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The Jahn–Teller Split HOMO of the Cyclohexane Cation in Selectively Alkyl-Substituted Cyclohexanes: An ESR and MNDO/INDO MO Study

Masaru Shiotani,*,† Mikael Lindgren,‡ and Takahisa Ichikawa†

Contribution from the Department of Applied Physics and Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 0724, Japan, and Department of Physics, Chemical Physics, University of Linköping, S-581 83 Linköping, Sweden. *Received June 1, 1989*

Abstract: Radical cations of various alkyl-substituted cyclohexanes have been radiolytically generated and stabilized in a solid perfluoromethylcyclohexane matrix at low temperature for ESR studies. The pertinent ESR spectra recorded at 4 K were successfully analyzed in terms of isotropic ^{1}H hyperfine (hf) splittings: 56 G (4 H) for 1,*trans*-4-dimethylcyclohexane (1,*t*-4-Me$_2$-cC6$^+$), 71 G (2 H) and 34 G (2 H) for 1-methyl,*trans*-4-ethylcyclohexane (1Me, *t*-4Et-cC6$^+$), 122 G (1 H), and 62 G (1 H) for 1,*cis*-3,*trans*-5-trimethylcyclohexane (1,*c*-3,*t*-5-Me$_3$-cC6$^+$), 37 G (2 H) and 24 G (2 H) for 1,*cis*-3,*cis*-5-trimethylcyclohexane (1,*c*-3,*c*-5-Me$_3$-cC6$^+$), 59 G (2 H) and 33 G (2 H) for the cis and trans isomers of 1,2-dimethylcyclohexane (1,*c*-2-Me$_2$-cC6$^+$ and 1,*t*-2-Me$_2$-cC6$^+$), 31 G (2 H) and 18 G (1 H) for isopropylcyclohexane (*i*-Pr-cC6$^+$), and 31 G (3 H) for *tert*-butylcyclohexane (*t*-Bu-cC6$^+$). The experimental hf splittings are correlated with theoretical ones calculated by semiempirical MNDO/INDO MO methods. The cations can be classified into ^{2}A$_g$-, ^{2}B$_g$-, and ^{2}A″-like electronic states with structural resemblance to the cyclohexane cation: ^{2}B$_g$-like for 1,*t*-4-Me$_2$-cC6$^+$, ^{2}A″-like for 1Me,*t*-4Et-cC6$^+$ and 1,*c*-3,*c*-5-Me$_3$-cC6$^+$, and finally ^{2}A$_g$-like for 1,*c*-3,*t*-5-Me$_3$-cC6$^+$, 1,*t*-2-Me$_2$-cC6$^+$, 1,*c*-2-Me$_2$-cC6$^+$, *i*-Pr-cC6$^+$, and *t*-Bu-cC6$^+$.

Techniques to generate and stabilize organic radical cations in solid halocarbon matrices at low temperature for the purpose of ESR spectroscopy were developed by Shida's[1] and other groups[2-4] in the late 1970s. Since then, the electronic structures of a large number of radiolytically oxidized saturated organic compounds have been studied.[5-8] In alkanes, several of the highest situated occupied molecular orbitals (MOs) are close in energy. One often finds more than two orbitals (doubly occupied) within ca. 1.0 eV.[9] This is particular evident in molecules of high symmetry in which some of the MOs are degenerate. Quantum mechanical MO calculations have suggested that the ionization is sometimes followed by severe distortions of the geometrical structures (see e.g., ref 10–14). The unpaired electron (hole) is largely confined into σ-bonds which can make them weakened and elongated. The degeneracy or near degeneracy can thus give rise to several possible distorted structures since each candidating electronic state is associated with a particular symmetry and charge distribution.

Radical cations of cyclic alkanes have attracted much attention,[10,12,15-21] since in the neutral form they usually have a degenerate highest occupied molecular orbital (HOMO). An ionization is followed by a geometrical distortion, well-known as the Jahn–Teller (J–T) effect,[22] which demonstrates the instability of degenerate electronic states.

The radical cation of cyclohexane (cC6$^+$) is of particular interest. Ab initio MO calculations reported by Lunell et al.[10] have suggested an electronic ground state of lower symmetry (^{2}A″ in C_s symmetry) than expected from a static J–T distortion (^{2}A$_g$ or ^{2}B$_g$ in C_{2h} symmetry[18]). Iwasaki and Toriyama[18,19] have, on the other hand, proposed a ^{2}A$_g$ state based on their experimental ESR data and INDO MO calculations: the hyperfine (hf) splittings for the rigid structure were extrapolated from the spectra showing dynamic behavior above 4.2 K, and the partially averaged hf splittings observed at 1.5 K were explained in terms of zero-point vibrations. Because of such fundamental interest more experimental data seem necessary to elucidate the electronic ground state for the cyclohexane cation and its analogues.

The introduction of substituents to cyclohexane in a certain symmetrical or asymmetrical manner is a chemically intuitive way to remove orbital degeneracy, and electronic states similar to those predicted by the J–T theorem can be studied separately.[21] This is the main purpose of the present study. In this paper, we report isotropic ESR spectra of various radical cations of alkyl-substituted cyclohexanes such as 1,*trans*-4-dimethylcyclohexane (1,*t*-4-Me$_2$-cC6), 1-methyl,*trans*-4-ethylcyclohexane (1Me,*t*-4Et-cC6), 1,*cis*-3,*trans*-5- and 1,*cis*-3,*cis*-5-trimethylcyclohexane (1,*c*-3,*t*-5- and 1,*c*-3,*c*-5-Me$_3$-cC6), 1,*trans*-2- and 1,*cis*-2-dimethylcyclohexane (1,*t*-2- and 1,*c*-2-Me$_2$-cC6), isopropylcyclohexane (*i*-Pr-

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* Address correspondence to Department of Applied Physics and Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 0724, Japan.

† Hiroshima University.

‡ University of Linköping.

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(21) Shiotani, M.; Ohta, N.; Ichikawa, T. *Chem. Phys. Lett.* **1988**, *149*, 185. After this article was submitted, we observed that the methylcyclohexane radical cation showed a temperature-dependent ESR line shape: Me-d_3-cC6$^+$ shows a triplet of ca. 74 G (2 H) which, for Me-cC6$^+$, further splits to a doublet of ca. 36 G (1 H) at 4 K. Therefore, the ^{2}A″ state in C_s, which was attributed to in the paper, may correspond to a dynamically averaged structure. The details can be found in *Chem. Phys. Lett.* **1989**, *161*, 127.

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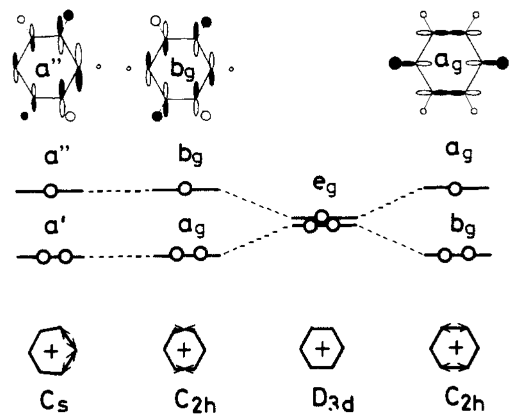

Figure 1. A schematic representation showing how the $4e_g$ degenerate orbital in $cC6^+$ changes by a distortion from the original D_{3d} to either C_{2h} or C_s symmetry. The unpaired electron in the cation occupies either the a_g (C_{2h}), b_g (C_{2h}); or a″ (C_s) orbital.

cC6), and *tert*-butylcyclohexane (*t*-Bu-cC6). The cations were generated in perfluoromethylcyclohexane (CF_3-cC6F11) by hole transfer from the irradiated solid matrix to the solute at 77 or 4 K.

The Fermi contact hyperfine interaction between the unpaired electron and hydrogen nuclei provides an accurate measure of the electron distribution in terms of measurable hf splitting constants in the ESR spectra. Their assignments are, however, not trivial, unless we possess some knowledge about the candidating cation ground states. Of the cation structures presented in this study, none have been reported previously, and we have adopted semiempirical MO calculations to examine possible electronic structures. It is emphasized on the distribution of the unpaired electron and its relation to certain geometrical distortions. The electronic states can be classified into ^2A_g-, ^2B_g-, and $^2A''$-like ones based on structural similarities to the cyclohexane cation: ^2B_g-like for 1,*t*-4-Me_2-$cC6^+$, $^2A''$-like for 1Me,*t*-4Et-$cC6^+$ and 1,*c*-3,*c*-5-Me_3-$cC6^+$, and ^2A_g-like for 1,*c*-3,*t*-5-Me_3-$cC6^+$, 1,*t*-2-Me_2-$cC6^+$, 1,*c*-2-Me_2-$cC6^+$, *i*-Pr-$cC6^+$, and *t*-Bu-$cC6^+$. It is essential to achieve a detailed knowledge of the ground-state structures before discussing the dissociation to other radical fragments as well as radiation chemistry in general of this important class of compounds.

Experimental Section

In this study we have chosen to use CF_3-cC6F11 as the matrix, which has been proved useful for generation and stabilization of radical cations at low temperature.[7,21,23] CF_3-cC6F11 (>95%) was obtained from Tokyo Kasei Co. The following solute molecules were obtained from Tokyo Kagaku Seiki Co. and used without further purification: 1,*t*-4-Me_2-cC6 (>99%), 1Me,*t*-4-Et-cC6 (>99%), 1,*c*-3,*t*-5-Me_3-cC6 (>99%), 1,*c*-3,*c*-5-Me_3-cC6 (>99%), 1,*t*-2-Me_2-cC6 (>99%), 1,*c*-2-Me_2-cC6 (>99%), *i*-Pr-cC6 (>99%), and *t*-Bu-cC6 (>99%). Samples of the degassed frozen solutions containing ca. 1 mol % of solute were irradiated by γ- or X-rays at 4.2 and 77 K. This is a well-known procedure to generate the solute radical cations by hole transfer to the solute from the irradiated matrix molecules and subsequent stabilization in a chemically inert medium.[5-8] The ESR spectra were recorded at various temperatures from 4 up to 180 K where a phase transition occurs in the matrix[24] and the cations change into neutral radicals usually by a deprotonation. Here we concentrate on the structure of the radical cations, the neutral radicals will be fully described in forthcoming reports.[25]

Theoretical

The geometry optimizations were carried out with the MNDO semiempirical MO method developed by Dewar and Theil.[26] For

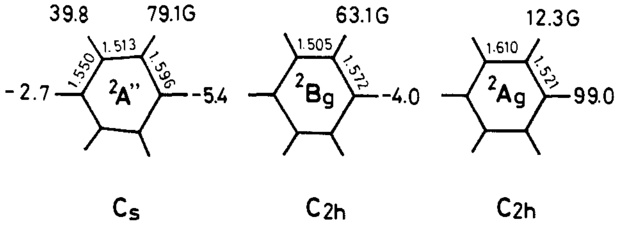

Figure 2. Calculated isotropic ^1H hf splittings (in G) for the equatorial hydrogens in the optimized geometries (MNDO) of $cC6^+$ in the possible ^2A_g, ^2B_g, and $^2A''$ states. The calculated C–C bond lengths (in Å) are inserted in the figure. For further details see the text.

Table I. Experimental Isotropic ^1H hf Splittings and the Corresponding Electronic States of Radical Cations

radical cation	isotropic ^1H hf[a] (G)	state[b]
1,*t*-2-Me_2-$cC6^+$	59 (2 H); 33 (2 H)	^2A_g
1,*c*-2-Me_2-$cC6^+$	59 (2 H); 32 (2 H)	^2A_g
1,*t*-4-Me_2-$cC6^+$	56 (4 H)	^2B_g
1Me,*t*-4Et-$cC6^+$	71 (2 H); 34 (2 H)	$^2A''$
1,*c*-3,*t*-5-Me_3-$cC6^+$	122 (1 H); 62 (1 H)	^2A_g
1,*c*-3,*c*-5-Me_3-$cC6^+$	37 (2 H); 24 (2 H)	$^2A''$
i-Pr-$cC6^+$	31 (2 H); 18 (1 H)	^2A_g
1Me,*t*-4-*i*-Pr-$cC6^+$	35 (2 H)	^2A_g
1Me,*c*-4-*i*-Pr-$cC6^+$	34 (2 H); 19 (1 H)	^2A_g
t-Bu-$cC6^+$	31 (3 H)	^2A_g

[a] Matrix, CF_3-cC6F11; temperature, 4 K; 10 G = 1 mT. [b] The states refer to the similar states of $cC6^+$. ^2A_g and ^2B_g belong to C_{2h}, while $^2A''$ belongs to C_s. For further details see the text.

the radical cations an UHF scheme was adopted. The particular program used is contained in the commercially available AMPAC quantum chemical calculation package.[27] In all calculations symmetry restrictions were imposed. The spin density, in terms of isotropic ^1H hf splittings, was calculated for the optimized geometries with the INDO method developed by Pople et al.[28] The program used in this study is an open shell version modified by Oloff and Hüttermann.[29] The usefulness of this procedure to discuss the electronic structure of radical cations of alkanes was recently shown.[13,14]

Results and Discussion

^2A_g, ^2B_g, and $^2A''$ States of $cC6^+$. Before going into the details of the ionized alkyl-substituted cyclohexanes it is helpful to first give a brief summary on the cyclohexane cation. The removal of one electron from the highest occupied degenerate e_g orbital of cC6 in D_{3d} symmetry (chair conformation) can give either the ^2A_g or ^2B_g state in C_{2h} symmetry according to the J–T effect, as shown in Figure 1. Here, the ^2A_g and ^2B_g states correspond to the elongation and compression, respectively, of the chair conformation along the direction producing the C_{2h} symmetry. It has been suggested by Lunell et al.[10] that a $^2A''$ state with C_s symmetry might be lower in energy. The geometries of the possible electronic structures were reexamined with MNDO calculations.[30] The main geometrical distortions upon ionization are changes in the carbon–carbon bond lengths (compared to those of the neutral molecule[31]), and these are inserted in the schematics in Figure 2. These and other geometrical parameters are essentially the same as those found in more sophisticated theoretical studies[10]

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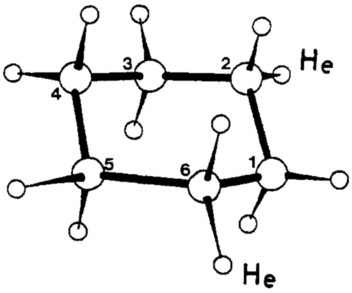
Table II. Total Energy (E_{tot}) and Heat of Formation (ΔH_f) Calculated with the MNDO MO Method for Different Electronic States of the Radical Cations

radical cation	calculation state[a]	 E_{tot} (eV)	 ΔH_f (kcal/mol)	observation state[a]
$cC6^+$	^2A_g	−927.89	220.60	^2A_g[b]
$cC6^+$	^2B_g	−927.88	220.81	
$cC6^+$	$^2A''$	−927.91	220.10	$2A''$[c]
1,*t*-4-Me_2-$cC6^+$	^2A_g	−1240.58	215.87	
1,*t*-4-Me_2-$cC6^+$	^2B_g	−1240.71	212.85	^2B_g
1,*t*-4-Me_2-$cC6^+$	$^2A''$	−1240.75	211.76	
1,*c*-3,*c*-5-Me_3-$cC6^+$	$^2A''$	−1397.00	211.65	$^2A''$
1,*c*-3,*c*-5-Me_3-$cC6^+$	$^2A''$	−1397.07	210.28	
1,*c*-3,*c*-5-Me_3-$cC6^+$	$^2A'$	−1396.97	212.26	
1,*c*-3,*t*-5-Me_3-$cC6^+$	$^2A'$	−1396.97	212.37	$^2A'$
1Me,*t*-4-Et-$cC6^+$	$^2A''$[d]	−1397.15	208.14	$^2A''$
1Me,*t*-4-Et-$cC6^+$	$^2A''$[e]	−1397.19	207.38	

[a] The states refer to the similar states of $cC6^+$. ^2A_g and ^2B_g belong to C_{2h}, while $^2A'$ and $^2A''$ belong to C_s. [b] References 16 and 19. [c] Reference 10. [d] The "W" at the methyl group. [e] The "W" at the ethyl group. For further details, see the text.

and are not discussed further here. Similar to the previous theoretical study,[10] the MNDO calculations presented here place the $^2A''$ state lowest in energy, followed by the ^2A_g and ^2B_g state. The total energies and heat of formation are presented in Table II.

The hf splittings of the equatorial hydrogens calculated with the INDO are depicted in Figure 2. The magnitude of the splittings for all axial hydrogens is less than 4 G (not presented here). From this result it is possible to conclude that the following three different basic ESR patterns can be expected for the cC6 cations with various substituents: for the ^2A_g state, a triplet with large hf splitting of ca. 100 G (10 G = 1 mT) due to two equatorial hydrogens at the C_1 and C_4 positions; for the ^2B_g state, a quintet with ca. 60 G due to four equatorial hydrogens at C_i (i = 2, 3, 5, 6); for the $^2A''$ state, a triple triplets with ca. 80 and 40 G due to two pairs of equatorial hydrogens at C_2 (C_6) and C_3 (C_5), respectively (see below the labeling used). In the $^2A''$ state, the



singly occupied molecular orbital (SOMO) is localized mainly in the "W" shaped structure formed by the atoms H_e-C_2-C_1-C_6-H_e. Here, the H_e stands for an equatorial hydrogen. This orbital is similar to that of the lowest state of the propane cation ($^2B_1$ in C_{2v})[20,32] and cyclopentane ($^2A''$ in C_s),[12,19] as pointed out previously.[10]

The electronic structures of $cC6^+$ discussed so far can form a "basis" for the radical cations of cyclohexanes with various substituents, provided the chemical nature of the substituents does not greatly change the electronic structure of the ring. In the following sections it will be shown how they appear in the different cases.

1,*t*-4-Me_2-$cC6^+$: ^2B_g State. The ESR spectrum of 1,*t*-4-Me_2-$cC6^+$[33] radical in CF_3-cC6F11 recorded at 4 K is shown in Figure 3a. The ESR line shape did not change between 4 K and 170 K. The lower spectrum in the figure is a computer simulation with an isotropic hf splitting, a^H = 56 G, due to four equivalent hydrogens. As seen in Figure 3 (parts b and c), similar ESR spectra were observed when other halocarbons were used as matrices: spectrum c being disturbed by the superposition of signals due to the matrix, CF_3CCl_3. The observation indicates that, similarly to the cyclohexane cation,[19] the electronic structure of 1,*t*-4-Me_2-$cC6^+$ is not significantly affected by the choice of the matrix. This argument is valid for the other radical cations of alkyl-substituted cyclohexanes presented in this paper.

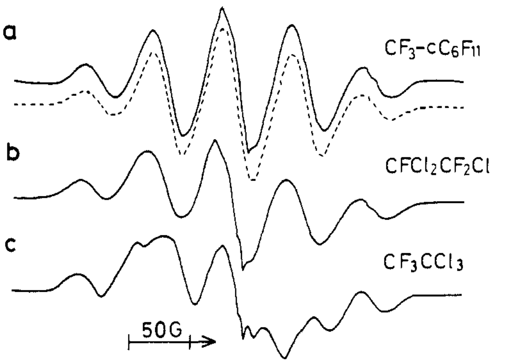


Figure 3. ESR spectra of 1,*t*-4-Me_2-$cC6^+$ recorded at 4 K: (a) in CF_3-cC6F11, (b) in $CFCl_2CF_2Cl$, and (c) in CF_3CCl_3. The dashed curve is a simulation spectrum calculated by using a ^1H hyperfine splitting, a^H = 56 G (4 H) and a Gaussian line width of ΔH_{msl} = 24 G.

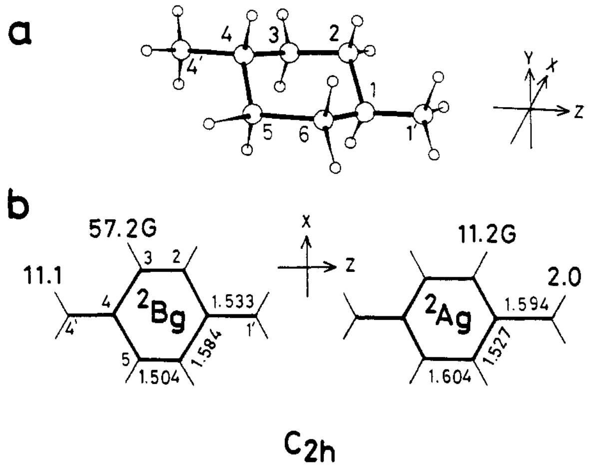


Figure 4. (a) The geometrical structure of 1,*t*-4-Me_2-cC6 in the C_{2h} chair conformation with both methyl groups in the equatorial position. (b) Calculated (INDO) isotropic ^1H hf splittings (in G) due to the equatorial ring hydrogens for the optimized geometries (MNDO) of 1,*t*-4-Me_2-$cC6^+$ with the ^2A_g and ^2B_g states. The C–C bond lengths (in Å) deduced from MNDO are also inserted in the figure. The hf splittings at the substituent methyl groups are for the hydrogens in the trans positions with respect to the methylene–methylene bonds. The experimental hf splitting is 56 G due to four magnetically equivalent hydrogens.

A chair form with both methyl groups in the equatorial position (C_{2h} symmetry) was adopted for the MO calculations (Figure 4a). This conformation is the most stable (e.g., ref 34) and also consistent with the experimental ESR results, as will be shown below. An MNDO geometry optimization was carried out adopting the following "standard" bond lengths and angles[28] as an initial input data: r_{C-C} = 1.54 Å, r_{C-H} = 1.09 Å, and ∠C–C–C = ∠C–C–H = 109.5°. The calculations resulted in an elongated C_{2h} chair conformation with an ^2A_g electronic ground state (Figure 4b, right-hand side). The major geometrical differences from the structure of neutral 1,*t*-4-Me_2-cC6[31] are as follows: an elongation of the methylene–methylene (C_2–C_3 and C_5–C_6) and methyl–methine (C_1–$C_{1'}$ and C_4–$C_{4'}$) bonds to 1.604 and 1.596 Å, respectively, and a shortening of the remaining four equivalent methylene–methine (C_1–C_2, C_3–C_4, C_4–C_5, and C_6–C_1) bonds to 1.527 Å. It should be noted that these bond lengths are very similar to those in the ^2A_g state of $cC6^+$ for the ring structure. The INDO calculations for this optimized geometry yielded an hf splitting of 11.2 G, due to the four equivalent equatorial hydrogens attached to the methylene carbons, as shown in Figure 4b, right-hand side. All other splittings were calculated to be less

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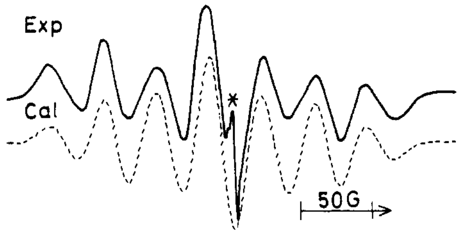


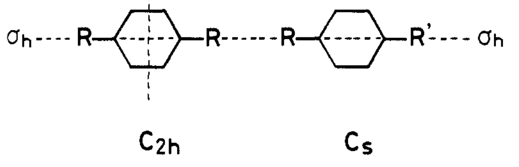
Figure 5. ESR spectrum of 1Me,*t*-4-Et-cC6$^+$ in CF_3-cC6F11 recorded at 4 K. The simulation spectrum (dashed curve) was obtained by using ^1H hyperfine splittings, 71 G (2 H) and 34 G (2 H) and a Gaussian line width, ΔH_{msl} = 28 G. The signal marked with an asterisk (*) is due to a paramagnetic species in the irradiated sample tube.

than a few gausses in magnitude and are not discussed here.

A compressed C_{2h} chair form with a ^2B_g electronic state was found by using a trial geometrical structure with slightly increased methylene–methine bond lengths (Figure 4b, left-hand side). For the optimized geometry they were found to be 1.584 Å. The methylene–methylene and methyl–methine bonds were shortened to 1.504 and 1.533 Å, respectively. The INDO calculations for the optimized geometry resulted in an hf splitting of 57.2 G due to the four equivalent equatorial hydrogens of the methylene groups. The calculations also predicted an hf splitting of 11.1 G due to the four equivalent methyl hydrogens in the trans position with respect to the elongated methylene–methine bonds, the splitting being less than the experimental line width of 28 G (Gaussian line shape). All other calculated splittings were less than 4 G in magnitude. The excellent agreement between the experimental and theoretical hf splittings (56 G (4 H) vs 57.2 G (4 H)) leads us to conclude that the 1,*t*-4-Me_2-cC6$^+$ radical has the ^2B_g electronic ground state in C_{2h} symmetry. The heat of formation of the ^2B_g state, ΔH_f, was evaluated ca. 3 kcal/mol lower than the ^2A_g state by the present MNDO calculations. However, allowing the ^2B_g structure to relax under C_s symmetry a $^2A''$ state with electron distribution similar to that of cyclohexane is achieved, being ca. 1 kcal/mol lower in energy. The hf pattern for this structure is dominated by two pairs of large splittings, a_1^H = 66.5 G (2 H) and a_2^H = 39.0 G (2 H), being inconsistent with the experimental data and thus rejected. The calculated energies for the various states are summarized in Table II.

1Me,*t*-4-Et-cC6$^+$: $^2A''$-like State. The ESR spectrum of 1Me,*t*-4-Et-cC6$^+$ in CF_3-cC6F11 at 4 K is shown in Figure 5. The ESR line shape did not change for samples being between 4 and 170 K. The spectrum of seven hf lines is well reproduced by a simulation using a_1^H = 71 G (2 H), a_2^H = 34 G (2 H), and a line width of 18 G (Gaussian line shape).

In the previous section, the cation of 1,*t*-4-Me_2-cC6 was concluded to possess a chair conformation having the methyl groups in equatorial positions and a ^2B_g electronic state in C_{2h} symmetry. The chair conformation is the most probable also for 1Me,*t*-4-Et-cC6$^+$ (Figure 6a). However, in the hf pattern 1Me,*t*-4-Et-cC6$^+$ resembles cC6$^+$ with the $^2A''$ state (in C_s) which can be viewed as a distortion of the ^2B_g state (in C_{2h}). 1Me,*t*-4-Et-cC6 is obtained by substituting one *methyl hydrogen* of 1,*t*-4-Me_2-cC6 for one *methyl group*. This substitution leads to the C_s symmetry which is lower than the C_{2h} as shown schematically. Thus, by inference, we can conclude that the electronic state of 1Me,*t*-4-Et-cC6$^+$ is similar to the $^2A''$ state theoretically predicted for the cyclohexane cation.



MO calculations can support this proposal. In the MNDO optimization a gauche conformation was imposed: the ethyl group is twisted by 120° with respect to the mirror plane of the 1-methylcyclohexyl group, and the atoms (H_t)-C_6-C_5-C_4-$C_{4'}$-(H) are located in a plane such as extended *n*-pentane (Figure 6a). In the optimization of the cation geometry a mirror plane was kept within the ring structure. Using trial geometries with various elongated C–C bonds in the ring, two different types of $^2A''$-like states[35] were found with the "W"-type distortion located either on the side having the methyl or ethyl group. The energy (heat of formation, ΔH_f) is ca. 1 kcal/mol lower for the latter case. One half of the cation structure has geometrical parameters close to the neutral ones, and the other half is deformed with two elongated methylene–methine bonds of 1.620 Å. Thus, the part of the molecule where the unpaired electron is mostly distributed can be regarded as the propane-like "W" structure with arrangements similar to the $^2A''$ state suggested for cC6$^+$ by Lunell et al.,[10] however, with minor differences being caused by the presence of the methyl and ether groups.

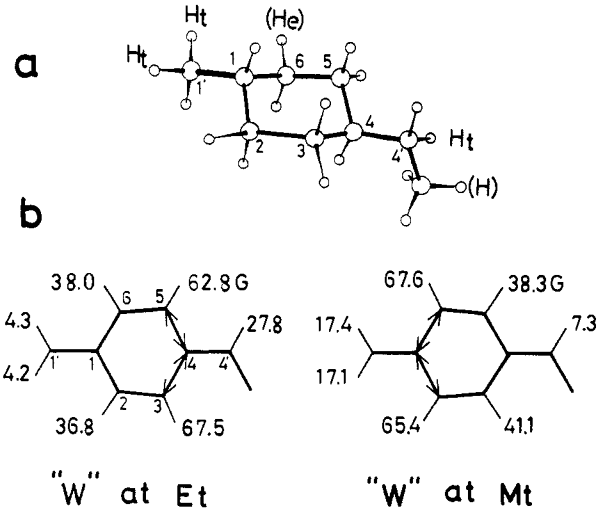
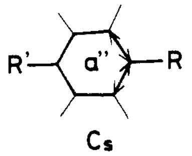


Figure 6. (a) The geometrical structure of 1Me,*t*-4-Et-cC6 in the chair conformation with the methyl and ethyl groups in equatorial positions. (b) Calculated (INDO) isotropic ^1H hf splittings (in G) due to the equatorial ring hydrogens and the hydrogens of the methyl and ethyl groups in the trans positions to the methylene–methine bonds. The two cases correspond to optimized geometries, "W" at the ethyl side (left) and "W" at the methyl side (right). The experimental hf splittings are given in Table I. For further details see the text.



The calculated hf splittings (INDO) for these two cases are inserted in the schematics in Figure 6b. The larger values in the ring are due to the four hydrogens in the equatorial position. For both cases, the "W" on the methyl or ethyl side, the calculated values are in rough agreement with the experimental data (71 G (2 H) and 34 G (2 H)). The "W" structure at the ethyl side is more likely compared with that at the methyl side according to the lower energy. The energy difference is, however, too small to be relied on. An unambiguous assignment can only be made from a clearly resolved substructure in the ESR hf pattern, due to the trans hydrogens on the substituents: the calculations suggest two trans hydrogens for the "W" at the methyl side (giving ca.

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(33) Shiotani, M.; Yano, A.; Ohta, N.; Ichikawa, T. *26th Japanese Symposium on ESR*; Nagoya, Japan, 1987; Abstract, 164.

(34) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon Inc.: Boston, MA, 1987; pp 447–463.

(35) Admitting C_s symmetry, the electronic state of 1Me,4-*t*-Et-cC6$^+$ is $^2A''$. However, the state should be referred to as $^2A''$-like since the C_s symmetry constraint was given only for the geometry of the ring structure (not including the twisted ethyl group).

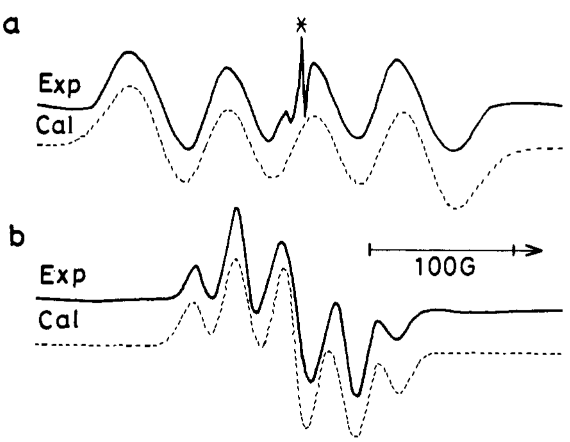

Figure 7. ESR spectra of 1,*c*-3,*t*-5-Me_3-cC6$^+$ (a) and 1,*c*-3,*c*-5-Me_3-cC6$^+$ (b) in CF_3-cC6F11 recorded at 4 K. The simulation spectra (dashed curves) were calculated by using the ^{1}H hyperfine splittings listed in Table I and Gaussian line shapes with ΔH_{msl} = 43 G and 20 G for 1,*c*-3,*t*-5-Me_3-cC6$^+$ and 1,*c*-3,*c*-5-Me_3-cC6$^+$, respectively. The signal marked with an asterisk (*) comes from the irradiated sample tube.

17 G) but only one for the "W" at the ethyl side (giving ca. 28 G). These are comparable to the line width and are not resolved in the present ESR spectrum.

1,3,5-Me_3-cC6$^+$: $^2\text{A}_\text{g}$- and ^{2}A″-like States. Two isomers of the 1,3,5-Me_3-cC6 radical cation with a chair conformation were examined, namely, 1,*c*-3,*t*-5-Me_3-cC6$^+$ and 1,*c*-3,*c*-5-Me_3-cC6$^+$. The experimental spectrum of 1,*c*-3,*t*-5-Me3-cC6$^+$[36] recorded at 4.2 K consists of a double doublet as shown in Figure 7a. The dashed curve below the experimental spectrum is a computer simulation having the following hf parameters: a_1^H = 122 G (1 H), a_2^H = 62 G (1 H), and a Gaussian line shape with ΔH_{msl} = 43 G. The 4 K spectrum of 1,*c*-3,*c*-5-Me_3-cC6$^+$ resolves five lines separated with an averaged isotropic splitting of ca. 31 G, as shown in Figure 7b. In computer simulations the quintet structure is best reproduced by using two pairs of hf splittings, a_1^H = 37 G (2 H) and a_2^H = 24 G (2 H), and a Gaussian line width of 20 G, resulting in the spectrum shown with dotted lines in Figure 7b. The ESR line shape of these radical cations remains essentially unchanged between 4 and 170 K, similarly to those of 1,*t*-4-Me_2-cC6$^+$ and 1Me,*t*-4-Et-cC6$^+$.

1,*c*-3,*t*-5-Me_3-cC6$^+$. First we describe the electronic structure of the 1,*c*-3,*t*-5-Me_3-cC6$^+$ radical. The energetically most preferable conformation of 1,*c*-3,*t*-5-Me_3-cC6 is depicted in Figure 8a.[34] Two of the methyl groups can be equatorial, but the third one must be axial. Thus, there are four equatorial hydrogens. Taking the molecular symmetry into consideration, we can now reasonably postulate that two equatorial hydrogens attached to the C_2 and C_5 carbons are responsible for the observed double doublet (122 G and 62 G). The electronic state is thus similar to the $^2\text{A}_\text{g}$ state of cC6$^+$, with two equatorial ring hydrogens in the trans position with respect to the elongated ring carbon–carbon bonds (C_3–C_4 and C_6–C_1) giving the large hf splittings. The nonequivalence of the hf splittings, compared with the expectation for a $^2\text{A}_\text{g}$ cyclohexane (C_{2h}) structure, is caused by the three methyl groups which lower the symmetry of the ring structure to C_s. Therefore the state should be correctly referred to as ^{2}A′ in C_s. Note that the sum of the experimental hf splittings, $a_1^\text{H} + a_2^\text{H}$ = 122 G + 62 G = 184 G, is in rough agreement with the corresponding ones expected for the $^2\text{A}_\text{g}$ state of cC6$^+$, 2 × 99 G = 198 G. MO calculations support the above assignment of the hf splittings and the $^2\text{A}_\text{g}$-like electronic state for 1,*c*-3,*t*-5-Me_3-cC6$^+$. The results are as follows. As a trial geometry in the MNDO optimization, the ring carbons were given a structure similar to that of the $^2\text{A}_\text{g}$ state found for cC6$^+$, with the methyl groups attached to the C_1, C_3, and C_5 positions having "standard" parameters.[28] The symmetry constrains was C_s with the mirror plane defined to contain the C_2, C_5, and $\text{C}_{5'}$ carbons. This resulted in the geometry having the C–C bond lengths as indicated in Figure 9a. Thus, the main distortions in the ring remained the same as in the $^2\text{A}_\text{g}$ state of cC6$^+$, i.e., elongation of the C_3–C_4 and the C_6–C_1 bond lengths. The INDO calculations for this geometry yielded hf splittings of a_1^H = 149 G (1 H) and a_2^H = 50 G (1 H) for the equatorial hydrogens at C_5 and C_2, respectively. These values are in rough agreement with the experimental splittings (122 and 62 G). The corresponding SOMO is schematically depicted in Figure 10a. All other calculated hf splittings were less than the experimental line width and are not discussed further.

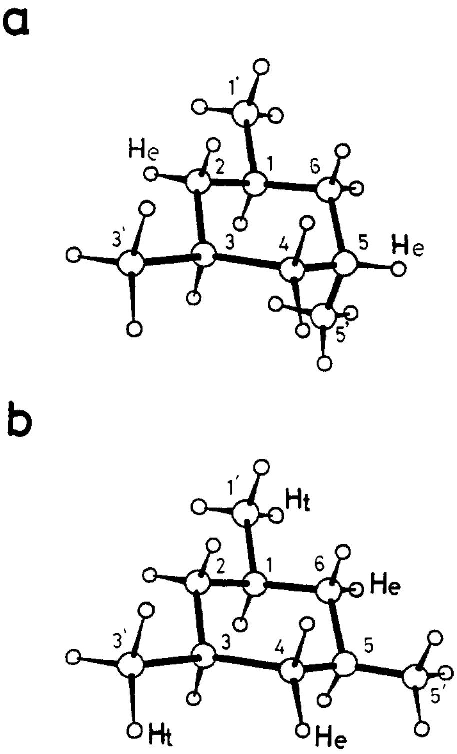

Figure 8. The geometrical structures of 1,*c*-3,*t*-5-Me_3-cC6 (a) and 1,*c*-3,*c*-5-Me_3-cC6 (b). 1,*c*-3,*t*-5-Me_3-cC6 has a chair conformation with two methyl groups in the equatorial position and one methyl group in the axial position, whereas 1,*c*-3,*c*-5-Me_3-cC6 has a chair conformation with three methyl groups in equatorial position.

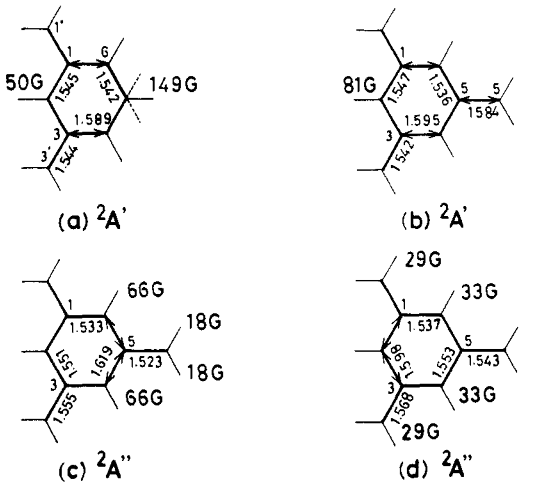

Figure 9. Calculated (INDO) isotropic ^{1}H hf splittings (in G) due to the equatorial ring hydrogens and the hydrogens of the methyl groups in the trans positions to the elongated methylene–methine bonds in the optimized geometries (MNDO): (a) 1,*c*-3,*t*-5-Me_3-cC6$^+$ with ^{2}A′ state; 1,*c*-3,*c*-5-Me_3-cC6$^+$ with (b) ^{2}A′ state and (c,d) two possible ^{2}A″ states. The two cases of ^{2}A″ correspond to the optimized geometries, (c) the "W" at the C_5 position and (d) the "W" at the C_2 position. The calculated C–C bond lengths (in Å) are inserted in the figure. For further details see the text.

1,*c*-3,*c*-5-Me_3-cC6. Next is to consider the cation of 1,*c*-3,*c*-5-Me_3-cC6. The neutral form of 1,*c*-3,*c*-5-Me_3-cC6 with the chair conformation can have all methyl groups in an equatorial position with the methyl groups perfectly staggered with respect to the

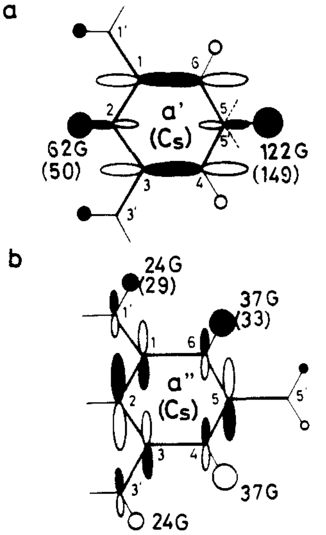

Figure 10. A schematic representation of the SOMOs in 1,c-3,t-5-Me_3-cC6$^+$ (a) and 1,c-3,c-5-Me_3-cC6$^+$ (b). The experimental ^{1}H hf splittings are compared with the theoretical ones (in parentheses). For further details see the text.

methine groups: the molecule belongs to the C_{3v} point group (Figure 8b). For this conformation the HOMO is a degenerate e orbital, and the ionization must give rise to a structural distortion with lower symmetry of C_s in accordance with the Jahn–Teller effect. In MO calculations three different distortions (in C_s) from the neutral molecular geometry (C_{3v}) were found as shown in Figure 9b–d. The first is a lengthening of the C_3–C_4 and C_6–C_1 bonds (Figure 9b). This resulted in a SOMO similar to that of 1,c-3,t-5-Me_3-cC6$^+$ (i.e., ^2A_g-like state) with an hf splitting of 81 G calculated for the equatorial hydrogen at the C_2 position and the remaining coupling constants less than the experimental line width of 20 G. The second is a distortion of the H_e-C_4-C_5-C_6-H_e fragment (Figure 9c) similar to the "W" shaped SOMO found for the $^2A''$ state of the cyclohexane and 1Me,t-4-Et-cC6 cations in earlier sections. For this structure the INDO hf splittings are 66 G for two equatorial hydrogens at the C_4 and C_6 positions and 18 G for two methyl hydrogens at the C_5 position, each located in trans position with respect to the elongated C_4–C_5 and C_5–C_6 bonds, respectively. The third is the same structure as (c), but with the "W" SOMO centered at C_2 instead of C_5 (Figure 9d). The larger hf splitting for this structure is due to the same hydrogens as (c) but with the different magnitude: 33 G for the pair attached to the ring. The smaller splitting of 29 G is calculated for the pair of methyl hydrogens at the $C_{1'}$ and $C_{3'}$ positions, one for each methyl group in the trans position to the elongated C_1–C_2 and C_2–C_3 bonds. The hf splittings calculated for the third case are in best agreement with the experimental ones, and conclusively the "W" structure at C_2 is the most probable for the 1,c-3,c-5-Me_3-cC6$^+$ radical. The corresponding SOMO is schematically represented in Figure 10b together with the experimental and calculated (in parentheses) hf splittings. Interestingly, the measured hf splitting (37 G) of the pair of equatorial hydrogens at the C_4 and C_6 positions is nearly the same as for the corresponding hydrogens in 1Me,t-4-Et-cC6$^+$ (34 G). This indicates that these two cations have a similar unpaired electron distribution and that the experimental results of 1,c-3,c-5-Me_3-cC6$^+$ as well as 1Me,t-4-Et-cC6$^+$ are consistent with the electron distribution of the cyclohexane $^2A''$ state. Other trial geometries were also examined under C_s symmetry, and they all resulted in one of the three structures discussed above.

A RHF/MNDO calculation of the high symmetrical conformation of the neutral molecule (C_{3v}) resulted in a HOMO of e symmetry. Thus, the $^2A''$ state for 1,c-3,c-5-Me_3-cC6$^+$ most likely arises from the Jahn–Teller distortion by which the highest e orbital splits into a' and a'' in C_s and the unpaired electron resides in the latter orbital. In Table II the energy and heat of formation for each state is presented. As for 1,t-4-Me_2-cC6$^+$, a state other than the observed one is calculated to have the lowest energy.

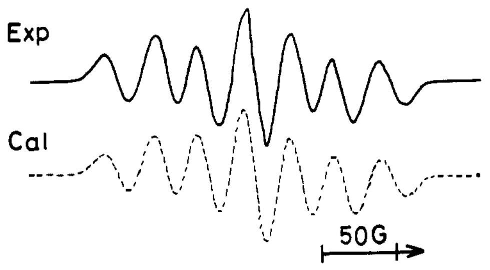

Figure 11. (a) ESR spectrum of 1,t-2-Me_2-cC6$^+$ in CF_3-cC6F11 recorded at 4 K. The simulation spectrum (dashed curve) was obtained by using the ^{1}H hf splittings listed in Table I and a Gaussian line width, ΔH_{msl} = 21 G.

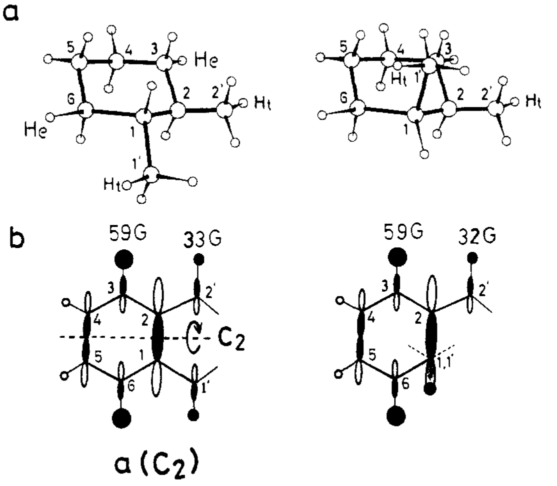

Figure 12. (a) The geometrical structures of two isomers of 1,2-Me_2-cC6: 1,t-2-Me_2-cC6 (left) in a chair conformation with two methyl groups in equatorial positions and 1,c-2-Me_2-cC6 (right) in the chair form with one methyl group in the equatorial position and the other methyl group in the axial position. (b) A schematic representation of the SOMOs in 1,t-2-Me_2-cC6$^+$ (left-hand side) and 1,c-2-Me_2-cC6$^+$ (right-hand side) originating from the ^2A_g state of cC6$^+$. The experimental ^{1}H hf splittings are given in the figure.

Other Radical Cations of Alkyl-Substituted Cyclohexanes with a ^2A_g-like State: 1,2-Me_2-cC6$^+$, i-Pr-cC6$^+$, and t-Bu-cC6$^+$. The experimental results for other alkyl-substituted cyclohexane cations having a SOMO originating from an A_g-like ring structure are summarized here. The ESR spectrum of 1,t-2-Me_2-cC6$^+$ [33] recorded at 4 K is shown in Figure 11. The spectrum consists of seven lines and can be analyzed as a triplet of triplets with isotropic ^{1}H hf splittings of a_1^H = 59 G (2 H) and a_2^H = 33 G (2 H). The computer simulation is shown as a dashed curve below the experimental spectrum. The ESR spectrum of 1,c-2-Me_2-cC6$^+$ was found to be essentially the same as that of 1,t-2-Me_2-cC6$^+$.

The chair form is the most stable conformation for 1,t-2-Me_2-cC6 and 1,c-2-Me_2-cC6 (Figure 12a). For 1,t-2-Me_2-cC6 the position of both methyl groups is equatorial, whereas for 1,c-2-Me_2-cC6 one of them has to be axial. Following the earlier discussions related to the ^2A_g state of the cyclohexane cation, one of the hf splittings observed, a_1^H = 59 G (2 H), is attributed to the equatorial hydrogens at C_3 and C_6. The second pair of hf splittings, a_2^H = 33 G (2 H), is due to two hydrogens, one of each methyl group, in the trans position to this bond. Interestingly, the a_1^H splitting is almost twice that of the a_2^H. This demonstrates that hyperconjugation is a predominant mechanism to yield the spin density in the hydrogen 1s orbitals: the two C_1–C_2 and C_4–C_5 bonds with almost equal unpaired electron density contribute to yield the a_1^H value, whereas only the C_1–C_2 bond contributes to the a_2^H value. Thus, it is suggested that the electronic state of both 1,2-Me_2-cC6$^+$ radicals originates from the ^2A_g state of cC6$^+$ with the methyl groups attached to the C_1 and C_2 carbons. The SOMO of the 1,t-2-Me_2-cC6$^+$ and 1,c-2-Me_2-cC6$^+$ is schematically shown in Figure 12b. 1,t-2-Me_2-cC6 has a 2-fold symmetry

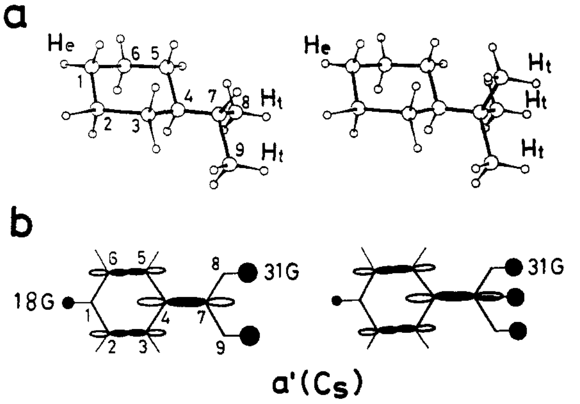

Figure 13. (a) The geometrical structures of *i*-Pr-cC6 (left) and *t*-Bu-cC6 (right) in a chair conformation and the *i*-Pr and *t*-Bu groups in equatorial positions. (b) A schematic representation of the SOMO in *i*-Pr-cC6$^+$ and *t*-Bu-cC6$^+$ originating from the ^2A_g state of cC6$^+$. The experimental ^1H hf splittings are given in the figure.

axis and belongs to the C_2 point group, so that the SOMO should be correctly referred to as an a orbital in C_2 symmetry.

Another example which shows a ^2A_g-like state are the cations of isopropylcyclohexane (*i*-Pr-cC6) and *tert*-butylcyclohexane (*t*-Bu-cC6).[37] The spectrum of *i*-Pr-cC6$^+$ consists of a triplet of doublets with isotropic hf splittings of 31 G (2 H) and 18 G (1 H), respectively. The triplet is attributed to two hydrogens, each belonging to a methyl group and located in the trans position with respect to the bond connecting the equatorially positioned *i*-Pr with the cyclohexyl group (i.e., the C_4–C_7 bond). The doublet of 18 G is assigned to an equatorial hydrogen attached to the C_1 atom (see Figure 13), This interpretation is consistent with the experimental results for 1Me,*t*-4-*i*-Pr-cC6$^+$ and 1Me,*c*-4-*i*-Pr-cC6$^+$: for 1Me,*t*-4-*i*-Pr-cC6$^+$, a triplet with 35 G (2 H), and, for 1Me,*c*-4-*i*-Pr-cC6$^+$, a triplet of doublets with 34 G (2 H) and 19 G (1 H), respectively.[37] In 1Me,*t*-4-*i*-Pr-cC6$^+$ the methyl group occupies the equatorial position at the C_1 carbon, and no additional doublet is observed. In 1Me,*c*-4-*i*-Pr-cC6$^+$ the CH_3 group occupies an axial position, and the doublet can be assigned to the equatorial hydrogen at the C_1 position.

Similarly, the *t*-Bu-cC6$^+$ radical has an ESR spectrum consisting of a quartet with a^H = 31 G (3 H). The quartet is attributed to three hydrogens, each being on one of the three methyl groups and all located in the trans position with respect to the bond to the equatorially positioned *t*-Bu group (i.e., the C_4–C_7 bond). These results suggest that the *i*-Pr-cC6$^+$ and *t*-Bu-cC6$^+$ have a ^2A_g-like electronic state as schematically shown in Figure 13b. The sum of the hf splittings due to methyl hydrogens is larger in *t*-Bu-cC6$^+$ than in Pr-cC6$^+$: 93 G vs 62 G. Thus, the unpaired electron is more confined to the C_4–C_7 bond between the substituent with a tertiary carbon and the cyclohexane ring than that in *i*-Pr-cC6$^+$. It should be noted that the hf splittings observed for the *i*-Pr-cC6$^+$ and *t*-Bu-cC6$^+$ are consistent with those for methyl-substituted *n*-butane cations. The unpaired electron in the latter cations are mostly confined to the central C–C bond to maximize the delocalization through the hyperconjugative mechanism, and relatively large hf splittings (29–61 G) have been observed for the trans C–H hydrogens with respect to this bond.[32,38,39]

A ^2A_g-like state has been observed also for other radical cations of alkyl-substituted cyclohexanes such as methylcyclohexane, ethylcyclohexane, 1,1-dimethylcyclohexane, 1-methyl-1-ethylcyclohexane, and 1,*trans*-3-dimethylcyclohexane.[40] The details will be published elsewhere.

Conclusions

All of the alkyl-substituted cyclohexane cations reported in this study have a SOMO which is closely related to the Jahn–Teller distorted e HOMO of cyclohexane itself. Thus, the alkyl groups cause only minor changes in the electronic structure of the cyclohexane ring. The presented cations, therefore, provide approximative experimental evidence for the possible electronic ground states of the cyclohexane cation. This is the reason for classifying the various cation structures into ^2A_g, ^2B_g, and $^2A''$ states in cC6$^+$.

From the bulk of experimental data given here it is evident that a small substituent, such as a methyl or ethyl group, gives rise to a SOMO with the unpaired electron largely confined into σ-bonds within the ring structure, in which at least one of the methine groups participates. For 1,2-Me_2-cC_6 the unpaired electron is largely distributed in the bond between the two methine groups. However, if the alkyl group has a secondary or tertiary carbon bonded to the ring as in *i*-Pr- and *t*-Bu-cC6, the unpaired electron is largely confined into the bond between the cyclohexyl group and the substituent.

With these structures, the unpaired electron can be efficiently delocalized into the substituent via the hyperconjugative mechanism. This is demonstrated by the appearance of rather large hf splittings for methyl protons in the cations such as 1,2-Me_2-cC6$^+$, 1,*c*-3,*c*-5-Me_3-cC6$^+$, *i*-Pr-cC6$^+$, and *t*-Bu-cC6$^+$. We conclude that the stabilization of a particular ground state is governed not only by the molecular symmetry but also the chemical nature of the functional groups. This parallels the common knowledge about radicals and radical ions of, e.g., unsaturated hydrocarbons. However, since the spin and charge densities of the saturated hydrocarbon radical cations are mostly confined to σ-bonding orbitals, the electronic interactions between various molecular fragments are different compared to radicals with lone paired and π-electrons. These must be carefully investigated before we can make successful predictions of the chemical properties. Here we have presented a study on how various alkyl substituents affect the intrinsically higher laying molecular orbitals of the cyclohexane ring.

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