Radical Cations of *cis*- and *trans*-1,3-Di- and 1,3,5-Trimethylcyclohexanes. Matrix Influence on Two Nearly Degenerate SOMOs

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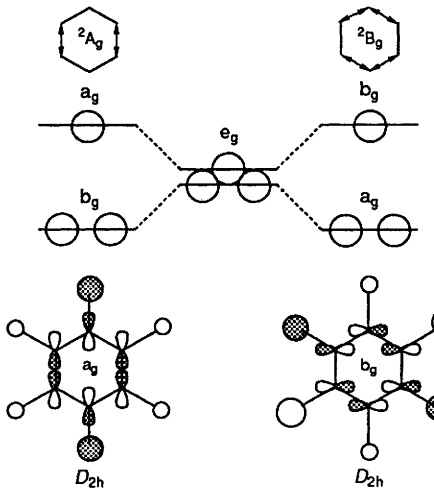
Radical cations of *cis* and *trans* isomers of 1,3-di- and 1,3,5-tri-methylcyclohexane, stabilized in various γ-irradiated solute–halocarbon matrices at 77 K and above, have been investigated by means of EPR spectroscopy. The hfs constants have been compared with those calculated using semiempirical methods, INDO (spin density) and MNDO (geometry optimizations). The SOMOs of the methyl-substituted cyclohexane cations are all similar to either of the orbitals, a_g or b_g, following a Jahn–Teller split of the e_g orbital (HOMO) of cyclohexane. The selection of SOMO depends on matrix and isomer. The *trans* isomers have one axial methyl group and the cations were found to take an a_g-like SOMO in all matrices used, with large spin density on the equatorial hydrogen attached to the axially substituted ring-carbon. Using CF_3CCl_3 as matrix the EPR signal due to the *trans*-1,3,5-trimethylcyclohexane cation contains (in addition) a spectrum of the b_g-like SOMO superimposed. The cation of *cis*-1,3-dimethylcyclohexane shows contributions from both SOMOs in the matrices CF_3-cC_6F_{11}, $CF_2ClCFCl_2$ and CF_3CCl_3, but exclusively a b_g-like SOMO in cC_6F_{12}. A b_g-like SOMO is observed for the *cis*-1,3,5-trimethylcyclohexane cation in all matrices. The abundance ratios, $[a_g]/[b_g]$, for the cases where the matrix-stabilized cation shows contribution from both b_g- and a_g-like SOMOs simultaneously, are found to be *ca.* 1/4 from line shape simulations. No prominent temperature dependence of this ratio is detected.

A method to generate and stabilize otherwise very reactive radical cations for the purpose of EPR spectroscopy was introduced with the halocarbon matrix isolation technique at the end of the seventies.[1–4] Since then, the electronic structures of a large number of saturated cations have been characterized.[5–9] Radical cations of cyclic alkanes with degenerate HOMO (Highest Occupied Molecular Orbital) have attracted much attention owing to the possible characterization of Jahn–Teller distorted ground states.[10–15] The high symmetry leading to the degenerate HOMO can also be lifted by introducing substituents. This has encouraged us to investigate a variety of alkyl-substituted cyclohexane cations,[16–21] which, in each case, were found to have an unpaired electron distribution within the ring-structure similar to either the a_g or b_g SOMO (Singly Occupied Molecular Orbital) of the cyclohexane cation following a Jahn–Teller distortion of the e_g HOMO.

Cations of alkanes can exist in different conformations, formed by the possible rotation of molecular fragments around certain methylene–methylene bonds. It has been established that particularly for linear alkanes[9b,d] the same molecular cation can exist with several different electronic ground states, each associated with a specific conformation. It is also known that the same cation conformation can exist with different ground states; recent studies of the *cis* and *trans* decalin cations revealed the existence of two different ground states in each case with the relative populations determined by the matrix and temperature.[22,23] There is also a case in which the matrix can distort the cation geometry to lower symmetry in certain matrices. Two different SOMOs of the propane cation can be stabilized at low temperature,[24] one of highest possible symmetry (C_{2v}) exclusively in the SF_6 matrix, the other as a distorted form (C_s) in certain halocarbon matrices.

In this report it is shown that two different ground state SOMOs of the same symmetry can be stabilized in radical cations of *cis*-1,3-di- and *trans*-1,3,5-trimethylcyclohexane.

We give first a brief review of the structure of the cyclohexane cation[13–15] and the cations of *cis*- and *trans*-1,3,5-trimethylcyclohexane in the CF_3-cC_6F_{11} matrix which has been reported on previously.[18] Thereafter the new data on *cis* and *trans* isomers of 1,3-di- and 1,3,5-trimethylcyclohexane cations in various matrices, are presented. The results are discussed with reference to semiempirical calculations and previous findings, concerning the cyclohexane cation and alkyl-substituted derivatives thereof.



The Ionization of Cyclohexane.—It has been established that the ionization of the cyclohexane chair conformation can give rise to two possible electronic states, ^2A_g and ^2B_g (in C_{2h}), originating from a Jahn–Teller split of the degenerate ^2E_g (D_{3d} chair) structure.[13–15,18] Each state is associated with a particular geometrical distortion and distribution of the unpaired electron.[15,18] These are summarized as shown above

Table 1 Experimental and calculated ^{1}H hfs constants of the radical cations presented in this study

Radical cation[b]	Matrix	State	Isotropic ^{1}H hfs constants[a]/G Experimental	 Calculated[c]
1,*c*3-Me$_2$-*c*C6	*c*C$_6$F$_{12}$	^{2}A″(C_s)	36 (2 H); 29 (2 H)	32.6 (2 H); 32.1 (2 H)
	CF$_3$CCl$_3$	^{2}A′(C_s)	93 (2 H); 12 (2 H)	88.3 (2 H); 16.3 (2 H)
	CF$_3$CCl$_3$	^{2}A″(C_s)	38 (2 H); 29 (2 H)	32.6 (2 H); 32.1 (2 H)
1,*t*3-Me$_2$-*c*C6	*c*C$_6$F$_{12}$	^{2}A′(C_1)	107 (1 H); 64 (1 H); 35 (1 H)	[d]153 (1 H); 57 (1 H); 21.5 (1 H) [d]82 (1 H); 63 (1 H); 38.6 (1 H)
1,*c*,*t*5-Me$_3$-*c*C6	*c*C$_6$F$_{12}$	^{2}A′(C_s)	125 (1 H); 58 (1 H)	[e]149.5 (1 H); 50.2 (1 H)
	CF$_3$CCl$_3$	^{2}A′(C_s)	156 (1 H); 63 (1 H)	[e]149.5 (1 H); 50.2 (1 H)
	CF$_3$CCl$_3$	^{2}A″(C_s)	45 (2 H); 31 (2 H)	[e]32.9 (2 H); 29.4 (2 H)
1,*c*3,*c*5-Me$_3$-*c*C6	*c*C$_6$F$_{12}$	^{2}A″(C_s)	35 (2 H); 28 (2 H)	[e]32.9 (2 H); 29.4 (2 H)

[a] 10 G = 1 mT. [b] 1,*c*3-Me$_2$-*c*C6: 1,*c*-3-dimethylcyclohexane; 1,*t*3-Me$_2$-*c*C6: 1, *t*-3-dimethylcyclohexane; 1,*c*3,*t*5-Me$_3$-*c*C6: 1,*c*-3,*t*-5-trimethylcyclohexane; 1,*c*3,*c*5-Me$_3$-*c*C6: 1,*c*-3,*c*-5-trimethylcyclohexane. [c] Calculated by INDO for the MNDO optimized geometry. [d] Comparing with and without symmetry condition in geometry optimization, see text for details. [e] From ref. 18.

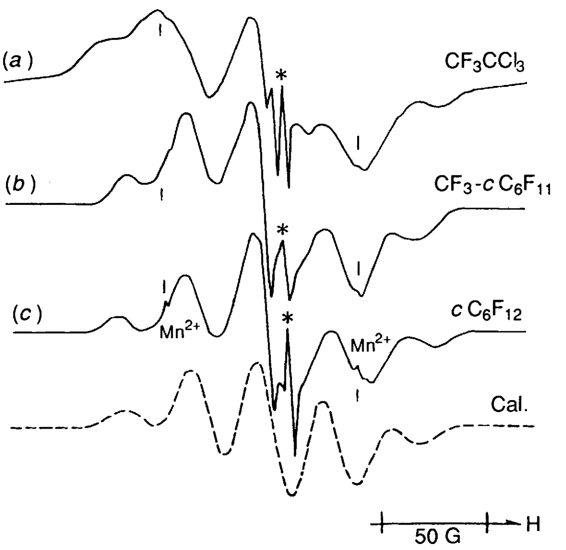


Fig. 1 EPR spectra of the radical cation of 1,*c*-3,*c*-5-trimethylcyclohexane at 77 K in the matrices (*a*) CF$_3$CCl$_3$, (*b*) CF$_3$-*c*C$_6$F$_{11}$ and (*c*) *c*C$_6$F$_{12}$. The dashed curve is a simulation of (*c*) using the following hf parameters: a_H = 35 G (2 H), a_H = 28 G (2 H), gaussian linewidth 20 G.

with schematical SOMOs as projected in the averaged ring plane.

The arrows indicate elongated bonds, typically 1.55–1.60 Å,[15–18] and large hydrogen hyperfine (hf) splitting constants (in gauss) are expected from those hydrogens of equatorial C–H bonds being coaxial with respect to elongated bonds in the ring structure. In earlier reports it has been shown how selective introduction of alkyl substituents stabilizes one of the two possible states.[17–19] The hyperconjugation mechanism for spin transfer from an a$_g$- or b$_g$-like SOMO in the ring structure onto various alkyl substituents has been clarified for monosubstituted, 1,1-disubstituted, 1,2-disubstituted, 1,4-disubstituted and 1,3,5-trisubstituted (methyls) cyclohexane cations.[17–19]

The a$_g$- *and* b$_g$-*like SOMOs of* cis- *and* trans-1,3,5-*Trimethyl-Cyclohexane Cations*.—The *cis*- and *trans*-1,3,5-trimethylcyclohexane cations in CF$_3$-*c*C$_6$F$_{11}$ have been discussed previously,[9c,18] and a short summary is given below. The EPR spectrum of 1,*c*-3,*c*-5-trimethylcyclohexane showed a hf pattern interpreted as a triplet of triplets due to hf splittings, a_H = 37 G (2 H) and a_H = 24 G (2 H). By comparison with the hf parameters calculated using MNDO/INDO calculations, the cation was concluded to take an ^{2}A″ state (in C_s), with the larger of the hf splittings assigned to the two identical equatorial ring hydrogens, and the other to two identical hydrogens on the methyl groups (one on each).

The cation of 1,*c*-3,*t*-5-trimethylcyclohexane was found to have an entirely different EPR spectrum. The hf structure exceeds a field width of 200 G, which is more than 50% larger than for the *cis* isomer, and a doublet of doublets is the only resolved splitting. This could be explained by the appearance of an a′ SOMO in C_s (a$_g$-like). The hf splittings, a_H = 122 G (1 H) and a_H = 62 G (1 H), were assigned to the two unique equatorial hydrogens, that with the larger spin density being the one attached to the carbon substituted with the axial methyl group.

As will be shown in the following section, the two characteristic EPR hf features associated with the ^{2}A′ and ^{2}A″ states discussed above, *i.e.* one wide and one narrower component, appeared also for *cis* and *trans* isomers of cations of both 1,3,5-trimethyl- and 1,3-dimethyl-cyclohexane in various matrices.

Experimental

The solutes and matrices were obtained commercially (Fluka and/or Tokyo Kagaku Seiki Co.) and used without further purification. The solutes were mixed with the matrix (< 1 mol%) on a vacuum line using standard techniques. The radical cations were generated at 77 K by γ-ray irradiation. This is a well established method to generate and stabilize the solute radical cation. The EPR spectra were recorded using a JEOL Spectrometer and analysed with standard techniques.

The semiempirical calculations were performed on a VAX 780 computer. The calculations using the MNDO method developed by Dewar *et al.* were performed using the utilities available within the AMPAC quantum chemical calculation package.[25] Parts of the calculations were performed using the library program MOPAC written by J. P. Stewart and converted by E. Osawa at the Computer Center, Institute for Molecular Science, Okazaki National Research Institute. The spin density was calculated using the INDO method developed by Pople *et al.* using a program of Oloff and Huttermann.[26]

Results

The experimental hf splitting constants are summarized in Table 1. For more details concerning assignments, see text and figure captions.

cis- *and* trans-1,3,5-*Trimethylcyclohexane Cations in Various Matrices*.—The EPR spectra of 1,*c*-3,*c*-5-trimethylcyclohexane in γ-irradiated matrices CF$_3$CCl$_3$, CF$_3$-*c*C$_6$F$_{11}$ and *c*C$_6$F$_{12}$ at 77 K are shown in Fig. 1, respectively. The spectra are similar, but a closer line shape analysis shows that the hfs constants are slightly different. The spectrum in Fig. 1(*c*) (*c*C$_6$F$_{12}$) is well simulated (dashed curve) using hf splittings: a_H = 35 G (2 H)

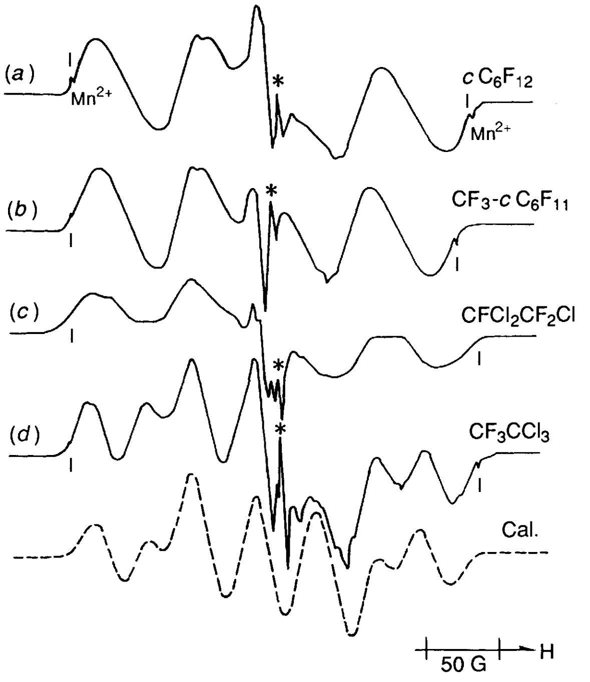


Fig. 2 EPR spectra of the radical cation of 1,*c*-3,*t*-5-trimethylcyclohexane at 77 K in the matrices (*a*) cC_6F_{12}, (*b*) CF_3-cC_6F_{11}, (*c*) $CF_2ClCFCl_2$ and (*d*) CF_3CCl_3. The dashed curve is a simulation of (*d*) using two components with the following hf parameters: (*i*) 25% of total intensity, a_H = 156 G (1 H), a_H = 62.5 G (1 H), gaussian linewidth 22 G; (*ii*) 75% of total intensity, a_H = 45 G (2 H), a_H = 31 G (2 H), gaussian linewidth 22 G.

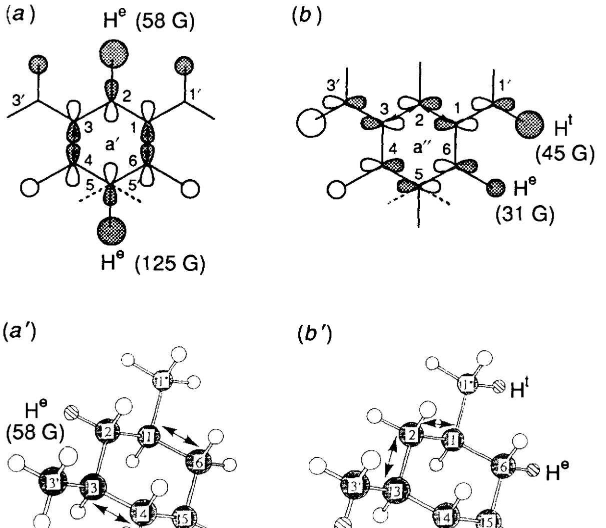


Fig. 3 The assignment of hf splittings and schematics of SOMOs of the radical cation states of 1,*c*-3,*t*-5-trimethylcyclohexane in CF_3CCl_3 at 77 K. (*a*) The a′ SOMO originating from an a_g SOMO of the 'unsubstituted' cyclohexane cation. (*b*) The a″ SOMO resembling the b_g SOMO of the cyclohexane cation. (*a*′) and (*b*′) The molecular conformations of the $^2A'$ and $^2A''$ ground states (C_s symmetry) with hydrogens of high spin density indicated.

and a_H = 28 G (2 H). This should be compared to the previous reported values for the CF_3-cC_6F_{11} matrix, a_H = 37 G and a_H = 24 G, respectively.[18] The small variation in the magnitude of the hf splittings does not contradict the assignment which was given previously,[18] *i.e.* a $^2A''$ state with the hf splittings assigned to the two identical equatorial hydrogens and two methyl hydrogens. The lines of the EPR spectrum found using CF_3CCl_3 are too broad to allow an accurate analysis; however, the resemblance to spectra 1(*b*) and 1(*c*) allows us to deduce a similar electronic structure in this case.

The EPR spectra of the 1,*c*-3,*t*-5-trimethylcyclohexane cation in the matrices *c*-C_6F_{12}, CF_3-cC_6F_{11}, $CF_2ClCFCl_2$ and CF_3CCl_3 at 77 K are shown in Fig. 2. The best resolved spectrum, Fig. 2(*a*) (cC_6F_{12}) was analysed using hfs constants: a_H = 125 G (1 H) and a_H = 58 G (1 H) (not shown); which are similar to the splittings obtained using the CF_3-cC_6F_{11} matrix;[18] a_H = 122 G and 62 G. The $CF_2ClCFCl_2$ matrix gives broader lines, but essentially the same hf splittings can be assumed by comparing the spectra in Figs. 2(*a*) and (*b*). The spectrum obtained using the CF_3CCl_3 matrix [Fig. 2(*d*)] cannot be simulated with only one component.

Being acquainted with the spectral features of the *cis* and *trans* isomers of 1,3,5-trimethylcyclohexane cations in CF_3-cC_6F_{11} and cC_6F_{12}, spectrum 2(*d*) was assumed to contain evidence of two species. Thus, the observed spectrum is well simulated (dashed curve) by superimposing two spectra: (*i*) a_H = 156 G (1 H) and a_H = 62.5 G (1 H), 25% of total intensity; (*ii*) a_H = 45 G (2 H) and a_H = 31 G (2 H), 75% of total intensity. The two components (*i*) and (*ii*) found using the CF_3CCl_3 matrix can be assigned to SOMO similar to those of the $^2A'$ and $^2A''$ states of the trimethylcyclohexane cations in CF_3-cC_6F_{11} and cC_6F_{12}. Schematic diagrams of the SOMOs and assignment of hf splittings for the possible structures of the 1,*c*-3,*t*-5-trimethylcyclohexane cation in CF_3CCl_3 are depicted in Fig. 3.

To summarize and conclude the experimental results for 1,3,5-trimethylcyclohexane cations, an extension of the study of *cis* and *trans* isomers by employing in addition the matrices $CF_2ClCFCl_2$, CF_3CCl_3 and cC_6F_{12}, shows that the same electronic ground states with essentially the same hfs constants are stabilized. In one case, the 1,*c*-3,*t*-5-trimethylcyclohexane cation in CF_3CCl_3, contributions from two 'ground states' are present simultaneously, where the magnitude of the largest hfs constant for each state is *ca.* 20% larger than in the cases where only one state is observed.

Cations of cis- *and* trans-1,3-*Dimethylcyclohexanes.*—The EPR spectra of the 1,*t*-3-dimethylcyclohexane cation in CF_3CCl_3, CF_2ClCF_2Cl, CF_3-cC_6F_{11} and cC_6F_{12} are shown in Fig. 4. All spectra show broad features resembling those found for the $^2A'$ state of the 1,*c*-3,*t*-5-trimethylcyclohexane cation in, *e.g.* cC_6F_{12}. The simulation of spectrum 4(*d*) (dashed curve) was composed using the hfs parameters; a_H = 106.7 G (1 H), a_H = 64.3 G (1 H) and a_H = 34.8 G (1 H). The splittings of 106 G and 64 G are similar to the splittings of 122 G and 62 G found for the 1,*c*-3,*t*-5-trimethylcyclohexane cation in cC_6F_{12} and CF_3-cC_6F_{11}. Furthermore, the splitting of 34 G is the same as reported for one methyl-hydrogen splitting of the methylcyclohexane cation,[17,20] which is known to take a 'distorted' a_g-like SOMO with the methyl group positioned asymmetrically (referring to the unsubstituted C_{2h} cyclohexane cation). Thus, the electronic structure of 1,*t*-3-dimethylcyclohexane cation is concluded to originate from an a_g-like SOMO of the ring structure, having the axial methyl group positioned symmetrically with respect to the 'undistorted' a_g SOMO. The equatorial methyl group is positioned asymmetrically (with reference to the a_g SOMO of the unsubstituted C_{2h} cyclohexane cation), just as in the methylcyclohexane cation. The assignments of splittings and a schematic of the SOMO are depicted in Fig. 5.

The EPR spectra of the 1,*c*-3-dimethylcyclohexane cation in cC_6F_{12}, CF_3-cC_6F_{11}, $CFCl_2CF_2Cl$ and CF_3CCl_3 at 77 K are shown in Fig. 6. Only one component can be observed using the cC_6F_{12} matrix [Fig. 6(*a*)], whereas the remaining spectra [Figs. 6(*b*)–(*d*)] contain contributions from several components. From a line shape analysis of the spectrum in Fig. 6(*a*) the

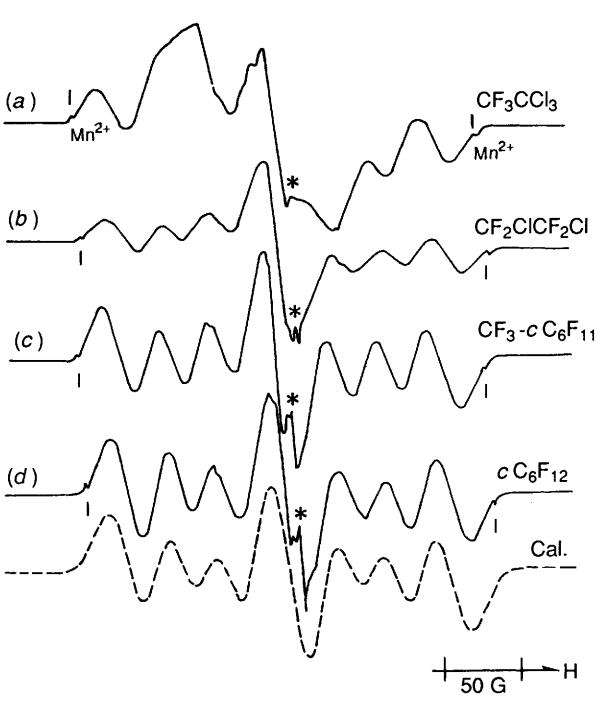


Fig. 4 EPR spectra of the radical cation of 1,*t*-3-dimethylcyclohexane at 77 K in the matrices (*a*) CF_3-cC_6F_{11}, (*b*) CF_3CCl_3, (*c*) $CF_2ClCFCl_2$ and (*d*) cC_6F_{12}. The dashed curve is a simulation of (*d*) using the following hf parameters: a_H = 106.7 G (1 H), a_H = 64.3 G (1 H), a_H = 34.8 G (1 H), gaussian linewidth 25.6 G.

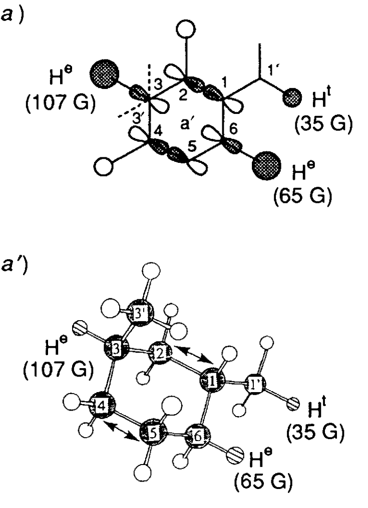


Fig. 5 The assignment of hf splittings and schematic diagrams of SOMOs of the radical cation states of 1,*t*-3-dimethylcyclohexane in cC_6F_{12} at 77 K. (*a*) The SOMO resembling the a_g SOMO of the 'unsubstituted' cyclohexane cation. (*a*′) The molecular conformations with hydrogens of high spin density indicated.

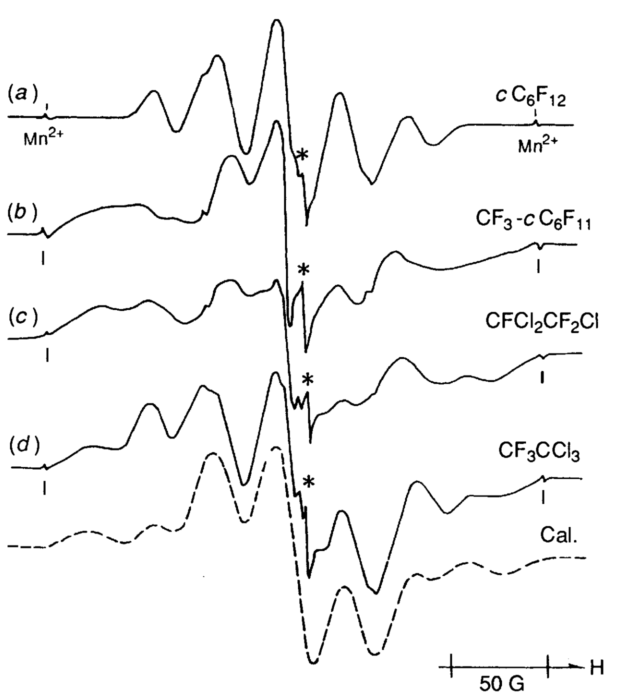


Fig. 6 EPR spectra of the radical cation of 1,*c*-3-dimethylcyclohexane at 77 K in the matrices (*a*) cC_6F_{12}, (*b*) CF_3-cC_6F_{11}, (*c*) $CF_2ClCFCl_2$ and (*d*) CF_3CCl_3. The dashed curve is a simulation of (*d*) using two components with the following hf parameters: (*i*) 15% of total intensity, a_H = 93.3 G (2 H), a_H = 12.2 G (2 H), gaussian linewidth 23.8 G; (*ii*) 85% of total intensity, a_H = 37.8 G (2 H), a_H = 28.7 G (2 H), gaussian linewidth 23.8 G.

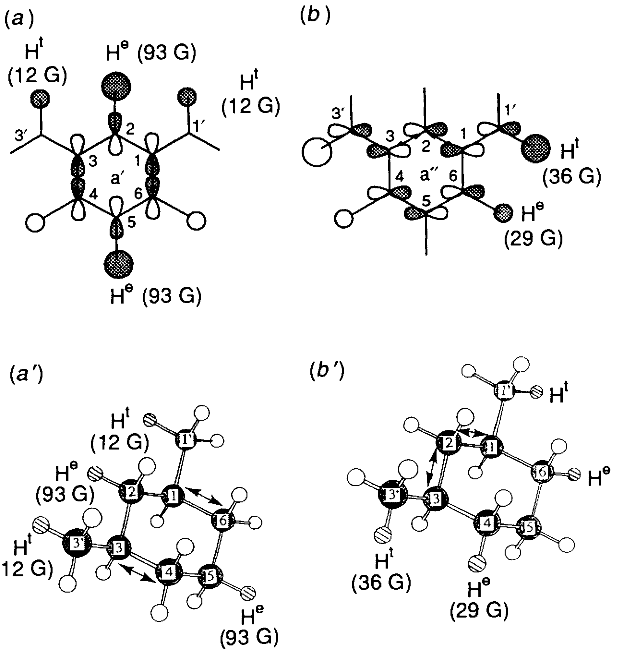
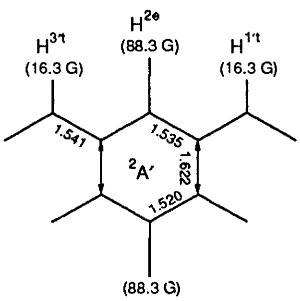


Fig. 7 The assignment of hf splittings and schematic diagrams of SOMOs of the radical cation states of 1,*c*-3-dimethylcyclohexane in CF_3CCl_3 at 77 K. (*a*) The a′ SOMO (in C_s) resembling the a_g SOMO of the 'unsubstituted' cyclohexane cation. (*b*) The a″ SOMO (in C_s) resembling the b_g SOMO of the cyclohexane cation. (*a*′) and (*b*′) The molecular conformations of the $^2A'$ and $^2A''$ ground states (C_s symmetry) with hydrogens of high spin density indicated.

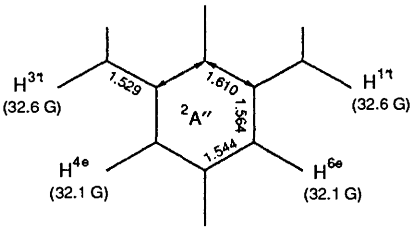
following splittings were concluded, a_H = 36.0 G (2 H) and a_H = 28.7 G (2 H) which almost coincide with the splittings obtained for the a″ (b_g-like) SOMO of 1,*c*-3,*c*-5-trimethylcyclohexane cation in CF_3-cC_6F_{11} or cC_6F_{12} (see Table 1, and the previous subsection). The spectrum obtained using CF_3CCl_3 was analysed assuming two superimposed spectra. The best fit simulation (dashed curve) contains the two components: (*i*) a_H = 93 G (2 H) and a_H = 12 G (2 H), 15% of total intensity; (*ii*) a_H = 38 G (2 H) and a_H = 29 G (2 H), 85% of total intensity. Thus, we may conclude that the 1,*c*-3-dimethylcyclohexane cation exists in two ground states, $^2A''$ and $^2A'$, having SOMOs and corresponding assignment of hyperfine splittings as in analogous electronic structures of the *trans*-1,3-di- and 1,3,5-trimethylcyclohexane, and *cis*-1,3,5-trimethylcyclohexane cations. The assignment of hf splittings and schematic diagrams of the SOMOs for the two electronic structures of the 1,*c*-3-dimethylcyclohexane cation are summarized in Fig. 7.

The hf structure of the EPR spectra of the cation in CF_3-cC_6F_{11} and $CFCl_2CF_2Cl$ [Figs. 6(*b*) and (*c*)] are not well enough resolved to allow an accurate analysis. However, they



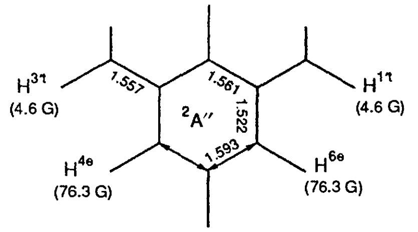
ΔHf/kcal 213.549
Etot/eV −67.034

1



ΔHf/kcal 213.479
Etot/eV −67.031

2



ΔHf/kcal 215.774
Etot/eV −67.024

3

clearly contain contribution from the 'wide' component associated with the a′ SOMO, and at least one narrower component associated with an a″ SOMO. By a comparison with the bulk of collected data discussed in this and earlier sections we may suggest that these spectra contain contributions from both a_g- and b_g-like SOMOs as well.

The discussion is continued in the next section which presents the results of semiempirical calculations of some key structures.

Semiempirical Calculations

The use of combined MNDO (geometry optimization) and INDO (unpaired electron spin density) calculations to guide in the analysis of experimental hf splitting constants from EPR data of alkyl-substituted cyclohexane cations were exemplified recently.[18] The detailed geometrical distortions and spin distributions of the candidate ground state structures of alkyl derivatives of cyclohexane cations, and in particular *cis* and *trans* isomers of 1,3,5-trimethylcyclohexane cations, were treated. Here only some brief comments are given, together with the presentation of results concerning 1,*c*-3-dimethylcyclohexane and 1,*t*-3-dimethylcyclohexane. The calculated hf splitting constants discussed are summarized together with the experimental ones in Table 1.

1,*c*-3-*Dimethylcyclohexane*.—As concluded in the previous section the hf patterns associated with the cation of 1,*c*-3-dimethylcyclohexane in various matrices indicate the existence of two different ground states, $^2A'$ and $^2A''$. MNDO optimizations of input geometries of the ring structure close to those of the geometries of the ^2A_g and ^2B_g states of the cyclohexane cation, yielded three possible distorted structures, as shown above. The carbon–carbon bond lengths are indicated together with the calculated hf splittings [see also Figs. 7(*a*′) and (*b*′)].

Structure **1** corresponds to the a_g-like SOMO a′ (in C_s), observed for the cation of 1,*c*-3,*t*-5-trimethylcyclohexane in cC_6F_{12} and CF_3-cC_6F_{11} [Fig. 7(*a*)]. Structures **2** and **3** both have b_g-like SOMOs [Fig. 7(*b*)], a″ (in C_s), where **2** corresponds to the structure deduced for the 1,*c*-3,*c*-5-trimethylcyclohexane cation in cC_6F_{12} and CF_3-cC_6F_{11}. Structures **2** and **3** can be viewed as the 'W-shaped' SOMO predicted for a C_s structure of the cyclohexane cation[15] where three carbons adopt a geometrical and electronic structure similar to the b_1 orbital of the propane cation.

The difference between the structures **2** and **3** is that the former has the 'W' over three ring carbons and the two methyl groups, whereas structure **3** is mostly confined in a 'W' over the three adjacent unsubstituted ring carbons and the two identical equatorial hydrogens. The calculated hyperfine splittings are collected in Table 1 together with experimental ones. (Only the largest calculated splittings for each structure are given. In each case the remaining ones are all less than *ca.* 5 G in magnitude and irrelevant in comparison with our experimental spectra where the line-width is *ca.* 15 G or larger).

The calculated splittings for the $^2A''$ state, structure **2**, a_H = 32.6 G (2 methyl hydrogens) and a_H = 32.1 G (pair of identical equatorial ring hydrogens) justifies the assignment of experimental splittings, a_H = 36.0 G and 28.7 G using cC_6F_{12}, and a_H = 37.8 G and 29.3 G using CF_3CCl_3. The experimental value a_H = 93.3 G agrees well with the calculated value of 88.3 G for the suggested $^2A'$ state (structure **1**), better than the value of 76.3 G calculated for the $^2A''$ state of structure **3**. Additional support for structure **1** is that the calculated heat of formation is 2.2 kcal mol^{-1} higher in structure **3**.*

It is emphasized that the $^2A'$ state can only be deduced in the case where the CF_3CCl_3 matrix has been used. Structure **3** cannot be ruled out in other cases in which several components were detected for the 1,*c*-3-dimethylcyclohexane cation, such as in the cases where CF_3-cC_6F_{11} and $CF_2ClCFCl_2$ have been used as matrix.

1,*t*-3-*Dimethylcyclohexane*.—In the geometry (MNDO) optimization it was assumed that the carbon–carbon bonds of the ring structure retained the C_{2h} symmetry associated with the a_g structure of cyclohexane. With the methyl groups introduced as outlined in the presentation of the experimental data (Fig. 5), *i.e.* the axial one symmetric and the equatorial one asymmetric with respect to the expected a_g-like SOMO, the optimized carbon–carbon bond lengths became as follows: 1.611 Å for the extended bonds [C(1)–C(2) and C(4)–C(5)]; 1.530 Å for the remaining carbon bonds within the ring; 1.535 Å for the axial methyl group; and finally, 1.544 Å for the equatorial methyl group. The calculated splittings: a_H = 153 G (1 H) for the equatorial hydrogen on C(3); a_H = 57.2 G (1 G) for the equatorial hydrogen on C(6); and a_H = 21.5 G (1 H) for the methyl hydrogen being coaxial with the elongated C(1)–C(2) bond. The remainder are less than the experimental linewidth. Comparing with the experimental data it is clear that the calculated splitting constants are overestimated for the equatorial hydrogen on C(3), whereas the splittings on the equatorial hydrogen on C(6) and on one methyl hydrogen are lower in magnitude (see Fig. 5).

Several other attempts were made to improve the calculated splittings by reducing the symmetry constraint of the ring

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* 1 cal = 4.184 J.

structure and only one will be discussed here. Releasing all symmetry constraints from the geometry 'C_{2h}' presented above gave rise to a distorted structure with a considerable elongation of the C(1)–C(2) bond (1.932 Å), a pronounced shortening of the bonds C(2)–C(3) and C(6)–C(1) to *ca.* 1.508 Å and 1.514 Å, respectively, and the remaining carbon–carbon bonds in the range 1.533–1.555 Å. The hf splitting constants of this structure were as follows: a_H = 82 G (1 H) for the equatorial hydrogen on C(3); a_H = 63 G (1 H) for the equatorial hydrogen on C(6); and a_H = 38 G (1 H) for the methyl hydrogen being coaxial with the elongated C(1)–C(2) bond.

The structure calculated with the symmetry condition overestimates the spin density over the ring fragment C(2)–C(3)–C(4) containing the axial methyl group, with the remaining parts having the spin density underestimated. For the structure calculated using no symmetry condition the reverse is the case. Thus, the calculated hf pattern for both structures agree qualitatively with experimental data and the question of the ring-distortion must remain for further experimental and/or theoretical investigations.

Conclusions

This study presents experimental data on the radical cations of *cis* and *trans* isomers of 1,3-di- and 1,3,5-tri-methylcyclohexanes. The assignment of spectra is based on semiempirical calculations and/or earlier conclusions concerning radical cations of related alkyl-substituted cyclohexane cations.[16–20]

Previously we have elucidated the electronic structures of cations of a variety of alkyl-substituted derivatives, and particularly for the cases with alkyl groups in two positions, such as *cis* and *trans* isomers of 1,1-, 1,2- and 1,4-substitution.[18–20] Concerning the substitution with two methyl groups the data reported herein complete the full range of possible isomers with the addition of the *cis* and *trans* 1,3-disubstituted cases. It has been found that disubstitution in 1,1- and 1,2-positions always gives a SOMO resembling the a_g SOMO of the ring (C_{2h} cyclohexane) structure. On the other hand, the 1,4-substitution stabilizes electronic structures similar to the cyclohexane cation states having b_g (C_{2h}) or a″ (C_s) SOMO.

Interestingly, the 1,3-substituted cations presented herein showed SOMOs of both kinds; exclusively an a_g-like SOMO for the isomer having an axial methyl group (1,*t*-3-) and a b_g-like for the isomer with both methyl groups equatorial (1,*c*-3-), although contribution from the a_g-like SOMO was observed in almost all examined matrices. Thus, if we regard the *trans* isomer as formed by shifting one of the methyl groups from being equatorial to axial in the *cis* structure, and remembering that the isomer with one axial methyl group stabilizes the A_g-like structure regardless of matrix used, we may conclude that the difference in stabilization energy between the levels in the *cis* isomer should be lower than, or at least of the same order of magnitude as, the conformational energy difference between a cyclohexane ring having an equatorial or axial methyl group, the latter well known to be *ca.* 1.8 kcal mol^{-1}. The same argument was introduced to estimate the energy difference between the electronic states in *cis* and *trans* isomers of 1,3,5-trimethylcyclohexane cations in CF_3-cC_6F_{11}.[9c]

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