESR line shape was found for 1,1-Me_2-*c*C6$^{\cdot +}$. The observation could be explained by the same dynamic model as described for Me-*c*C6$^{\cdot +}$ in an earlier section.[32] In this case too, no methyl group rotation occurred at higher temperature (*ca.* 170 K). No such temperature effect was observed for 1-Me-1-Et-*c*C6$^{\cdot +}$.

N-*Propylcyclohexane and Isopropylcyclohexane*.—The ESR spectra of the cations of n-propylcyclohexane (Pr^n-*c*C6) and isobutylcyclohexane (Bu^i-*c*C6) in the CF_3-*c*C_6F_{11} matrix are shown in Figs. 7(*a*) and 7(*b*), respectively. The dashed curves are computer simulations having the following ESR parameters: 67 G (2H) and 17 G (1H) for Pr^n-*c*C6$^{\cdot +}$ and 55 G (2H) and 24 G (1H) for Bu^i-*c*C6$^{\cdot +}$. The larger splittings are of the same magnitude as found for the cations presented in earlier sections (see Table 1) and it is reasonable to postulate an a_g-like SOMO in the ring structure for these two cations too. Thus, the hf triplet is due to the interaction between the unpaired electron and the equatorial hydrogens at C-3 and C-6 (H_e in Fig. 8). Following our earlier discussions, the doublet of 17 and 24 G can be assigned to a hydrogen in the *trans* position to the elongated C(1)–C(2) bond in the ring. Conformations giving rise to such situations are depicted in Fig. 8 for Pr^n-*c*C6$^{\cdot +}$.

We suggest that alkyl substituents with a long tail can take several possible conformations, and that it is difficult to make up an unambiguous structure without employing specifically

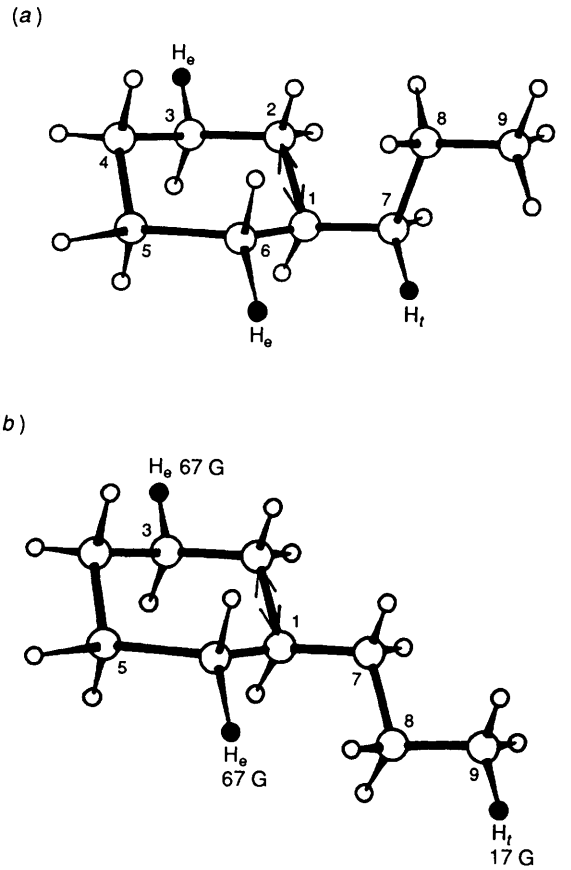


Fig. 8 Cation conformations of Pr^{n}-*c*C6$^{\cdot +}$ which can explain the experimental hf pattern shown in Fig. 7. See the text for more details.

deuteriated compounds.* The hypothetical conformations which are depicted in Figs. 8(*a*) and 8(*b*) can explain the hf substructure observed for Pr^{n}-*c*C6$^{\cdot +}$. By analogy with earlier discussions, the hydrogen which might give rise to the hf substructure is located in the *trans* position to an elongated bond in the ring structure having high spin density. However, more systematic studies have to be undertaken in order to clarify the details concerning the local conformation of the substituent.

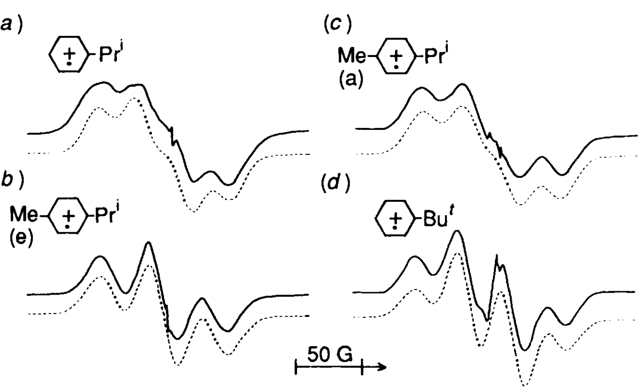
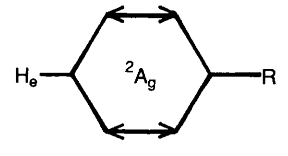


Fig. 9 The ESR spectra of the cations of (*a*) isopropylcyclohexane, (*b*) *trans*-4-methylisopropylcyclohexane, (*c*) *cis*-4-methylisopropylcyclohexane and (*d*) *tert*-butylcyclohexane in a CF$_3$-*c*C$_6$F$_{11}$ matrix at 4 K. The dashed curves are computer simulations with linewidths of 24 G in (*a*) and (*c*), and (*d*) and 28 G in (*b*). The ^{1}H hf splittings are collected in Table 1.

Isopropylcyclohexane and tert-*Butylcyclohexane*.—The ESR spectra for the isopropylcyclohexane (Pr^{i}*c*C6) and *tert*-butylcyclohexane (Bu^{t}-*c*C6) cations in CF$_3$-*c*C$_6$F$_{11}$ at 4 K are shown in Figs. 9(*a*) and 9(*d*), respectively. The dashed curves below each of the experimental spectra are computer simulations with the following hf parameters: 31 G (2H) and 18 G (1H) for Pr^{i}-*c*C6$^{\cdot +}$, and 31 G (3H) for Bu^{t}-*c*C6$^{\cdot +}$. We now propose that the SOMO of the ring structure is similar to the a$_g$ orbital of the cyclohexane cation, but symmetrical with respect to the position of the substituent, as shown in the diagram below.



In Pr^{i}-*c*C6$^{\cdot +}$ two secondary carbons, C-1 and C-7, are connected to each other, whereas in Bu^{t}-*c*C6$^{\cdot +}$ a secondary carbon, C-1, is connected to a tertiary carbon, C-7 [see Figs. 10(*a*) and 10(*d*)]. Such bonds have been found to attract a considerable amount of the unpaired electron in branched alkane cations, and the spin density can be transferred to other parts of the molecule through hyperconjugation effects.[22,24,27,28] From these considerations it is reasonable to expect that the unpaired electron in Pr^{i}-*c*C6$^{\cdot +}$ and Bu^{t}-*c*C6$^{\cdot +}$ is mainly confined to the C(1)–C(7) bond and the C(2)–C(3) and C(5)–C(6) bonds in the ring to form a symmetrically disorted A$_g$ structure.

Thus, the hf quartet of 31 G (3H) observed for Bu^{t}-*c*C6$^{\cdot +}$ can be assigned to three hydrogens, one on each of the methyl groups, located axially with respect to the C(1)–C(7) bond. No splittings due to ring hydrogens can be detected for this cation. This means that most of the unpaired electron is confined to the C(1)–C(7) bond. Similarly, the hf triplet of 31 G (2H) observed for Pr^{i}-*c*C6$^{\cdot +}$ can be attributed to two methyl hydrogens located axially with respect to the C(1)–C(7) bond. The additional doublet which can be resolved in the ESR spectrum of Pr^{i}-*c*C6$^{\cdot +}$ can be assigned to the equatorial hydrogen at C-4. The latter assignment was confirmed by measuring the *cis* and *trans* isomer cations of 4-methylisopropylcyclohexane in which the methyl group takes the axial and equatorial positions, respectively [see Figs. 10(*b*) and 10(*c*)]. The ESR spectrum of the *cis* isomer cation resolved a triplet of doublets with 34 G (2H) and 19 G (1H), respectively, whereas only a triplet of 35 G (2H) could be detected for the *trans* isomer cation [see Figs. 9(*b*) and 9(*c*)]. Thus, the splittings due to the two isopropyl hydrogens (the hf triplet) have nearly the same value of Pr^{i}-*c*C6$^{\cdot +}$, but no additional doublet was resolved for the cation of *trans*-4-methylisopropylcyclohexane since it has no hydrogen in the equatorial position at C-4.

The magnitude of the doublet splitting due to the equatorial hydrogen at C-4 gives a measure of the spin localization in the ring. The splittings of 18 G detected for Pr^{i}-*c*C6$^{\cdot +}$ is *ca.* 20% of that expected for the corresponding splitting in the ^{2}A$_g$ state of the cyclohexane cation (*ca.* 100 G). Thus, by comparison with the cyclohexane cation itself, *ca.* 80% of the unpaired electron in the C(3)–C(4)–C(5) fragment has been attracted towards the substituent. By estimating the spin density distribution from other considerations, further support to this statement is given.

The radical cation of 2,3-dimethylbutane (2,3-Me$_2$-B)[24,27] has a 'local' structure which is analogous to Pr^{i}-*c*C6$^{\cdot +}$. Schematics of their SOMOs are depicted in Figs. 11(*a*) and 11(*c*), together with the assignment of certain hf splittings due to the methyl hydrogens being axial to the C–C bond of high spin

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* The ESR spectrum of Pr^{n}-*c*C6$^{\cdot +}$ in a CF$_3$Cl matrix at 4 K is essentially the same as that in a CF$_3$-*c*C$_6$F$_{11}$ matrix at the same temperature. When the matrix is changed to CF$_2$ClCFCl$_2$ or CF$_3$CCl$_3$, however, the triple doublet is replaced by a triplet of *ca.* 67 G with broader linewidth, suggesting that, in the latter matrices, the Pr^{n} group can take various conformations.

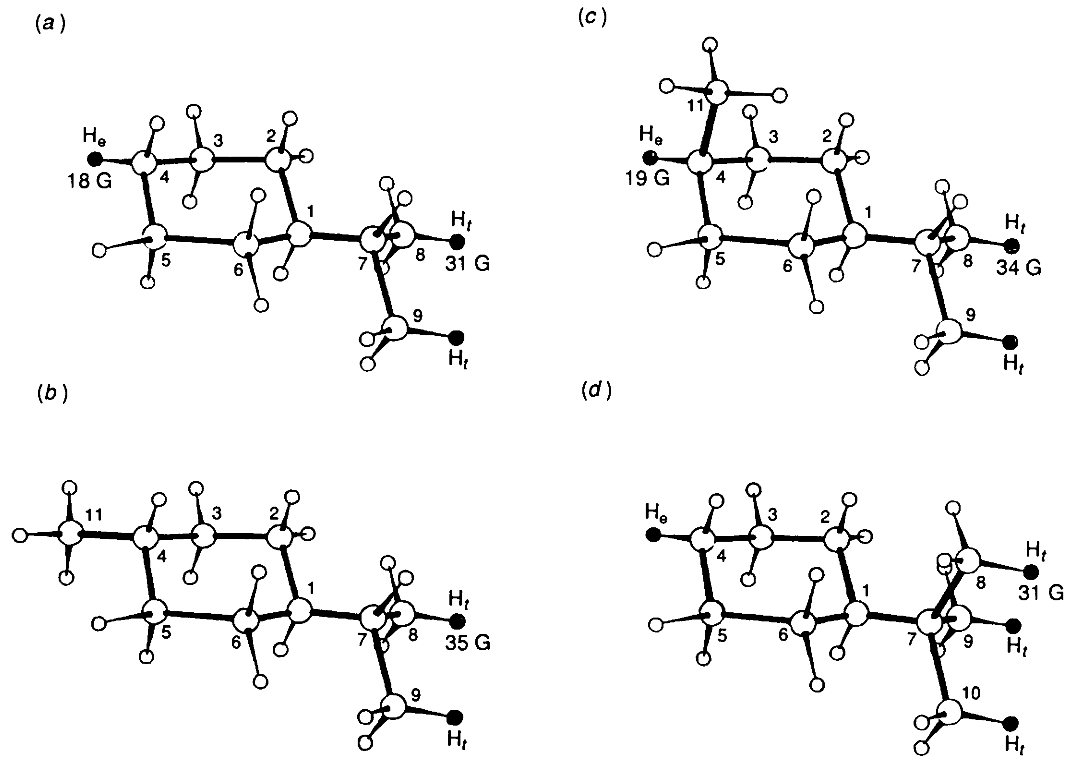


Fig. 10 The proposed conformations and assignment of hf splittings for the cations of (*a*) isopropylcyclohexane, (*b*) *trans*-4-methylisopropylcyclohexane, (*c*) *cis*-4-methylisopropylcyclohexane and (*d*) *tert*-butylcyclohexane

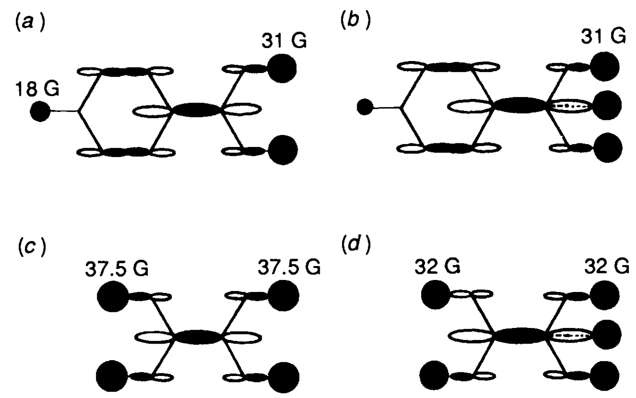
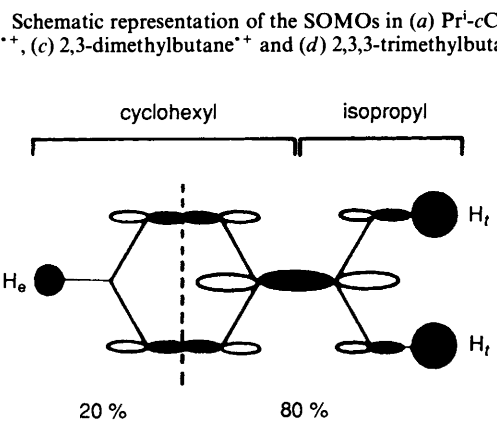


Fig. 11 Schematic representation of the SOMOs in (*a*) Pr^i-cC6$^{\bullet+}$, (*b*) Bu^t-cC6$^{\bullet+}$, (*c*) 2,3-dimethylbutane$^{\bullet+}$ and (*d*) 2,3,3-trimethylbutane$^{\bullet+}$



density. The hf splitting of Pr^i-cC6$^{\bullet+}$ is *ca.* 80% of the corresponding value for 2,3-Me$_2$-B$^{\bullet+}$ (37.5 G). This is consistent with the estimate of the spin density made by comparing the hf splitting due to the equatorial ring hydrogen at C-4 with the analogous ones for the ^2A_g state of the cyclohexane cation.

Table 1 Isotropic ^{1}H hf splittings of the radical cations discussed in this study. Unless otherwise indicated, CF$_3$-cC$_6$F$_{11}$ was used as matrix and the sample temperature was 4.2 K.

Radical cation[a]	^{1}H hf/G[b]	References
Me-cC6$^{\bullet+}$	74 (2H); 34 (1H)	Ref. 12
Me-cC6$^{\bullet+}$	48.8 (2 H); 42.7 (2H); 20.1 (2H)	140 K, refs. 11 and 12
[^{2}H$_3$]$_2$Me-cC6$^{\bullet+}$	74 (2H)	Ref. 12
[^{2}H$_3$]Me-cC6$^{\bullet+}$	48.8 (2H); 42.7 (2H)	140 K, refs. 11 and 12
[3,3,5,5-^{2}H$_4$]Me-cC6	74 (1H); 34 (1H)	This work
1,1-Me$_2$-cC6$^{\bullet+}$	61 (2H); 29 (2H)	This work
Et-cC6$^{\bullet+}$	69 (2H)	This work
1-Me-1-Et-cC6$^{\bullet+}$	60 (2H); 29 (1H)	This work
Pr^n-cC6$^{\bullet+}$	67 (2H); 17 (1H)	This work
Bu^i-cC6$^{\bullet+}$	55 (2H); 24 (1H)	This work
1,t2-Me$_2$-cC6$^{\bullet+}$	59 (2H); 33 (2H)	Ref. 13
1,c2-Me$_2$-cC6$^{\bullet+}$	59 (2H); 32 (2H)	Ref. 13
Pr^i-cC6$^{\bullet+}$	31 (2H); 18 (1H)	This work
1-Me,t4-Pr^i-cC6$^{\bullet+}$	35 (2H)	This work
1-Me,c4-Pr^i-cC6$^{\bullet+}$	34 (2H); 19 (1H)	This work
Bu^t-cC6$^{\bullet+}$	31 (3H)	This work
2,3-Dimethylbutane$^{\bullet+}$	37.5 (4H)[c]	77 K, ref. 24
2,2,3-Trimethylbutane$^{\bullet+}$	32.0 (5H)[c]	77 K, ref. 24

[a] cC6: cyclohexane. [b] 1 G = 10 mT. [c] Matrix: CF$_2$ClCFCl$_2$.

In a similar way it is also possible to obtain a rough estimate of the unpaired electron distribution in the other cases. The SOMOs and hf splittings due to 'axial' methyl hydrogens on the *tert*-butyl fragments for the cations of *tert*-butylcyclohexane and 2,2,3-trimethylbutane are depicted in Figs. 11(*b*) and 11(*d*), respectively. The hf splittings are nearly the same, indicating that almost all of the unpaired electron is attracted towards the substituent, most of it being in the bond between the cyclohexyl and *tert*-butyl fragments.

The conformations of the cations and schematics of the SOMOs are depicted in Figs. 10 and 11, respectively. The hf splittings are summarized in Table 1.

Conclusions

This report presents the electronic structures of cations for some alkylcyclohexanes with the substituent(s) on one carbon. All have a common feature, namely, the alkyl group(s) is (are) bonded to a ring structure whose electronic state resembles the ^2A_g state of the cyclohexane cation itself. Furthermore, the various cations presented in this study can be grouped into two classes depending on how the substituent(s) is (are) located with respect to an a_g-like SOMO in the ring structure, namely asymmetrically or symmetrically. The asymmetrical case occurs for cations with alkyl groups such as methyl, ethyl, n-propyl or isobutyl and the cations of 1,1-dimethylcyclohexane and 1-methyl-1-ethylcyclohexane. The hf pattern is dominated by a triplet with a splitting ranging from 55–75 G, depending on the size and conformation of the substituent. The hf splitting is attributed to two equatorial hydrogens at the C-3 and C-6 positions, one of them being adjacent to the C-1 atom with the alkyl group. The magnitude of the splitting decreases as the size of the substituent increases. The unpaired electron resides largely in the C(1)–C(2) bond, and the bond probably becomes weaker and longer. If the substituent has a coaxial carbon–hydrogen bond to the elongated bond with high spin density, an additional hf splitting due to the hydrogen, <34 G, can be observed in the ESR spectrum. The symmetrical case occurs for cations with an alkyl group such as isopropyl and *tert*-butyl; a secondary or tertiary carbon is attached to the ring. The ESR hf pattern is dominated by splittings due to the methyl hydrogens being axial with respect to the bond connecting the substituent to the ring.

In both cases, the unpaired electron favours a localization in bonds to tertiary or quarternary carbons, giving rise to a 'local' structure resembling the analogous carbon–carbon bonds of branched n-alkane cations. The unpaired electron can delocalize efficiently by hyperconjugation from such bonds of high spin density into σ-bonds which are coaxial. Thus, the unpaired electron is delocalized both in the ring structure and into the substituent(s).

The mechanism for spin delocalization is similar to that suggested in the early work of Williams and coworkers.[22] They stated an empirical rule: 'For an unpaired electron occupying a σ-orbital in the carbon chain, spin delocalization will occur mainly to those (axial) hydrogens which are coplanar with the largest number of carbon atoms in the extended chain'. Here we have presented experimental data which show that the only necessary condition is that such hydrogens (of high spin density) are coaxial with respect to the σ-bond(s) in the carbon–carbon framework having large spin density. The mechanism for spin delocalization is consistent with the results of the *gauche* conformer of the n-butane cation which has the carbon chain folded at the C(2)–C(3) bond. The hf splitting due to the *trans* hydrogen in the *gauche* conformer[28] was found to be essentially the same as the splittings reported for the extended conformer.*

The asymmetrical structure proposed for the first class of cations can give a simple model of the dynamic features for the cations of methylcyclohexane and 1,1-dimethylcyclohexane. In this model, a distorted A_g-like structure changes to its own mirror image. This process causes two methyl hydrogens and two pairs of equatorial ring hydrogens (at C-3 and C-5, and at C-6 and C-2) to become equivalent in the fast exchange limit on the ESR time scale.

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* The hf splitting reported for the n-butane cation in ref. 22(*b*) is overestimated owing to a reorientational motion of the methyl groups which affects the ESR line shape at highest temperatures, *cf.*, M. Iwasaki and K. Toriyama, *J. Am. Chem. Soc.*, 1986, **108**, 6441. The true hf splitting is between 60 and 63 G, depending on the choice of matrix.

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