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Notes

2-Chloroallyl Cation. Structure, FT-IR Spectra, and Matrix Isolation

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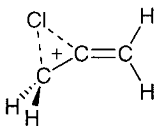
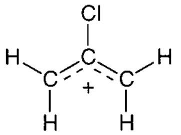
Although a series of chloro-substituted allyl cations were already characterized by NMR and IR spectra,[1] the problem of the structure of the 2-chloroallyl cation (**1**) still remained an open question.[2] It is known that allyl cations are sensitive to the electron donating capabilities of their substituents. Chlorine bound to the terminal C-atom of the allyl group has a stabilizing effect that can be ascribed to the back-donation of n-electrons. This effect is manifested in the lowering of the rotational barrier observed for the *cis*−*trans* isomerization of 1-chloroallyl cations.[1a] Moreover, the extent of the stabilization by a terminal chlorine is almost the same as by a terminal methyl group.

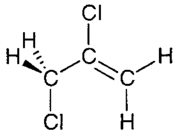
However, an electron donating substituent bound to the central carbon atom of the allyl group has no stabilizing effect by π-conjugation. It was found[3] that the solvolysis rate of 2-chloro- and 2-bromoallyl esters is much lower than that of the parent allyl tosylate. This inter alia may be a consequence of the π-orbital noninteraction between the halogen n-electrons and the allyl cation LUMO. The orbital that describes halogen lone pair electrons lies in the bisecting nodal plane of the LUMO of the allyl cation. From such a point of view, it may be expected that the preferred effect of chlorine in **1** is bridging rather than a back-donation of n-electrons, and the C_s structure **1a** seemed to be more favorable.



1a (C_s)



1b (C_{2v})



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This structure could also be considered as a kind of allene chloronium ion. Previously published ^{1}H NMR spectra of **1** in a SbF_5/SO_2 solution were explained by such a structure.[2] The more symmetric C_{2v} structure **1b** has not been taken into account in an explanation of these spectral data. However, in spite of the lack of π-interaction between the allyl group and the chlorine atom, the structure **1b** could be considered to be at least as stable as isomer **1a**. Stability of **1b** may originate from a perfect allyl group π-electron delocalization. Additionally, the destabilizing sterical and strain effects are absent in this structure.

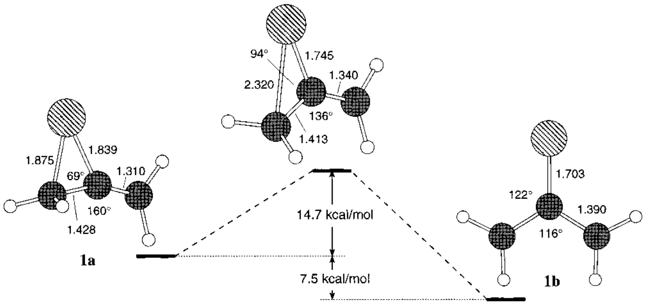

Figure 1. MP2(fc)/6-311G(d,p) optimized geometries and relative energies (including ZPVE correction) of cations **1a** and **1b** and transition structure for their interconversion.

In this work, we represent a reinvestigation of the structure of **1** by ab initio calculations on the MP2 and DFT level of theory. The results of the calculations are supplemented with the experimental approach to the isolation and FT-IR characterizations of the ion.

Results and Discussion

Results of Calculations. The energies of cations **1a** and **1b** and the transition structure for their interconversion were calculated at the MP2(fc)/6-311G(d,p) level of theory (Figure 1). The C_{2v} structure **1b** is 7.5 kcal/mol (ZPVE-corrected value) more stable than the chlorine-bridged isomer **1a**. The activation energy for the isomerization of **1a** to **1b** is calculated to be 14.7 kcal/mol. At the DFT level (B3LYP/6-311G(d,p)), the stability relation between **1a** and **1b** is not much different than at the MP2 level. Isomer **1b** (C_{2v}) is 10.1 kcal/mol (ZPVE-corrected value) more stable than **1a**. Theoretically, both of the carbocations are isolable. Noninteraction of the chlorine n-electrons in **1b** could be demonstrated by unchanged values of the C−Cl bond distance. It is less shortened (1.703 Å, compared to 1.640 Å in 1-chloroallyl cation, 1.747 Å in 2-chloropropene, or 1.735 Å in 2,3-dichloropropene (**2**), all at MP2(fc)/6-311G(d,p)) than could be expected for the structures with more significant chlorine interaction. A decrease in the C−Cl bond length by 0.067[4a] and 0.058[4b] Å in going from a neutral chloride to an α-chlorocarbocation has been observed by X-ray dif-

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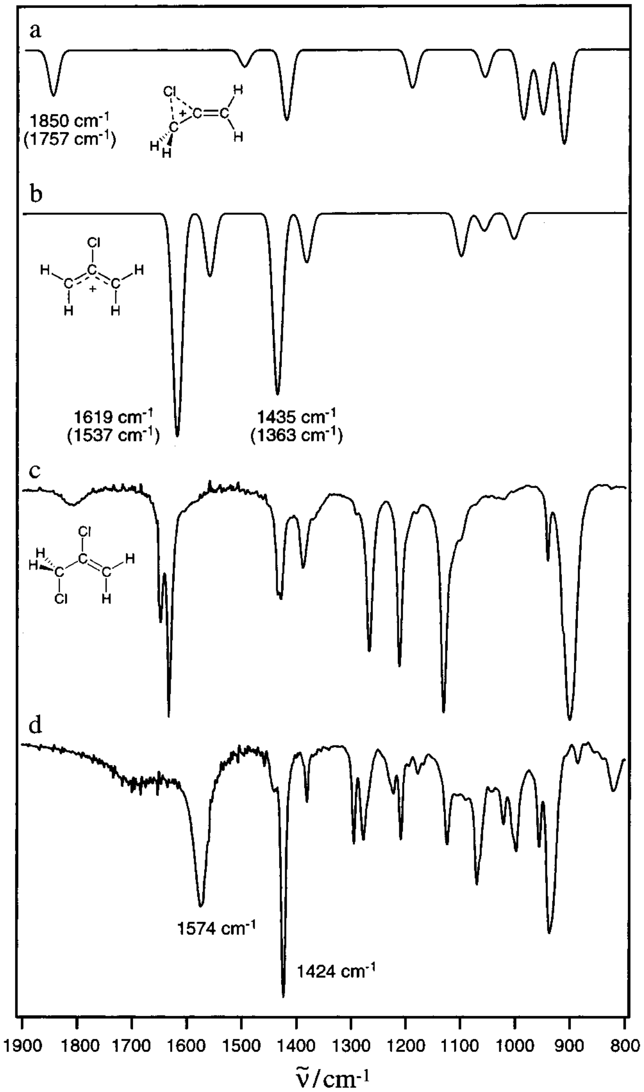

Figure 2. IR spectra calculated at MP2(fc)/6-311G(d,p) level of theory (in parentheses scaled[6] values) of (a) C_s cation **1a** and (b) C_{2v} cation **1b**, (c) experimental FT-IR spectrum of 2,3-dichloropropene in an $SbCl_5$ matrix at 77 K, and (d) reaction product after the matrix was warmed to 120 K.

fraction measurements. The same conclusion also follows from results of the NPA[4c] and AIM[4d] analyses of MP2 densities at the same level of theory. In going from the *trans*-1-chloroallyl cation to the 2-chloroallyl cation **1b**, the charge on chlorine decreases from 0.333 to 0.156 (NPA) or from 0.127 to −0.001 (AIM), respectively. Also, the C−Cl bond order, calculated by the AIM method, changes from 1.445 in the *trans*-1-chloroallyl cation to 1.183 in the 2-chloroallyl cation **1b**.

The less stable structure **1a** possess characteristics of the allene chloronium ion. Its C=C bond is shorter than in nonbridged allyl cations. The Cl-atom takes a central position between carbons above the C−C bond with almost equal C−Cl bond distances (see Figure 1).

Starting from these geometries, the frequencies and intensities of IR-active vibrations are calculated for both **1a** and **1b**. The corresponding simulated spectra are represented in Figure 2 (spectra a and b). Characteristic signals assigned to the C=C stretching vibrations are calculated at 1850 cm^{-1} (1757 cm^{-1} scaled by 0.950[6]) for **1a** and at 1619 cm^{-1} (1537 cm^{-1} scaled) for the structure **1b**. The former frequency is typical for the allene chloronium ion and the second for the allyl cation, respectively.

Experimental Approach. Preparation of **1** in solid SbF_5 failed. The expected characteristic signals for an asymmetric stretching mode of the CCC^+ group (in the 1500−1600 cm^{-1} region) or of the $C{=}C^+$ group (in the 1800−1900 cm^{-1} region) did not appear in the spectra. Instead, broad absorptions, typical for polymeric materials, were recorded. This failure encouraged us to test other Lewis acids, such as $SbCl_5$, as a superacid matrix material for the preparation of these sensitive cations.

The precursor of **1**, 2,3-dichloropropene (**2**), was codeposited[5] with an excess of $SbCl_5$ (500:1) on the CsI window cooled to 77 K. The spectrum changed, by warming the matrix to 120 K and the dominant peaks at 1574 and 1424 cm^{-1} started to grow. The spectra are shown in Figure 2c,d. All the new peaks were compared with the spectra calculated for the structures **1a** and **1b** on the MP2(fc)/6-311G(d,p) level of theory. A good agreement with experimental frequencies and intensities was found only for the spectrum calculated for structure **1b**. Comparison between experimental and calculated frequencies for the four peaks that can be readily identified, two C−H stretching modes (3023 and 2967 cm^{-1}) and two stretching modes of the CCC^+ group (1574 and 1424 cm^{-1}), gives a correlation coefficient of 0.9997 and a scaling factor of 0.94, in agreement with the published value.[6] The characteristic CCC^+ asymmetric stretching vibration of **1b** (1574 cm^{-1}) is almost the same as in the parent allyl cation (1577 cm^{-1}).[7] This supports the theoretical prediction that the nodal position of the chlorine has no direct effect on the π-electron density in the ground-state allyl cation. For structure **1a**, which may be perceived as an allene chloronium ion, calculation predicts the high-frequency signal of C=C stretching at 1850 cm^{-1} (Figure 2, part a), but in our experiments, no signal appeared in this spectral region (see Figure 2, part d).

Alternative assignment of the spectrum in part b of Figure 2 to the complex **2**·$SbCl_5$ rather than to the carbocation **1b** can be excluded because a change in the C=C frequency in going from the precursor **2** to such a complex is calculated to be only 9 cm^{-1}! Namely, calculated C=C stretching frequencies at the MP2(fc)/6-31G(d) level of theory are 1714 cm^{-1} in **2** and 1705 cm^{-1} in **2**·SbF_5 (Figure 3). On the other hand, a typical decrease in the C=C stretching frequency in going from an alkene to the allyl cation is nearly 70 cm^{-1}, as it has already been found in a series of simple acyclic allyl cations. In the case of **1b**, we have measured a 65 cm^{-1} frequency downshift (from 1639 cm^{-1} in 2,3-dichloropropene to 1574 cm^{-1} in **1b**).

To support the assignment of the spectrum of **1b**, we have also prepared its cyclic chloroallyl cation analogue **5**. The ion was independently prepared in the SbF_5 matrix from two different precursors **3**[8a] and **4**[8b] under similar experimental conditions used in preparation of **1b** (Figure 4). The asymmetric CCC^+ stretching signal

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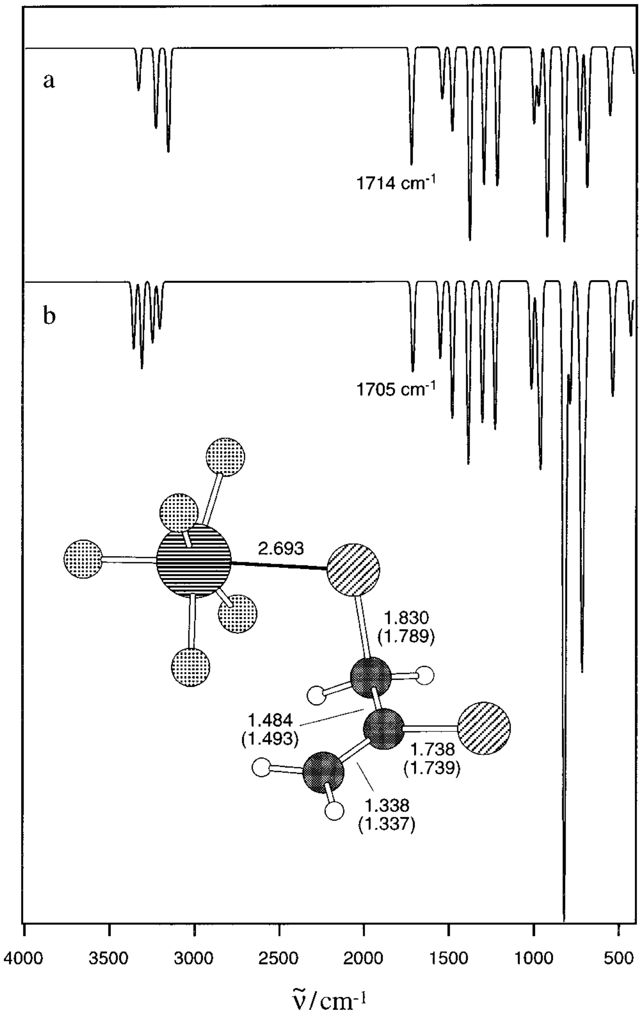
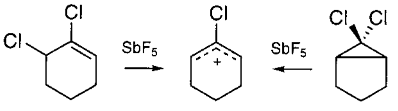


Figure 3. IR spectra (nonscaled) calculated at MP2(fc)/6-31G-(d) level of theory of (a) 2,3-dichloropropene (**2**) and (b) complex of 2,3-dichloropropene with SbF_5 (**2**·SbF_5). Bond distances given in parentheses correspond to 2,3-dichloropropene.



3 **5** **4**

was found in the same spectral region, i.e. at 1523 cm^{-1}. Again, this frequency is very close to that measured for the unsubstituted cyclohexenyl cation (1521 cm^{-1}),[9] implying that the central position of the chlorine atom does not significantly change π-electron distribution in the allyl group.

Conclusions

Among the two possible isomers of a 2-chloroallyl cation, it was found that the C_{2v} structure **1b** is 7.5 kcal/mol (MP2) or 10.1 kcal/mol (DFT) more stable than the C_s isomer **1a**.

Our FT-IR experiments in the cryogenic solid $SbCl_5$ matrix have shown that the ion **1b** is a major product under these conditions. It can be characterized by a typical absorption at 1574 cm^{-1} assigned to the allyl CCC^+ asymmetric stretching mode. Another isomer, **1a**, has not been observed because no signal of the expected allene chloronium ion C═C stretching vibration appeared in 1800−1900 cm^{-1} spectral region.

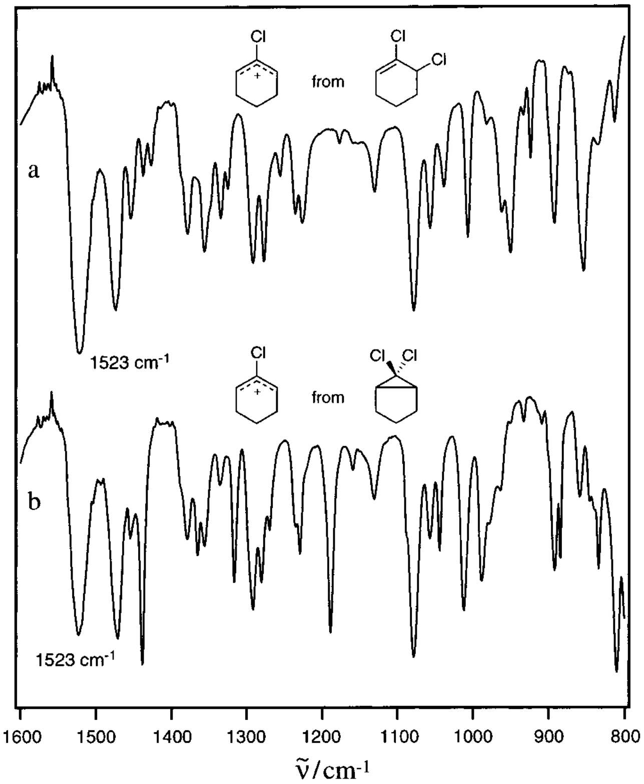


Figure 4. FT-IR spectra of 2-chlorocyclohexenyl cation (**5**) in an SbF_5 matrix from the precursors (a) 2,3-dichlorocyclohexene and (b) 6,6-dichlorobicyclo[3.1.0]hexene.

The calculated decrease in the C═C stretching frequencies (9 cm^{-1}) expected by the formation of the complex of the precursor with a Lewis acid is small in comparison with the frequency downshift (65 cm^{-1}) measured for the ionization of **2**. Consequently, such a complex has not been observed.

Experimental Section

General. All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification. Infrared spectra were recorded on Perkin-Elmer 1725x FT-IR spectrometer with 2 cm^{-1} resolution. The ^{13}C and ^{1}H NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 75 and 300 MHz, respectively, with $CDCl_3$ as solvent.

6,6-Dichlorobicyclo[3.1.0]hexane.[10] Chloroform (9 mL), cyclopentene (9.2 mL; 0.1045 mol), 50% sodium hydroxide (20 mL), and triethylbenzylammonium chloride (0.2 g) were placed in a 100 mL flask fitted with a stirrer. The mixture was vigorously stirred for 1 h. Then, the cooled reaction mixture was added in water (50 mL). The layers were separated, and the water layer was extracted with dichloromethane (25 mL). The combined organic layers were washed with water (25 mL), dried over sodium sulfate, and evaporated. Distillation at 20 mmHg gave 6.70 g of product, bp 70−72 °C in 42% yield. ^{13}C NMR (δ/ppm): 24.88; 27.46; 37.92; 68.01.

2,3-Dichlorocyclohexene.[11] 6,6-dichlorobicyclo[3.1.0]hexane (2.5 g; 0.016 mol) was heated for 3 h under nitrogen at 210 °C. Distillation gave 2.5 g of 2,3-dichlorocyclohexene, bp 81 °C, 15 mmHg, in 100% yield. IR (cm^{-1}): 1641 (C═C str.). ^{13}C NMR (δ/ppm): 15.84; 25.89; 32.84; 59.00; 129.80; 131.28.

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Matrix Experiment. All the matrices were prepared on a CsI window cooled by a closed cycle cryostat ROK 10-300 Leybold Heraeus connected to vacuum line, equipped with an oil diffusion pump. During the deposition, the temperature was held at 70 K and the vacuum at 10−5 mmHg. The flow of the sample was regulated by a Teflon valve. The deposition times were 6 min in all experiments. The matrix material (SbF_5 or $SbCl_5$) to sample ratio was estimated to be 500:1.

Methods of Calculations

Full geometry optimizations and harmonic vibrational frequency calculations were, for all molecules, performed with Gamess[12] and Gaussian 94[13] programs at MP2(fc) and B3LYP level of theory. Split-valence basis set 6-311G(d,p) was used for cations and the precursor molecule, and the structure and spectra of the **2**·SbF_5 complex was calculated using the 6-31G(d) basis set for **2** and 3-21G(d) for the SbF_5 moiety. The existence of a true minima or saddle point was, in each case, verified by the absence or presence of imaginary vibrational frequencies. Natural population analysis (NPA)[4c] and atoms in molecules theory (AIM)[4d] calculations, both based on MP2(fc)/6-311G(d,p) densities, were performed by Gaussian 94.

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