0 °C was treated with *N*-ethyl-*N'*-(3-(dimethylamino)propyl)carbodiimide methiodide (1.0 equiv) and stirred overnight while the solution was allowed to warm to room temperature. The supernatant solution was concentrated and flash-chromatographed with appropriate solvent. The product obtained was triturated in hexanes.

**2,4,5-Trichlorophenyl Ester 5a**: 23% yield; mp 177–178 °C; IR (KBr) 1775, 1696, 1457, 1350, 1234 $cm^{-1}$; $^1$H-NMR (250 MHz, $CDCl_3$) $\delta$ 8.30 (br, 1 H), 7.58 (s, 1 H), 7.37 (s, 1 H), 7.01 (m, 1 H), 4.73 (s, 2 H), 1.96 (d, $J$ = 1.3 Hz, 3 H).

**Phenyl Ester 5b**: 41% yield; mp 193–194 °C; IR (KBr) 1756, 1696, 1652, 1457, 1203 $cm^{-1}$; $^1$H-NMR (250 MHz, $CDCl_3$) $\delta$ 8.35 (br, 1 H), 7.40 (t, $J$ = 7.3 Hz, 2 H), 7.26 (t, $J$ = 7.4 Hz, 1 H), 7.13 (d, $J$ = 7.4 Hz, 2 H), 7.02 (m, 1 H), 4.69 (s, 2 H), 1.95 (d, $J$ = 1.0 Hz, 3 H); HRMS calcd for $C_{13}H_{12}N_2O_4$ 260.0797, found 260.0795.

**Diaminotriazine–Thymine Template 6.** Diaminotriazine amine **3** (61 mg, 0.118 mmol) and the trichlorophenyl ester **5a** (43 mg, 1.0 equiv) were allowed to react for 20 min in 6 mL of dry $CH_2Cl_2$ and $Et_3N$ (100 $\mu$L) under argon. Flash chromatography of the concentrated residue with 5–10% MeOH in $CH_2Cl_2$ gave 81 mg (100%) of **3** as a white powder: mp 200–205 °C; IR (KBr) 3340, 3217, 2960, 2850, 1684, 1652, 1538, 1535, 1432 $cm^{-1}$; $^1$H-NMR (250 MHz, $CDCl_3$) $\delta$ 12.9 (br, 1 H), 8.34 (t, 1 H), 8.08 (d, $J$ = 2.2 Hz, 1 H), 7.75 (br, 2 H), 7.57 (d, $J$ = 2.3 Hz, 1 H), 7.52 (d, $J$ = 2.1 Hz, 1 H), 7.47 (d, $J$ = 2.1 Hz, 1 H), 7.31 (br, 1 Hr), 7.07 (s, 1 H), 5.43 (br, 2 H), 4.31 (s, 2 H), 3.3–3.5 (m, 4 H), 1.90 (s, 3 H), 1.67 (s, 6 H), 1.34 (s, 18 H); HRMS calcd for $C_{36}H_{45}N_9O_5$ 683.3544, found 683.3543.

**Kinetic Studies.** The reaction of thymine ester **5b** with diaminotriazine amine **3** in the presence or absence of template **6** was performed in $CHCl_3$ solution containing 18 equiv of triethylamine (TEA). A Waters 600 HPLC (Multisolvent Delivery System) equipped with a UV detector (Waters, Lambda-Max, Model 481 LC spectrophotometer) set at 254 nm (AUFS = 1.0) was used for analysis of reaction mixtures. Analyses were performed using a reverse-phase column (Beckman C18 column, Ultrasphere ODS dp, 5 $\mu$, 4.6 mm, i.d. × 25 cm, flow rate = 1.0 mL/min) and a mixture of water/methanol/TEA (16:84:0.6) as a mobile phase. The integration of peaks and calculation of concentrations were performed using an NEC computer and Waters 820 Baseline software. Chloroform was dried over molecular sieves. All experiments were performed at ambient temperature (21.5–23.0 °C). Each run was performed two or three times to obtain average values for data.

**Typical Reaction Procedures.** A Wheaton reaction vial (0.3 mL) equipped with a Microflex Miniert valve and Microflex stir vane was charged with 40 $\mu$L of diaminotriazine amine **3** stock solution ($2.0 \times 10^{-2}$ M), 20 $\mu$L of $CHCl_3$, 2 $\mu$L of TEA, and finally 40 $\mu$L of thymine ester **5b** stock solution ($2.0 \times 10^{-2}$ M). Aliquots (2.0 $\mu$L) were withdrawn periodically and analyzed by HPLC. The retention times of product (template) **6**, diaminotriazine amine **3**, and thymine active ester **5b** were 7.4, >12, and 2.4 min, respectively.

**Acknowledgment.** We are grateful to the National Institutes of Health and the National Science Foundation for financial support of this research and to M. Conn for experimental assistance.

**Registry No. 1a**, 130525-39-2; **1b**, 140663-26-9; **1c**, 140663-27-0; **1d**, 140663-28-1; **2**, 140663-23-6; **3**, 140663-24-7; **4**, 20924-05-4; **5a**, 140676-57-9; **5b**, 140663-29-2; **6**, 140663-25-8; biguanide, 56-03-1; ethylenediamine, 107-15-3.

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# Ab Initio Study of Vibrationally Preferred Deuteration Sites in the Cyclopropane-$d_2$ Radical Cation

**Leif A. Eriksson and Sten Lunell***

*Contribution from the Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20 Uppsala, Sweden.* *Received December 3, 1991*

**Abstract:** The relative stabilities of various positional isomers of partially deuterated cyclopropane cations have been studied theoretically, using ab initio UHF/6-31G** calculations, and compared with the results of low-temperature matrix-isolation ESR (electron spin resonance) experiments. Deuteration at the top carbon is, from differences in zero-point vibrational energies (ZPE), calculated to be more favorable than in any of the basal positions, in agreement with experiments on the cyclopropane-*1,1*-$d_2$ cation (the ground state of the cation being an obtuse, equilateral triangle). The relative abundance of the isomers, observed at 4 K in the absence of annealing, is found to correspond to the calculated Boltzmann distribution at 100 K, indicating that thermal equilibration is hindered at temperatures below this. This agrees with experimental studies of the dynamic Jahn–Teller effect, as well as experiments involving annealing at 20–77 K. Somewhat unexpectedly, the preferred deuteration sites are in the longer C–H bonds, in contrast to, e.g., the methane or *n*-butane cations, where the opposite is true. It is shown that this is caused by strong interactions in the low-frequency (bending) part of the vibrational spectrum.

## 1. Introduction

Partial deuteration has been applied very successfully during recent years in connection with electron spin resonance (ESR) studies of hydrocarbon radical cations.[1] As an example, it was possible by this technique, in combination with accurate quantum-chemical calculations, to resolve the long-standing discussion about the ground-state conformation of the methane radical cation.[2-4] By studying the doubly deuterated species, $CH_2D_2^+$, it was shown that the methane cation has a $C_{2v}$ distorted ground state and that the deuterium atoms preferentially occupy the two shorter bonds, whereas the protons occupy the two longer bonds. In certain cases, however, it has been impossible to associate the observed ESR spectra with any unique nuclear arrangement even at low temperatures, and thus a mixture of conformations has had to be assumed in order to obtain satisfactory simulations of the spectra.[5-9]

We have, in a recent paper,[10] analyzed one such case in detail, namely, the *n*-butane cation (more precisely, the *n*-butane-*1,1,4,4*-$d_4$ and *n*-butane-*1,4*-$d_2$ radical cations), and shown that

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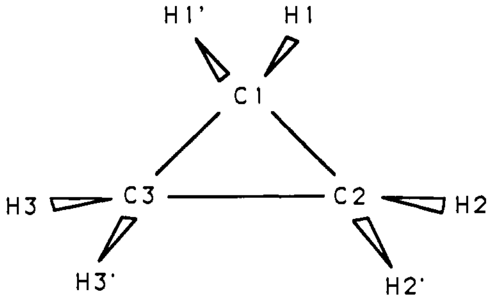

**Figure 1.** Structure and labeling of the cyclopropane radical cation ($C_{2v}$ symmetry).

the experimentally deduced abundances of the various conformational isomers follow a Boltzmann distribution based on their zero-point vibrational energies (ZPE). For example, for the *n*-butane-*1,1,4,4*-$d_4$ cation there are three different possible arrangements of the protium atoms on the terminal methyl groups. These are in-plane–in-plane, in-plane–out-of-plane, and out-of-plane–out-of-plane, where the "plane" is the local plane defined by the three adjacent carbon atoms. The statistical abundance ratio between these isomers is 1:4:4, whereas experimentally a superposition of the corresponding spectra in the ratio 3.0:4.9:2.1 was observed in a $CF_3CCl_3$ matrix at 77 K.[5] Calculating the ZPE for the different conformations at the HF/6-31G** level and using Boltzmann statistics based on these energies to calculate the relative abundance ratios at $T = 77$ K led to the ratio 2.9:4.7:2.4 for the gauche form (2.5:5.2:2.3 for the trans conformation), in excellent agreement with the observed ratios. Estimates were also made of the temperature below which deviations from Boltzmann statistics should be expected, in good agreement with observations.

In the present paper, a similar analysis is made of the doubly deuterated cyclopropane cation, and the results are related to experimental observations made in low-temperature matrix-isolation ESR measurements.[9] As will be seen below, the vibrational motion is in a sense more complex in the cyclopropane cation than in the butane and methane cations, giving rise to some important differences between the two systems.

## 2. Theory

To a first approximation, the ZPE of a particular C–H stretching vibration is proportional to the energy of a harmonic oscillator, $E_{ZPE} \propto (k/m)^{1/2}$, where *k* is the force constant and *m* is the mass of the hydrogen nucleus. In order for the system to lower its ZPE, the deuterium atoms in a partially deuterated compound will hence, at low enough temperatures, preferentially occupy sites with larger force constants. As the temperature increases, other conformations do, however, become accessible when the rotational and vibrational motions become strong enough to overcome the barriers separating different conformational isomers. For high enough temperatures, the population of these new conformations, or states, can be assumed to follow a Boltzmann distribution.

In a more accurate treatment, the true potential energy hypersurface governing the nuclear motion must be calculated, within the Born–Oppenheimer approximation. The ZPE are then obtained from the calculated potential energy surface by performing separate normal coordinate analyses for each isomer of the partially deuterated compound. The calculations in the present paper follow this procedure and were all done at the HF/6-31G** level of approximation.[11] The geometry was first optimized within the $C_{2v}$ point group symmetry, after which the protons were substituted by deuterons at appropriate positions, and the vibrational frequencies and total ZPE were calculated. The harmonic approximation was used, and the force constants were calculated from finite differences of analytical first derivatives. The program package GAMESS[12] was used throughout the study.

In a typical matrix-isolation ESR experiment, the sample is cooled to temperatures between 4 and 100 K, and it may happen that, at a certain temperature, the internal motions become too slow to overcome the rotational or vibrational barriers between the different conformers. If the cooling is fast enough, a certain distribution between isomeric forms may in such cases become "frozen" and can be observed at lower temperatures than initially expected.[7,8,10] This will be discussed further below.

**Table I.** Geometries and Total Energies Obtained from the UHF/6-31G*, UHF/6-31G**, and MP2/6-31G** Geometry Optimization Calculations[a]

| | UHF/6-31G*[b] | UHF/6-31G**[c] | MP2/6-31G**[d] |
|---|---|---|---|
| *R*(C1–C2) | 1.4765 | 1.4760 | 1.4746 |
| *R*(C2–C3) | 1.8744 | 1.8730 | 1.8420 |
| *R*(C1–H1) | 1.0779 | 1.0782 | 1.0833 |
| *R*(C2–H2) | 1.0743 | 1.0751 | 1.0804 |
| ∠(C2–C1–C3) | 78.8 | 78.8 | 77.3 |
| *E* | −116.749 204 | −116.759 694 | −117.157 305 |

[a] Bond lengths are in angstroms, angles in degrees, and energies in atomic units (1 au = 2.6255 × $10^3$ kJ/mol). [b] Reference 16. [c] This work. [d] Reference 15.

**Table II.** Zero-Point Energies and Statistical Abundance Ratios for the Different Substitutional Isomers of the Cyclopropane-$d_2$ Radical Cation[a]

| deuterated position | ZPE, kJ/mol | isomer | statistical abund ratio |
|---|---|---|---|
| 1,1 | 200.5118 | I | 1 |
| 2,2 | 201.6652 | II | 2 |
| 1,2 cis | 201.0888 | III | 4 |
| 1,2 trans | 201.1319 | III | 4 |
| 2,3 cis | 201.6947 | IV | 2 |
| 2,3 trans | 201.7385 | IV | 2 |

[a] The labeling of the deuterated positions refers to the carbon atoms of Figure 1.

**Table III.** Boltzmann Distributions and, within Parentheses, Calculated Abundance Ratios for the 1,1 and 2,2 (3,3) Isomers of the Cyclopropane-$d_2$ Cation

| temp, K | 1,1 | 2,2 (3,3) |
|---|---|---|
| 100 | 1.0000 (6.7) | 0.4995 (3.3) |
| 77 | 1.0000 (7.5) | 0.3306 (2.5) |
| 50 | 1.0000 (8.9) | 0.1248 (1.1) |
| 20 | 1.0000 (10.0) | 0.0010 (0.0) |

## 3. Results and Discussion

Cyclopropane in its cationic form is Jahn–Teller active and distorts from the structure of $D_{3h}$ symmetry to an isosceles, obtuse triangle of $C_{2v}$ symmetry (Figure 1). The singly occupied molecular orbital (SOMO) of the cyclopropane radical cation is the $6a_1$ orbital,[13,14] as has been confirmed by extensive ab initio studies (see, e.g., ref 15 and references therein). The electronic ground state of the cation is thus ${}^2A_1$.

The geometrical parameters and UHF energy, obtained in the present study, are listed in Table I together with results from previous HF/6-31G*[16] and MP2/6-31G**[15] geometry optimization calculations. From the HF/6-31G** calculations performed in the present study, the geometry *R*(C1–C2) = 1.476 Å, *R*(C2–C3) = 1.873 Å, and ∠(C2–C1–C3) = 78.77° was obtained for the carbon framework. The C1–H bonds are found to be 1.078 Å, and the C2–H (C3–H) bonds are 1.075 Å. It can be seen that the inclusion of polarization functions on the hydrogen atoms (i.e., comparing the HF/6-31G* and HF/6-31G** results, listed in Table I) leaves the calculated equilibrium geometry of the cation virtually unaffected. If electron correlation is taken into account (MP2/6-31G**, Table I), the effects on the geometry are also rather small. In the MP2 calculations (as compared to HF), the C2–C1–C3 angle decreases slightly, as do the three carbon–carbon

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**Table IV.** Boltzmann Distributions and, within Parentheses, Calculated Abundance Ratios for the 1,2 (1,3) and 2,3 Isomers of the Cyclopropane-$d_2$ Cation

| temp, K | 1,2 (1,3) | 2,3 |
|---|---|---|
| 100 | 7.7978 (8.1) | 1.8805 (1.9) |
| 77 | 7.7394 (8.4) | 1.5011 (1.6) |
| 50 | 7.6059 (9.0) | 0.8847 (1.0) |
| 4 | 5.0938 (10.0) | 0.0000 (–) |

bond distances. The C–H bonds, instead, increase by about 0.006 Å. The geometry of the cyclopropane radical cation can thus be considered as relatively insensitive as far as basis set effects and electron correlation are concerned.

**A. Comparison with Experimental Data.** The ZPE of the various substitutional isomers of the cyclopropane-$d_2$ cation, calculated in the present study, are listed in Table II. The statistical abundance ratio (degeneracy factors) of the four isomeric types I (1,1), II (2,2), III (1,2), and IV (2,3) is 1:2:8:4. Isomers I and III, where the C1 carbon is deuterated, are seen to be more stable than those where the deuterium atoms only occupy the basal carbon atoms.

The Boltzmann populations corresponding to these ZPE (including degeneracy factors) are shown for different temperatures in Tables III and IV. As can be seen, the calculated populations differ strongly from the pure statistical ratios quoted above. For example, the 1,1-substituted isomer is at all temperatures predicted to be more populated than the 2,2-substituted (3,3-substituted) isomers, rather than the opposite. A similar systematic trend can be observed also for the 1,2-substituted isomers.

Experimentally, the cyclopropane-*1,1*-$d_2$ cation has been studied by ESR at temperatures from 4 to 100 K by Matsuura et al.[9] They found that, at low temperatures, 1,1 substitution is preferred, whereas at higher temperatures the C1 carbon (cf. Figure 1), through vibrational motions, may become one of the "basal" carbon atoms, giving a "pseudo"-2,2 substitution. The ESR spectrum obtained at 4 K was attributed by Matsuura et al. to a superposition of isomers I and II in the ratio 2:1. As shown in Table III, this ratio corresponds to the calculated Boltzmann populations at 100 K, rather than 4 K. From this, one can conclude that the vibrational motion responsible for the thermal equilibrium between isomeric forms I and II is quenched at temperatures lower than 100 K, on the time scale defined by the ESR experiment. This is confirmed by the analysis performed by Matsuura et al., which does show the onset of a dynamical averaging between isomers I and II (dynamic Jahn–Teller effect), leading to a qualitative change of the form of the ESR spectrum, at temperatures above 100 K.

After annealing at a temperature between 20 and 77 K (different temperatures for different matrices), the spectra were found[9] to change irreversibly to the 1,1 form. Also, this is in accord with the predictions of Table III. As the temperature is increased above 4 K, enough vibrational motion will be available to overcome the energy barrier connecting the two forms 1,1 and 2,2. At 20 K, only the 1,1 isomer is populated, according to Table III, so that the probe containing the "frozen" 2:1 distribution from 100 K, on annealing for a long enough period of time, will attain the equilibrium distribution valid for that specific temperature. It should be noted that it is not possible to reach the 1,2 (1,3) and 2,3 isomers from the 1,1 isomer by vibrational motions alone, but that a true hydrogen-exchange reaction is required for this transformation.

**B. The 1,2 and 2,3 Isomers. Ring Opening.** Although no experimental data are available as yet for the 1,2 and 2,3 isomers of the cyclopropane-$d_2$ cation, the Boltzmann populations of these conformations at various temperatures were calculated. The results are listed in Table IV. The conformation with a deuterated 1-position (1,2) is, in this case, even more stable relative to the isomers with only the basal carbon atoms deuterated (2,3) than what was observed for the 1,1 vs 2,2 isomers. At 100 K, the abundance ratio between the 1,2 and 2,3 isomers is obtained as 4:1, to be compared with the ratio of 2:1 obtained for the 1,1 and 2,2 (3,3) isomers (Table III). The vibrational barriers should be nearly identical for the 1,1- and 1,2-substituted cations, so that the distribution between the conformations can be assumed to be frozen at approximately 100 K also for the 1,2 isomer. This leads to a predicted abundance ratio of approximately 4:1 for isomers III and IV at temperatures lower than 100 K.

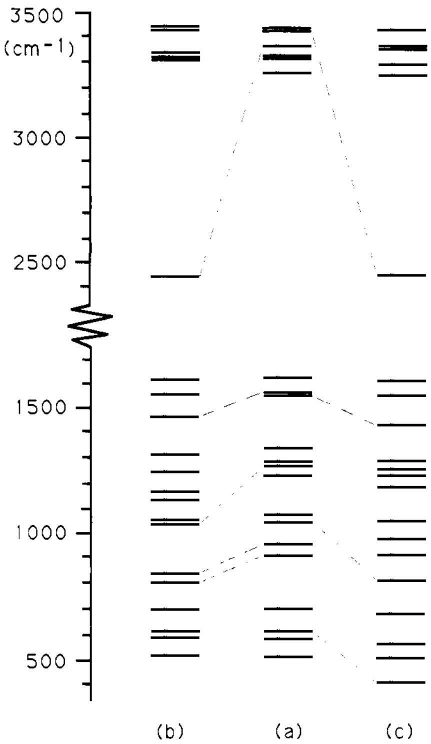

**Figure 2.** Frequency distributions (cm$^{-1}$) of the undeuterated (a) and C1 and C2 singly deuterated (b and c, respectively) cyclopropane radical cations.

As the temperature is lowered, the calculated abundance ratio is increased further, in favor of the 1,2 isomer. At 4 K, the ratio between the 1,2 and 2,3 conformations is 10:0, and it is also found that the cis-1,2 conformation dominates over the corresponding trans form by a ratio of 4:1. At 100 K, the cis:trans ratio for the 1,2 isomer is 1:1. In the cyclopropane cation, the C2–C3 bond is already significantly elongated (cf. Table I), and a ring-opening process accompanied by a rotation of a (deuterated) methylene group around the remaining $\sigma$-bond is thus not improbable. The cis/trans isomerization reaction of the cyclopropane radical cation has been investigated previously by Lunell et al.[15] in a study of the ring-opening process leading to the trimethylene radical cation. They found that the trimethylene cation is a saddle point on the cyclopropane UHF/3-21G energy surface, with a transition energy of 20 kcal/mol. It was also found that, in the trimethylene cationic transition state, one of the terminal $CH_2$ groups is rotated 90° to lie in the plane formed by the carbon skeleton,[15] which strongly supports the possibility of cis/trans isomerization.

**C. Vibrational Analysis.** The longest C–H bonds in the cyclopropane cation are those connected to the C1 carbon atom (Table I). According to the approximation that the stretching vibrations can be described as harmonic oscillators, the deuterium atoms should preferentially occupy the positions bearing the shortest C–H bonds, in this case connected to the basal C2 and C3 carbon atoms (cf. Section 2), as has been found previously to be the case for, for example, $CH_2D_2^{+}$ [2] and partially deuterated *n*-butane cations.[10] However, as described above, the lowest ZPE are obtained instead for those isomers where the C1 carbon is deuterated. In order to investigate this disagreement between the simple theoretical model and the actual results from both experiments and calculations, a careful analysis of the individual vibrational frequencies of the undeuterated and singly deuterated cyclopropane radical cations, calculated at the HF/6-31G** level, was conducted. For a symmetry classification of the vibrations of the undeuterated cation, we refer to Bouma et al.[16] Since the

**Table V.** Vibrational Frequency Components in the High- and Low-Frequency Regions ($cm^{-1}$) along with the Total ZPE (kJ/mol), for the Undeuterated and Singly Deuterated Isomers of the Cyclopropane Cation[a]

| deuterated position | frequency range high (2000–3500 $cm^{-1}$) | frequency range low (0–2000 $cm^{-1}$) | ZPE (kJ/mol) |
|---|---|---|---|
| – (a) | 20 200.29 | 16 454.88 | 219.0673 |
| C1, apical (b) | 19 321.48 | 15 753.81 | 209.7940 |
| C2, basal (c) | 19 302.47 | 15 868.68 | 210.3704 |

[a] The results are from UHF/6-31G** calculations.

symmetry will be broken by the deuteration, it will not be used here.

In Figure 2, the individual frequencies for the (a) undeuterated, (b) C1 singly deuterated, and (c) C2 singly deuterated species are displayed. The top part of the spectrum, at 2400–3500 $cm^{-1}$, corresponds essentially to the C–H/C–D stretching vibrations. For the undeuterated cyclopropane radical cation, these all lie within 200 $cm^{-1}$, whereas if one of the protons is substituted for a deuteron, the energy of the stretching vibration of that particular bond is lowered by about 1000 $cm^{-1}$, in accordance with theory. In Table V, the contributions to the total ZPE have been shown separately for the high-frequency C–H/C–D stretch range 2000–3500 $cm^{-1}$ and for the low-frequency region below 2000 $cm^{-1}$, containing all other types of vibrational modes. When one of the long C–H bonds is deuterated (case b in Figure 2), the partial ZPE for the C–H/C–D stretching vibrations is actually found to be larger than when the deuteration occurs at one of the shorter bonds in the C2 or C3 position (case c). The simple harmonic model ($E_{ZPE} \propto (k/m)^{1/2}$) is thus valid as long as only the high-frequency range containing the C–H stretching vibrations is considered. The answer to the question of why the C1 deuterated species obtain a lower total ZPE than when a basal carbon is deuterated is hence to be found in the low-frequency part (0–2000 $cm^{-1}$) of the spectrum.

In the low-frequency region, the four lowest normal modes of the undeuterated cation primarily describe bending vibrations of the four basal hydrogens. Consequently, these frequencies are essentially unaffected by deuteration in the 1 or 1′ positions, whereas deuteration in one of the basal positions shifts one of the frequencies, $\nu_3$, downward by approximately 130 $cm^{-1}$. The next two vibrations, $\nu_5$ and $\nu_6$, have their largest amplitudes at the apical hydrogens H1 and H1′ and consequently are affected quite strongly by deuteration in these positions, while being less sensitive to deuteration in one of the basal positions. The opposite is true for $\nu_7$ and $\nu_8$, which describe symmetrical and antisymmetrical combinations of bending vibrations of the basal hydrogens; deuteration in this position consequently causes one of these frequencies to decrease, in this case also by 130 $cm^{-1}$.

Of the next four vibrations, $\nu_{10}$ and $\nu_{12}$ describe in-phase and out-of-phase "wagging" vibrations of H1 and H1′; deuteration at one of these positions decouples these vibrations and lowers one of the frequencies by ca. 240 $cm^{-1}$. The other two vibrations in this group, $\nu_9$ and $\nu_{11}$, involve all six hydrogens and are shifted slightly toward lower frequencies on deuteration at any position. Of the three remaining vibrations below 2000 $cm^{-1}$, $\nu_{13}$ involves only the basal carbons and is downshifted by 120 $cm^{-1}$ upon deuteration on one of these sites, and $\nu_{14}$ is localized to the apical hydrogens and is downshifted by deuteration at the 1 and 1′ positions, in this case also by 120 $cm^{-1}$, whereas $\nu_{15}$ involves all six hydrogens but is affected rather little by deuteration in any position.

It is evident from Figure 2 that the net effect of deuteration in any position will be a lowering of the contribution to the ZPE coming from the frequency region below 2000 $cm^{-1}$. A detailed calculation shows, in addition, that the lowering is significantly larger for deuteration in the 1 or 1′ positions than in any of the basal positions, in fact almost 20% larger (see Table V). This difference is large enough to overcome the opposite tendency in the high-frequency (C–H stretching) region, making the total ZPE lowering about 7% larger for 1 or 1′ deuteration, i.e., in the longer C–H bonds, than for deuteration at the other sites, where the C–H bonds are shorter.

At this moment we cannot suggest an easy, intuitive explanation for the results reported above, but only note that they are fully confirmed by the experiments by Matsuura et al.[9] Since both the methane[2] and *n*-butane[10] cations show the expected behavior, i.e., that deuteration is preferred at the short C–H bonds, it is natural to associate the unexpected results for the cyclopropane cation with its ring structure, which will cause stronger and more intricate couplings between the atomic vibrations than in an open system.

## 4. Conclusion

In the present paper, it has been shown that an analysis of the vibrational ZPE at the HF/6-31G** level, as outlined in a previous paper,[10] is capable of explaining the observed abundances of the different substitutional isomers of the cyclopropane-*1,1*-$d_2$ radical cation. The matrix-isolation ESR results at 4 K have been shown to correspond to freezing the distribution between the different conformations at about 100 K, below which the vibrational motion connecting the two isomers occurs at a very low rate. Since the 1,1 conformer is found to be the most stable of the two (Table III), annealing at temperatures below 100 K for long enough times inevitably leads to an increasing population of the 1,1 isomer, in agreement with the observations made in ref 9.

Considering only the 1,2 and 2,3 deuteration isomers, it is found that, at very low temperatures, the dominating conformation is the cis-1,2 conformation, relative to the trans-1,2 or cis/trans-2,3 isomers. It is suggested that, in accordance with a previous study,[15] ring opening by breaking the elongated C2–C3 $\sigma$-bond and rotation of a terminal methylene group is responsible for the isomerization process leading to an increased cis-1,2 population.

The species with lowest ZPE are those where the top (C1) carbon atom has been deuterated. This is despite the fact that these C–H bonds are longer than those connected to the basal carbons and give higher partial ZPE when only the C–H/C–D stretching vibrations are considered. The explanation of this unexpected result lies in the strong coupling between the different vibrations in the low-frequency range (450–2000 $cm^{-1}$), which cause the total ZPE to become lower when deuterating the C1 carbon than one of the basal carbon atoms.

**Acknowledgment.** This work was financed by the Swedish National Science Foundation (NFR). The National Supercomputer Centre (NSC) at the University of Linköping is acknowledged for a grant of computer time on the Cray X-MP/48 computer.

**Registry No.** Cyclopropane radical cation, 34496-93-0; 1,1-dideuteriocyclopropane radical cation, 91146-48-4; *cis*-1,2-dideuteriocyclopropane radical cation, 140849-63-4; *trans*-1,2-dideuteriocyclopropane radical cation, 140849-64-5.